$\alpha^4\mathcal{R}$ corrections to singlet states of helium

Krzysztof Pachucki*
Institute of Theoretical Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland

(Received 7 July 2006; published 31 August 2006)

Corrections of order $\alpha^4\mathcal{R}$ are calculated for the singlet states $1\,{}^1S_0$ and $2\,{}^1S_0$ of the helium atom. The result for the $1\,{}^1S_0$ state is in slight disagreement with that of Korobov and Yelkhovsky [Phys. Rev. Lett. **87**, 193003 (2001)]. The results obtained lead to a significant improvement of the transition frequencies between low-lying levels of the helium atom. In particular theoretical predictions for the $2\,{}^1S_0$-$1\,{}^1S_0$ transition are found to be in disagreement with experimental values.

DOI: 10.1103/PhysRevA.74.022512 PACS number(s): 31.30.Jv, 12.20.Ds, 31.15.Md, 32.10.Fn

I. INTRODUCTION

In this paper we present an approach for obtaining precise energy levels of light few-electron atoms and perform calculations for the singlet states $1\,{}^1S_0$ and $2\,{}^1S_0$ of the helium atom. This approach is based on quantum electrodynamic (QED) theory and relies on expansion in the fine structure constant α [1,2]. It allows one to systematically include nuclear recoil effects, electron self-energy, and vacuum polarization. Several calculations have already been performed for triplet states of helium, the most accurately known being the fine structure of $2\,{}^3P_J$, where all corrections up to order of $m\alpha^7$ have recently been obtained [3,4]. Other examples include energies of $1\,{}^1S_0$ [5,6], $2\,{}^3S_1$ [7], and $2\,{}^3P$ [8], which have been obtained up to the order of $m\alpha^6$. For other atoms like lithium [9] or beryllium [10], energy levels are less accurately known—namely, up to order $m\alpha^5$—but are still accurate enough to allow the nuclear charge radius to be determined from isotope shift measurements [11].

According to QED theory, the expansion of energy levels in powers of α has the following form:

$$E(\alpha) = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + O(\alpha^8), \qquad (1.1)$$

where $E^{(n)}$ is a contribution of order $m\alpha^n$ and may include powers of $\ln\alpha$. Each term $E^{(n)}$ can be expressed as an expectation value of some effective Hamiltonian or in some cases of a nonlocal operator. $E^{(2)}\equiv E_0$ is the eigenvalue of the nonrelativistic Hamiltonian H_0, which for the infinite nuclear mass is

$$H_0 = \sum_a \left\{\frac{\vec{p}_a^{\,2}}{2m} - \frac{Z\alpha}{r_a}\right\} + \sum_{a>b}\sum_b \frac{\alpha}{r_{ab}}. \qquad (1.2)$$

$E^{(4)}$ is the expectation value of the Breit-Pauli Hamiltonian $H^{(4)}$ [12],

$$\begin{aligned}H^{(4)} = &\sum_a \left\{-\frac{\vec{p}_a^{\,4}}{8m^3} + \frac{\pi Z\alpha}{2m^2}\delta^3(r_a) + \frac{Z\alpha}{4m^2}\vec{\sigma}_a\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a\right\}\\ &+ \sum_{a>b}\left\{-\frac{\pi\alpha}{m^2}\delta^3(r_{ab}) - \frac{\alpha}{2m^2}p_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right)p_b^j\right.\\ &- \frac{2\pi\alpha}{3m^2}\vec{\sigma}_a\cdot\vec{\sigma}_b\delta^3(r_{ab}) + \frac{\alpha}{4m^2}\frac{\sigma_a^i\sigma_b^j}{r_{ab}^3}\left(\delta^{ij} - 3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right)\\ &+ \frac{\alpha}{4m^2 r_{ab}^3}\big[2(\vec{\sigma}_a\cdot\vec{r}_{ab}\times\vec{p}_b - \vec{\sigma}_b\cdot\vec{r}_{ab}\times\vec{p}_a)\\ &\left.+ (\vec{\sigma}_b\cdot\vec{r}_{ab}\times\vec{p}_b - \vec{\sigma}_a\cdot\vec{r}_{ab}\times\vec{p}_a)\big]\right\}. \qquad (1.3)\end{aligned}$$

$E^{(5)}$ is the leading QED contribution, which for singlet states is [13,14]

$$\begin{aligned}E^{(5)} = &\sum_{a>b}\left\langle\left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\frac{\alpha^2}{m^2}\delta^3(r_{ab}) - \frac{7m\alpha^5}{6\pi}P\left(\frac{1}{(m\alpha r_{ab})^3}\right)\right\rangle + \sum_a\left[\frac{19}{30} + \ln(\alpha^{-2})\right.\\ &\left. - \ln k_0\right]\frac{4Z\alpha^2}{3m^2}\langle\delta^3(r_a)\rangle, \qquad (1.4)\end{aligned}$$

where

$$\left\langle\phi\left|P\left(\frac{1}{r^3}\right)\right|\psi\right\rangle \equiv \lim_{a\to 0}\int d^3r\,\phi^*(\vec{r})\psi(\vec{r})\left[\frac{1}{r^3}\Theta(r-a) + 4\pi\delta^3(r)(\gamma+\ln a)\right], \qquad (1.5)$$

with Θ being the step function and γ the Euler constant. Equation (1.5) contains the many-electron Bethe logarithm $\ln k_0$ defined by

$$\ln k_0 = \frac{\left\langle\sum_a\vec{p}_a(H_0-E_0)\ln[2(H_0-E_0)/m\alpha^2]\sum_b\vec{p}_b\right\rangle}{2\pi Z\alpha\left\langle\sum_c\delta^3(r_c)\right\rangle}. \qquad (1.6)$$

The calculation of $E^{(6)}$ is the subject of this work. It can be represented as

$$E^{(6)} = \langle H^{(6)}\rangle + \left\langle H^{(4)}\frac{1}{(E_0-H_0)'}H^{(4)}\right\rangle, \qquad (1.7)$$

where $H^{(6)}$ is the effective Hamiltonian of order $m\alpha^6$. Its derivation is presented in the following section. Since individual terms in above equation are divergent, we follow the approach of Ref. [5] and use the technique of dimensional regularization, details of which are presented in Appendix A. $H^{(4)}$ in the above equation is therefore a Breit-Pauli Hamiltonian in d dimensions, the derivation of which is also in-

*Electronic address: krp@fuw.edu.pl; www.fuw.edu.pl/~krp

cluded in Sec. II. For the next-order term $E^{(7)}$ we will use an approximate formula based on hydrogenic values [15].

II. DERIVATION OF THE EFFECTIVE HAMILTONIAN

To derive the effective Hamiltonian, we follow Ref. [2], consider the Dirac equation with electromagnetic field, and perform a nonrelativistic expansion by the use of the Foldy-Wouthuysen transformation (see Appendix B for details):

$$H_{\rm FW} = eA^0 + \frac{\pi^2}{2m} - \frac{e}{4m}\sigma^{ij}B^{ij} - \frac{\pi^4}{8m^3} - \frac{e}{8m^2}(\vec{\nabla}\cdot\vec{E} + \sigma^{ij}\{E^i,\pi^j\}) + \frac{e}{16m^3}\{\sigma^{ij}B^{ij},p^2\} - \frac{e}{16m^3}\{\vec{p},\partial_t\vec{E}\} + \frac{3e}{32m^4}\{\sigma^{ij}E^ip^j,p^2\} + \frac{e}{128m^4}[p^2,[p^2,A^0]] - \frac{3e}{64m^4}\{p^2,\nabla^2A^0\} + \frac{p^6}{16m^5}, \tag{2.1}$$

where higher-order terms are neglected. This Hamiltonian defines an effective nonrelativistic QED theory with Lagrangian

$$\mathcal{L} = \sum_a \psi_a^\dagger(i\partial_t - H_{\rm FW})\psi_a + \mathcal{L}_{EM}, \tag{2.2}$$

where $\mathcal{L}_{EM}$ is the Lagrangian of the electromagnetic field and the summation goes over all particles. We consider now the equal time retarded Green function $G=G(\{\vec{r}_a'\},t';\{\vec{r}_a\},t)$, where by $\{\vec{r}_a\}$ we denote the set of coordinates for all particles of the system. In the absence of time-dependent perturbation $G=G(t'-t)$. The Fourier transform of G in the time variable $t'-t$ can be written as

$$G(E) \equiv \frac{1}{E - H_{\rm eff}(E)}, \tag{2.3}$$

which is the definition of the effective Hamiltonian $H_{\rm eff}(E)$. In the nonrelativistic case $H_{\rm eff}=H_0$,

$$H_0 = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} - \left[\frac{Z\alpha}{r_1}\right]_\epsilon - \left[\frac{Z\alpha}{r_2}\right]_\epsilon + \left[\frac{\alpha}{r_{12}}\right]_\epsilon, \tag{2.4}$$

where $[Q]_\epsilon$ is the $d=3-2\epsilon$ extension of the operator Q at $d=3$; see Appendix A for details. All the relativistic and QED corrections resulting from the Lagrangian $\mathcal{L}$ can be represented as

$$G(E) = \frac{1}{E-H_0} + \frac{1}{E-H_0}\Sigma(E)\frac{1}{E-H_0} + \frac{1}{E-H_0}\Sigma(E)\frac{1}{E-H_0}\Sigma(E)\frac{1}{E-H_0} + \cdots = \frac{1}{E-H_0-\Sigma(E)} \equiv \frac{1}{E-H_{\rm eff}(E)}, \tag{2.5}$$

where $\Sigma(E)$ is the n-particle irreducible contribution. The energy level can be interpreted as a pole of $G(E)$ as a function of E. It is convenient to consider the matrix element of G between the nonrelativistic wave function corresponding to this energy level. There is always such a correspondence, since relativistic and QED effects are small perturbations of the system. This matrix element is

$$\langle\phi|G(E)|\phi\rangle = \left\langle \phi \left| \frac{1}{E-H_0-\Sigma(E)} \right| \phi \right\rangle \equiv \frac{1}{E-E_0-\sigma(E)}, \tag{2.6}$$

where

$$\sigma(E) = \langle\phi|\Sigma(E)|\phi\rangle + \sum_{n\neq 0}\langle\phi|\Sigma(E)|\phi_n\rangle\frac{1}{E-E_n}\langle\phi_n|\Sigma(E)|\phi\rangle + \cdots . \tag{2.7}$$

Having $\sigma(E)$, the correction to the energy level can be expressed as

$$\delta E = E - E_0 = \sigma(E_0) + \sigma'(E_0)\sigma(E_0) + \cdots = \langle\phi|\Sigma(E_0)|\phi\rangle + \left\langle\phi\left|\Sigma(E_0)\frac{1}{(E_0-H_0)'}\Sigma(E_0)\right|\phi\right\rangle + \langle\phi|\Sigma'(E_0)|\phi\rangle\langle\phi|\Sigma(E_0)|\phi\rangle + \cdots \tag{2.8}$$

Since the last term in Eq. (2.8) can be neglected up to order $m\alpha^6$, one can consider only $\Sigma(E_0)$. In most cases, the explicit state dependence of Σ can be eliminated by the use of commutation relations. The only exception is the so called Bethe logarithm, which contributes only in order $m\alpha^5$. If we consider this term separately, the operator Σ gives an effective Hamiltonian

$$H_{\rm eff} = H_0 + \Sigma = H_0 + H^{(4)} + H^{(5)} + H^{(6)} + \cdots, \tag{2.9}$$

from which one can calculate corrections to energy levels. The calculation of Σ follows from the Feynman rules for the Lagrangian in Eq. (2.2). We will use the photon propagator in the Coulomb gauge:

$$G_{\mu\nu}(k) = \begin{cases} -\dfrac{1}{\vec{k}^2}, & \mu=\nu=0, \\[2ex] \dfrac{-1}{k_0^2-\vec{k}^2+i\varepsilon}\left(\delta_{ij} - \dfrac{k_ik_j}{\vec{k}^2}\right), & \mu=i,\nu=j, \end{cases} \tag{2.10}$$

and consider separately corrections due to exchange of the Coulomb G_{00} and the transverse G_{ij} photon. The typical one-photon exchange contribution between electrons a and b is

$$\langle\phi|\Sigma(E_0)|\phi\rangle = e^2\int\frac{d^Dk}{(2\pi)^Di}G_{\mu\nu}(k)\left\{\left\langle\phi\left|j_a^\mu(k)e^{i\vec{k}\cdot\vec{r}_a}\times\frac{1}{E_0-H_0-k^0+i\varepsilon}j_b^\nu(-k)e^{-i\vec{k}\cdot\vec{r}_b}\right|\phi\right\rangle + \left\langle\phi\left|j_b^\mu(k)e^{i\vec{k}\cdot\vec{r}_b}\frac{1}{E_0-H_0-k^0+i\varepsilon}\times j_a^\nu(-k)e^{-i\vec{k}\cdot\vec{r}_a}\right|\phi\right\rangle\right\}, \tag{2.11}$$

where $D=d+1$, ϕ is an eigenstate of H_0 and j_a^μ is the electromagnetic current for particle a. The first terms of the nonrelativistic expansion of j^0 component are obtained from Eq. (2.1) (terms involving coupling to A^0),

$$j^0(\vec{k}) = 1 + \frac{i}{4m}\sigma^{ij}k^i p^j - \frac{1}{8m^2}\vec{k}^2 + \cdots, \tag{2.12}$$

and of the $\vec{j}$ component (terms involving coupling to $\vec{A}$),

$$j^i(\vec{k}) = \frac{p^i}{m} + \frac{i}{2m}\sigma^{ji}k^j. \tag{2.13}$$

Most of the calculation is performed in the nonretardation approximation; namely, one sets $k^0=0$ in the photon propagator $G_{\mu\nu}(k)$ and $j(k)$. The retardation corrections are considered separately. Within this approximation and using the symmetrization $k^0 \leftrightarrow -k^0$, the k^0 integral is

$$\frac{1}{2}\int \frac{dk^0}{2\pi i}\left[\frac{1}{-\Delta E - k^0 + i\varepsilon} + \frac{1}{-\Delta E + k^0 + i\varepsilon}\right] = -\frac{1}{2}, \tag{2.14}$$

which leads to

$$\langle\phi|\Sigma(E_0)|\phi\rangle = -e^2\int \frac{d^dk}{(2\pi)^d}G_{\mu\nu}(k_0=0,\vec{k})\langle\phi|j_a^\mu(\vec{k}) \times e^{i\vec{k}\cdot(\vec{r}_a-\vec{r}_b)}j_b^\nu(-\vec{k})|\phi\rangle. \tag{2.15}$$

One recognizes that in the nonrelativistic limit G_{00} gives the Coulomb interaction. However, this term is already included in H_0, which means that this nonrelativistic Coulomb interaction has to be excluded from the perturbative expansion. Next-order terms resulting from j^0 and $\vec{j}$ lead to the Breit-Pauli Hamiltonian H_{BP}. This includes corrections to the electric as well as magnetic interactions between electrons and the nucleus. Corrections to the kinetic energy and electron-nucleus interaction are obtained from Eq. (2.1) by setting $eA^0=-[(Z\alpha)/r_a]_\epsilon$,

$$\delta_1 H^{(4)} = \sum_{a=1,2} -\frac{p_a^4}{8m^3} + \frac{\pi Z\alpha}{2m^2}\delta^d(r_a) - \frac{1}{4m^2}\sigma_a^{ij}\nabla^i\left[\frac{Z\alpha}{r_a}\right]_\epsilon p_a^j. \tag{2.16}$$

The derivation of electron-electron interactions is as follows. The j^0 component gives relativistic corrections of the form

$$\begin{aligned}\delta_2 H^{(4)} &= e^2\int \frac{d^dk}{(2\pi)^d}\frac{1}{\vec{k}^2}j_1^0(\vec{k})e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}j_2^0(-\vec{k})\\ &= e^2\int \frac{d^dk}{(2\pi)^d}\frac{1}{\vec{k}^2}\left(1 + \frac{i}{4m}\sigma_1^{ij}k^i p_1^j - \frac{\vec{k}^2}{8m^2}\right)\\ &\quad\times e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}\left(1 - \frac{i}{4m}\sigma_2^{ij}k^i p_2^j - \frac{\vec{k}^2}{8m^2}\right)\\ &= -\frac{\pi\alpha}{m^2}\delta^d(r) + \frac{1}{4m^2}\left(\sigma_1^{ij}\nabla^i\left[\frac{\alpha}{r}\right]_\epsilon p_1^j - \sigma_2^{ij}\nabla^i\left[\frac{\alpha}{r}\right]_\epsilon p_2^j\right),\end{aligned} \tag{2.17}$$

where $r \equiv r_{12} = |\vec{r}_1 - \vec{r}_2|$. We have left out in the above the pure Coulomb interaction between electrons and neglected higher-order terms. The $\vec{j}$ component gives the following corrections:

$$\begin{aligned}\delta_3 H^{(4)} &= -e^2\int \frac{d^dk}{(2\pi)^d}\frac{1}{\vec{k}^2}\left(\delta^{ij} - \frac{k^i k^j}{\vec{k}^2}\right)j_1^i(\vec{k})e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}j_2^j(-\vec{k})\\ &= -e^2\int \frac{d^dk}{(2\pi)^d}\frac{1}{\vec{k}^2}\left(\delta^{ij} - \frac{k^i k^j}{\vec{k}^2}\right)\\ &\quad\times\left(\frac{p_1^i}{m} + \frac{i}{2m}\sigma_1^{ij}k^j\right)e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}\left(\frac{p_2^i}{m} - \frac{i}{2m}\sigma_2^{ij}k^j\right)\\ &= -\frac{\alpha}{2m^2}p_1^i\left[\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right]_\epsilon p_2^j + \frac{1}{4m^2}\sigma_1^{ik}\sigma_2^{jk}\\ &\quad\times\left(\nabla^i\nabla^j - \frac{\delta^{ij}}{d}\nabla^2\right)\left[\frac{\alpha}{r}\right]_\epsilon - \frac{\pi\alpha}{dm^2}\sigma_1^{ij}\sigma_2^{ij}\delta^d(r)\\ &\quad-\frac{1}{2m^2}\left(\sigma_1^{ij}\nabla^i\left[\frac{\alpha}{r}\right]_\epsilon p_2^j - \sigma_2^{ij}\nabla^i\left[\frac{\alpha}{r}\right]_\epsilon p_1^j\right).\end{aligned} \tag{2.18}$$

The complete relativistic correction $H^{(4)}$ is a sum of Eqs. (2.16)–(2.18),

$$H^{(4)} = \delta_1 H^{(4)} + \delta_2 H^{(4)} + \delta_3 H^{(4)}. \tag{2.19}$$

Since spin-orbit terms do not lead to divergences in the second-order matrix element, one can assume for them $\epsilon=0$. The spin-spin tensor interaction, the second term of Eq. (2.18), vanishes for singlet states, as the total spin is zero; see Eq. (3.29) for the definition of a singlet state in d dimensions. Moreover, as a result of this definition one obtains $\sigma_1^{ij}\sigma_2^{ij} \to -d(d-1)$, so $H^{(4)}$ becomes

$$H^{(4)} = H_A + H_C, \tag{2.20}$$

$$\begin{aligned}H_A &= -\frac{p_1^4}{8m^3} - \frac{p_2^4}{8m^3} + \frac{\pi Z\alpha}{2m^2}\delta^d(r_1) + \frac{\pi Z\alpha}{2m^2}\delta^d(r_2)\\ &\quad-\frac{\alpha}{2m^2}p_1^i\left[\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right]_\epsilon p_2^j + \frac{\pi\alpha}{m^2}(d-2)\delta^d(r),\end{aligned} \tag{2.21}$$

$$\begin{aligned}H_C &= \frac{(\vec{\sigma}_1 - \vec{\sigma}_2)}{2}\left[\frac{Z}{4m^2}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1 - \frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)\right.\\ &\quad\left.+\frac{1}{4m^2}\frac{\vec{r}}{r^3}\times(\vec{p}_1 + \vec{p}_2)\right],\end{aligned} \tag{2.22}$$

in agreement with Ref. [6]. Both H_A and H_C contribute to $E^{(6)}$ through a second-order contribution—namely,

$$E_A = \left\langle H_A\frac{1}{(E_0 - H_0)'}H_A\right\rangle, \tag{2.23}$$

$$E_C = \left\langle H_C\frac{1}{E_0 - H_0}H_C\right\rangle. \tag{2.24}$$

Below we derive the higher-order term in the nonrelativistic expansion—namely, the $m\alpha^6$ Hamiltonian, which we call here the higher-order effective Hamiltonian $H^{(6)}$. It is expressed as a sum of various contributions,

$$H^{(6)} = \sum_{i=0,8} \delta H_i + H_H + H_R, \tag{2.25}$$

which are calculated in the following on the basis of the Foldy-Wouthuysen Hamiltonian from Eq. (2.1). A similar derivation has already been performed for the case $d=3$ in Ref. [2]. One can neglect here all spin-orbit terms and tensor spin-spin interactions, as they vanish for singlet states. δH_0 is the kinetic energy correction, the last term in Eq. (2.1),

$$\delta H_0 = \frac{p_1^6}{16m^5} + \frac{p_2^6}{16m^5}. \tag{2.26}$$

δH_1 is a correction due to the ninth and tenth terms in $H_{\rm FW}$ in Eq. (2.1). These terms involve only A^0, so the nonretardation approximation is strictly valid here. This correction δH_1 includes the Coulomb interaction between the electron and the nucleus and between electrons. So if we denote by V the nonrelativistic interaction potential

$$V \equiv \left[-\frac{Z\alpha}{r_1} - \frac{Z\alpha}{r_2} + \frac{\alpha}{r}\right]_\epsilon \tag{2.27}$$

and, for later use, by $\mathcal{E}_a$ the static electric field at the position of particle a which is produced by the nucleus and the other particle b,

$$e\vec{\mathcal{E}}_a \equiv -\nabla_a V \equiv \left[-Z\alpha\frac{\vec{r}_a}{r_a^3} + \alpha\frac{\vec{r}_{ab}}{r_{ab}^3}\right]_\epsilon, \tag{2.28}$$

then δH_1 can be written as

$$\delta H_1 = \sum_{a=1,2} \frac{1}{128m^4}[p_a^2,[p_a^2,V]] - \frac{3}{64m^4}\{p_a^2,\nabla_a^2 V\}. \tag{2.29}$$

δH_2 is a correction to the Coulomb interaction between electrons which comes from the fifth term in $H_{\rm FW}$ Eq. (2.1)—namely,

$$-\frac{e}{8m^2}(\vec{\nabla}\cdot\vec{E} + \sigma^{ij}\{E^i,p^j\}). \tag{2.30}$$

If the interaction of both electrons is modified by this term, it can be obtained in the nonretardation approximation, Eq. (2.15)—namely,

$$\begin{aligned}\delta H_2 &= \int \frac{d^d k}{(2\pi)^d}\frac{4\pi}{k^2}\frac{1}{64m^4}(k^2 - 2i\sigma_1^{ij}k_1^i p_1^j)e^{i\vec{k}\cdot\vec{r}}(k^2 + 2i\sigma_2^{kl}k^k p_2^l) \\ &= \frac{1}{64m^4}\left\{-4\pi\alpha\nabla^2\delta^d(r) + \frac{16\pi\alpha}{d(d-1)}\sigma_1\sigma_2 p_1^i[\delta_\perp^{ij}(r)]_\epsilon p_2^j\right\},\end{aligned} \tag{2.31}$$

where $[\delta_\perp^{ij}(r)]_\epsilon$ is defined in Eq. (A28) and we use the identity which is valid for singlet states:

$$\sigma_1^{ij}\sigma_2^{kl} = \sigma_1\sigma_2\frac{(\delta^{ik}\delta^{jl} - \delta^{il}\delta^{jk})}{d(d-1)}, \tag{2.32}$$

$$\sigma_1\sigma_2 \equiv \sigma_1^{ij}\sigma_2^{ij}. \tag{2.33}$$

δH_3 is the correction that comes from seventh term in Eq. (2.1):

$$-\frac{e}{16m^3}\{\vec{p},\partial_t\vec{E}\}. \tag{2.34}$$

To calculate this correction, we have to return to the original expression for one-photon exchange, Eq. (2.11). We assume that particle 1 interacts with the electromagnetic field by this term, while particle 2 by nonrelativistic coupling eA^0, and obtain

$$\begin{aligned}\delta E_3 = &-e^2\int\frac{d^D k}{(2\pi)^D i}\frac{1}{\vec{k}^2}\frac{1}{16m^3} \\ &\times\left(\left\langle\phi\left|\{\vec{p}_a,\vec{k}e^{i\vec{k}\cdot\vec{r}_a}\}\frac{k^0}{E_0 - H_0 - k^0 + i\varepsilon}e^{-i\vec{k}\cdot\vec{r}_b}\right|\phi\right\rangle\right. \\ &\left.-\left\langle\phi\left|e^{-i\vec{k}\cdot\vec{r}_b}\frac{k^0}{E_0 - H_0 - k^0 + i\varepsilon}\{\vec{p}_a,\vec{k}e^{i\vec{k}\cdot\vec{r}_a}\}\right|\phi\right\rangle\right) \\ &+(1\leftrightarrow 2).\end{aligned} \tag{2.35}$$

After performing the k^0 integral and commuting $(H_0 - E_0)$ with $e^{-i\vec{k}\cdot\vec{r}_b}$ one expresses this correction in terms of an effective operator

$$\delta H_3 = -\frac{1}{16m^4}\left[p_2^2,\left[p_1^2,\left[\frac{\alpha}{r}\right]_\epsilon\right]\right]. \tag{2.36}$$

δH_4 is the relativistic correction to transverse photon exchange. The first electron is coupled to $\vec{A}$ by the nonrelativistic term

$$-\frac{e}{m}\vec{p}\cdot\vec{A} - \frac{e}{4m}\sigma^{ij}B^{ij} \tag{2.37}$$

and the second one by the relativistic correction, the fourth and sixth terms in Eq. (2.1):

$$-\frac{1}{8m^3}\left(\pi^4 - \frac{e}{2}\{\sigma^{ij}B^{ij},p^2\}\right) \to \frac{e}{8m^3}\left\{p^2, 2\vec{p}\cdot\vec{A} + \frac{1}{2}\sigma^{ij}B^{ij}\right\}. \tag{2.38}$$

It is sufficient to calculate it in the nonretardation approximation

$$\begin{aligned}\delta H_4 = &\frac{\alpha}{8m^3}[2p_1^2 p_1^i + p_1^2\sigma_1^{li}\nabla_1^l]\left[\frac{p_2^j}{m} + \frac{1}{2m}\sigma_2^{kj}\nabla_2^k\right] \\ &\times\left[\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\right]_\epsilon + \text{H.c.} + (1\leftrightarrow 2).\end{aligned} \tag{2.39}$$

It is convenient at this point to introduce a notation for the vector potential at the position of particle a which is produced by particle b:

$$e\mathcal{A}^i_a \equiv \left[\frac{\alpha}{2r_{ab}}\left(\delta^{ij}+\frac{r^i_{ab}r^j_{ab}}{r^2_{ab}}\right)\frac{p^j_b}{m}+\frac{\alpha}{2m}\sigma^{ki}_b\frac{r^k_{ab}}{r^3_{ab}}\right]_\epsilon. \quad (2.40)$$

This correction can then be written as

$$\delta H_4 = \sum_{a=1,2}\frac{e}{8m^3}\{p^2_a, 2\vec{p}_a\cdot\vec{\mathcal{A}}_a+\sigma^{ij}_a\nabla^i_a\mathcal{A}^j_a\}$$
$$= \frac{(p_1^2+p_2^2)}{2}p^i_1\left[\frac{\alpha}{2r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)\right]_\epsilon p^j_2$$
$$+\frac{(p_1^2+p_2^2)}{8}\frac{\sigma_1\sigma_2}{d}4\pi\delta^d(r). \quad (2.41)$$

One notices that in the nonretardation approximation any correction can be simply obtained by replacing the magnetic field $\vec{A}$ by a static field $\vec{\mathcal{A}}_a$. We will use this fact in further calculations.

δH_5 comes from the coupling

$$\frac{e^2}{4m^2}\sigma^{ij}E^iA^j, \quad (2.42)$$

which is present in the fifth term in Eq. (2.1). The resulting correction is obtained by replacing the fields $\vec{E}$ and $\vec{A}$ by the static fields produced by the other electron:

$$\delta H_5 = \sum_a \frac{e^2}{4m^2}\sigma^{ij}_a\mathcal{E}^i_a\mathcal{A}^j_a = -\frac{Z\alpha^2}{8m^3}\frac{\sigma_1\sigma_2}{d}\left[\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_2}{r_2^3}\right]_\epsilon\left[\frac{\vec{r}}{r^3}\right]_\epsilon$$
$$+\frac{\alpha^2}{4m^3}\frac{\sigma_1\sigma_2}{d}\left[\frac{1}{r^4}\right]_\epsilon, \quad (2.43)$$

where $[1/r^4]_\epsilon \equiv (\nabla[1/r]_\epsilon)^2$.

δH_6 comes from the coupling

$$\frac{e^2}{2m}\vec{A}^2, \quad (2.44)$$

which is present in the second term of Eq. (2.1). Again, in the nonretardation approximation the $\vec{A}_a$ field is being replaced by the static fields produced by the other electron:

$$\delta H_6 = \sum_a \frac{e^2}{2m^2}\vec{\mathcal{A}}^2_a = \frac{\alpha^2}{8}p^i_1\frac{1}{r^2}\left(\delta^{ij}+3\frac{r^ir^j}{r^2}\right)p^j_1+\frac{\alpha^2}{8}p^i_1\frac{1}{r^2}$$
$$\times\left(\delta^{ij}+3\frac{r^ir^j}{r^2}\right)p^j_1+\frac{d-1}{4}\left[\frac{\alpha^2}{r^4}\right]_\epsilon, \quad (2.45)$$

where one used the identity

$$\sigma^{ij}\sigma^{ij} = d(d-1). \quad (2.46)$$

δH_7 is a retardation correction in the nonrelativistic single-transverse-photon exchange. To calculate this correction, we have to again return to the general one-photon exchange expression, Eq. (2.11), and take the transverse part of the photon propagator:

$$\delta E = -e^2\int\frac{d^Dk}{(2\pi)^Di}\frac{1}{(k^0)^2-\vec{k}^2+i\varepsilon}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)$$
$$\times\left\langle\phi\left|j^i_1(k)e^{i\vec{k}\cdot\vec{r}_1}\frac{1}{E_0-H_0-k^0+i\varepsilon}j^j_2(-k)e^{-i\vec{k}\cdot\vec{r}_2}\right|\phi\right\rangle$$
$$+(1\leftrightarrow 2). \quad (2.47)$$

We assume that the product $j^i_1(k)\,j^j_2(-k)$ 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

$$\delta E = e^2\int\frac{d^dk}{(2\pi)^d2k}\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)\left\langle\phi\left|j^i_1(\vec{k})e^{i\vec{k}\cdot\vec{r}_1}\right.\right.$$
$$\left.\left.\times\frac{1}{E_0-H_0-k}j^j_2(-\vec{k})e^{-i\vec{k}\cdot\vec{r}_2}\right|\phi\right\rangle+(1\leftrightarrow 2), \quad (2.48)$$

where $k=|\vec{k}|$. By using the nonrelativistic form of j^i and performing the retardation expansion

$$\frac{1}{E_0-H_0-k} = -\frac{1}{k}+\frac{H_0-E_0}{k^2}-\frac{(H_0-E_0)^2}{k^3}+\cdots, \quad (2.49)$$

where the first one contributes to the Breit-Pauli Hamiltonian, the second term to $E^{(5)}$, and the third term gives δE_7,

$$\delta E_7 = -e^2\int\frac{d^dk}{(2\pi)^d2k^4}\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)\left\langle\phi\left|\left(\frac{p^i_1}{m}+\frac{1}{2m}\sigma^{ki}_1\nabla^k_1\right)\right.\right.$$
$$\left.\left.\times e^{i\vec{k}\cdot\vec{r}_1}(H_0-E_0)^2\left(\frac{p^j_2}{m}+\frac{1}{2m}\sigma^{lj}_2\nabla^l_2\right)e^{-i\vec{k}\cdot\vec{r}_2}\right|\phi\right\rangle$$
$$+(1\leftrightarrow 2). \quad (2.50)$$

This is the most complicated term in the evaluation. After k integration one obtains

$$\delta H_7 = \frac{\alpha}{16m^4}\frac{\sigma_1\sigma_2}{d}\left[p_1^2,\left[p_2^2,\left[\frac{\alpha}{r}\right]_\epsilon\right]\right]$$
$$-\frac{\alpha}{8m^2}\left\{[p^i_1,V]\left[\frac{r^ir^j-3\delta^{ij}r^2}{r}\right]_\epsilon[V,p^j_2]\right.$$
$$+[p^i_1,V]\left[\frac{p_2^2}{2m},\left[\frac{r^ir^j-3\delta^{ij}r^2}{r}\right]_\epsilon\right]p^j_2$$
$$+p^i_1\left[\left[\frac{r^ir^j-3\delta^{ij}r^2}{r}\right]_\epsilon,\frac{p_1^2}{2m}\right][V,p^j_2]$$
$$\left.+p^i_1\left[\frac{p_2^2}{2m},\left[\left[\frac{r^ir^j-3\delta^{ij}r^2}{r}\right]_\epsilon,\frac{p_1^2}{2m}\right]\right]p^j_2\right\}, \quad (2.51)$$

where $[(r^ir^j-3\delta^{ij}r^2)/r]_\epsilon$ is defined in Eq. (A26).

δH_8 is the retardation correction to single-transverse-photon exchange, where one vertex is nonrelativistic, Eq. (2.13), and the second comes from the fifth term in Eq. (2.1):

$$-\frac{e}{8m^2}\sigma^{ij}\{E^i,p^j\}. \tag{2.52}$$

With the help of Eq. (2.48) one obtains the following expression for δE_8:

$$\delta E_8 = e^2\int\frac{d^dk}{(2\pi)^d}\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)\frac{i}{16m^3}\left\langle\phi\middle|\sigma_1^{ik}\{e^{i\vec{k}\cdot\vec{r}_1},p_1^k\}\right.\times\frac{1}{E_0-H_0-k}\left(p_2^j-\frac{i}{2}\sigma_2^{lj}k^l\right)e^{-i\vec{k}\cdot\vec{r}_2}|\phi\rangle + \text{H.c.}+(1\leftrightarrow 2). \tag{2.53}$$

In the expansion of $1/(E_0-H_0-k)$ in Eq. (2.49) the first term vanishes because it cancels out with its Hermitian conjugate and the second term is a correction of order $m\alpha^6$. After commuting (H_0-E_0) on the left one obtains the effective operator δH_8:

$$\delta H_8 = \sum_a\frac{e^2}{8m^2}\sigma_a^{ij}\{\mathcal{E}_a^i,\mathcal{A}_a^j\}-\frac{ie}{16m^3}[\sigma_a^{ij}\{p_a^i,\mathcal{A}_a^j\},p_a^2]$$
$$=\frac{\sigma_1\sigma_2}{d}\left\{-\frac{Z\alpha^2}{8}\left[\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_2}{r_2^3}\right]_\epsilon\left[\frac{\vec{r}}{r^3}\right]_\epsilon+\frac{1}{4}\left[\frac{\alpha^2}{r^4}\right]_\epsilon+\frac{1}{32}\left[p_1^2,\left[p_1^2,\left[\frac{\alpha}{r}\right]_\epsilon\right]\right]+\frac{1}{32}\left[p_2^2,\left[p_2^2,\left[\frac{\alpha}{r}\right]_\epsilon\right]\right]\right\}. \tag{2.54}$$

H_H is the high-energy contribution which is given by the forward three-photon exchange scattering amplitude. It was calculated for the $m\alpha^6$ correction to the parapositronium binding energy in [16]. Following [6], we define a d-dimensional spin-wave function in analogy to this parapositronium work [see Eq. (3.29)] and take the result with reversed sign:

$$H_H=\left(-\frac{1}{\epsilon}+4\ln m-\frac{39\zeta(3)}{\pi^2}+\frac{32}{\pi^2}-6\ln(2)+\frac{7}{3}\right)\frac{\pi\alpha^3}{4m^2}\delta^d(r), \tag{2.55}$$

where ζ is the Riemann zeta function and we follow the convention that a common factor $[(4\pi)^\epsilon\Gamma(1+\epsilon)]^2$ is pulled out from all matrix elements.

H_R is a radiative correction and its derivation requires a separate treatment. This is based on our former work for helium [17], and this result has also been obtained in Ref. [5]. It is a sum of one- and two-loop contributions:

$$H_R = H_{R1}+H_{R2},$$
$$H_{R1}=\frac{\alpha(Z\alpha)^2}{m^2}\left[\frac{427}{96}-2\ln(2)\right]\pi[\delta^3(r_1)+\delta^3(r_2)]+\frac{\alpha^3}{m^2}\left[\frac{6\zeta(3)}{\pi^2}-\frac{697}{27\pi^2}-8\ln(2)+\frac{1099}{72}\right]\pi\delta^3(r), \tag{2.56}$$

$$H_{R2}=\frac{\alpha^2(Z\alpha)}{m^2}\left[-\frac{9\zeta(3)}{4\pi^2}-\frac{2179}{648\pi^2}+\frac{3\ln(2)}{2}-\frac{10}{27}\right]\pi[\delta^3(r_1)+\delta^3(r_2)]+\frac{\alpha^3}{m^2}\left[\frac{15\zeta(3)}{2\pi^2}+\frac{631}{54\pi^2}-5\ln(2)+\frac{29}{27}\right]\pi\delta^3(r), \tag{2.57}$$

At this point we have obtained all contributions of the order of $m\alpha^6$.

III. ELIMINATION OF SINGULARITIES

The elimination of singularities will be performed in atomic units, which in d dimensions become little more complicated. The nonrelativistic Hamiltonian in natural units is

$$H_0=\frac{\vec{p}_1^{\,2}}{2m}+\frac{\vec{p}_2^{\,2}}{2m}-Z\alpha\frac{C_1}{r_1^{1-2\epsilon}}-Z\alpha\frac{C_1}{r_2^{1-2\epsilon}}+\alpha\frac{C_1}{r_{12}^{1-2\epsilon}}. \tag{3.1}$$

Using coordinates in atomic units,

$$\vec{r}\to(m\alpha)^{-1/(1+2\epsilon)}\vec{r}, \tag{3.2}$$

it can be written as

$$H_0=m^{(1-2\epsilon)/(1+2\epsilon)}\alpha^{2/(1+2\epsilon)}\times\left[\frac{\vec{p}_1^{\,2}}{2}+\frac{\vec{p}_2^{\,2}}{2}-Z\frac{C_1}{r_1^{1-2\epsilon}}-Z\frac{C_1}{r_2^{1-2\epsilon}}+\frac{C_1}{r_{12}^{1-2\epsilon}}\right]. \tag{3.3}$$

If one pulls out the factor $m^{(1-2\epsilon)/(1+2\epsilon)}\alpha^{2/(1+2\epsilon)}$ from H_0, then one will obtain the nonrelativistic Hamiltonian in atomic units. Similarly for $H^{(6)}$, the common factor in atomic units,

$$m^{(1-10\epsilon)/(1+2\epsilon)}\alpha^{6/(1+2\epsilon)}, \tag{3.4}$$

is pulled out from all the terms, which corresponds to the replacement $m\to 1, \alpha\to 1$. Such a factor will also be pulled out from H_H in Eq. (2.55), which will lead to the appearance of logarithmic terms.

We will explore now the power of dimensional regularization. All integrals of the form

$$\int d^dk\; k^\alpha \equiv 0 \tag{3.5}$$

vanish identically by definition. We will use this fact in the following. Consider the matrix element

$$\left\langle\phi\middle|\delta^d(r)\left[\frac{1}{r}\right]_\epsilon\middle|\phi\right\rangle=\int\frac{d^dp_1}{(2\pi)^d}\phi^\star(p_1)\int\frac{d^dp_2}{(2\pi)^d}\times\int\frac{d^dp_3}{(2\pi)^d}\frac{4\pi}{(\vec{p}_2-\vec{p}_3)^2}\phi(p_3), \tag{3.6}$$

and change the variable $\vec{p}_2=\vec{q}_2+\vec{p}_3$; then,

$$\left\langle \phi \left| \delta^d(r)\left[\frac{1}{r}\right]_\epsilon \right| \phi \right\rangle = \int \frac{d^d p_1}{(2\pi)^d}\phi^\star(p_1)\int \frac{d^d q_2}{(2\pi)^d}\frac{4\pi}{q_2^2} \times \int \frac{d^d p_3}{(2\pi)^d}\phi(p_3) = 0. \quad (3.7)$$

The integral with q_2 vanishes, so this matrix element is equal to 0; similarly,

$$\left\langle \phi \left| \delta^d(r_a)\left[\frac{1}{r_a}\right]_\epsilon \right| \phi \right\rangle = 0. \quad (3.8)$$

Let us introduce momenta $\vec{P}$ and $\vec{p}$,

$$\vec{p}_1 = \frac{\vec{P}}{2} + \vec{p}, \quad (3.9)$$

$$\vec{p}_2 = \frac{\vec{P}}{2} - \vec{p}, \quad (3.10)$$

where p_a is a momentum of the electron a, and consider the matrix element

$$\langle \phi | \vec{p}\,\delta^d(r)\vec{p}|\phi\rangle = \int \frac{d^d P}{(2\pi)^d}\left|\int \frac{d^d p}{(2\pi)^d}\phi(\vec{P},\vec{p})\vec{p}\right|^2 = 0. \quad (3.11)$$

This is equal to 0 because the integrand $\phi(\vec{P},\vec{p})\vec{p}$ is odd in $\vec{p}$ for the singlet states considered here. These matrix elements and the Schrödinger equation

$$\left(\frac{\vec{P}^2}{4} + \vec{p}^2 + V\right)\phi = E\phi \quad (3.12)$$

are used to derive various identities—for example,

$$\langle \nabla^2 \delta^d(r)\rangle = -\langle [\vec{p},[\vec{p},\delta^d(r)]]\rangle = -2\langle \delta^d(r)p^2\rangle = -2\left\langle \delta^3(r)\left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{\vec{P}^2}{4}\right)\right\rangle. \quad (3.13)$$

Similarly,

$$\left[\frac{Z^2}{r_1^4}\right]_\epsilon \equiv \left(\nabla_1\left[\frac{Z}{r_1}\right]_\epsilon\right)^2 = \vec{p}_1\frac{Z^2}{r_1^2}\vec{p}_1 - 2\left(E + \frac{Z}{r_2} - \frac{1}{r} - \frac{\vec{p}_2^2}{2}\right)\frac{Z^2}{r_1^2} - 2\left[\frac{Z}{r_1}\right]_\epsilon^3, \quad (3.14)$$

$$\left[\frac{1}{r^4}\right]_\epsilon \equiv \left(\nabla\left[\frac{1}{r}\right]_\epsilon\right)^2 = \frac{1}{2}\vec{p}_1\frac{1}{r^2}\vec{p}_1 + \frac{1}{2}\vec{p}_2\frac{1}{r^2}\vec{p}_2 - \left(E + \frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r^2} + \left[\frac{1}{r}\right]_\epsilon^3. \quad (3.15)$$

Since the electron-nucleus divergences cancel out algebraically, one does not need the matrix element of $\langle 1/r_1^3\rangle$. However, $\langle 1/r^3\rangle$ is needed and is calculated as follows:

$$\left\langle \left[\frac{1}{r}\right]_\epsilon^3\right\rangle = C_1^3\int d^d r\,\phi^2(r)r^{-3+6\epsilon} = C_1^3\phi^2(0)\int^\varepsilon d^d r\,r^{-3+6\epsilon} + \int_\varepsilon d^3 r\,\phi^2(r)r^{-3} = \left\langle \frac{1}{r^3}\right\rangle + \langle \pi\delta^d(r)\rangle\left(\frac{1}{\epsilon} + 2\right), \quad (3.16)$$

where $\langle 1/r^3\rangle \equiv P(1/r^3)$ is defined in Eq. (1.5). The matrix elements of $1/r^4$ can be obtained from Eq. (3.15), but it can also be calculated directly,

$$\left\langle \left[\frac{1}{r^4}\right]_\epsilon\right\rangle = C_1^2\int d^d r\,\phi^2(r)[\nabla(r^{-1+2\epsilon})]^2$$
$$= C_1^2(-1+2\epsilon)^2\phi^2(0)\int^\varepsilon d^d r\,r^{-4+4\epsilon}$$
$$(1 - C_2 r^{1+2\epsilon})^2 + \int_\varepsilon d^3 r\,\phi^2(r)r^{-4}$$
$$= \left\langle \frac{1}{r^4}\right\rangle + \langle \pi\delta^d(r)\rangle\left(\frac{1}{\epsilon} - 4\right), \quad (3.17)$$

where we assume that $1/\varepsilon$ and $\ln\varepsilon + \gamma$ are dropped. Similarly,

$$\left[\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\right]_\epsilon \nabla^i\nabla^j\left[\frac{1}{r}\right]_\epsilon = \frac{1}{r^4} + \pi\delta^d(r)\left(\frac{1}{\epsilon} - 5\right). \quad (3.18)$$

From Eqs. (3.16) and (3.17) one obtains the identity

$$\left\langle \frac{1}{r^4}\right\rangle = \left\langle \frac{1}{r^3}\right\rangle + \vec{p}_1\frac{1}{2r^2}\vec{p}_1 + \vec{p}_2\frac{1}{2r^2}\vec{p}_2 - \left(E + \frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r^2} + 6\pi\delta^3(r). \quad (3.19)$$

Other identities which will be used are

$$4\pi\delta_\perp^{ij}p^ip^j = -\pi\nabla^2\delta^d(r) - \frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + \frac{1}{2}\left[\frac{1}{r^4}\right]_\epsilon, \quad (3.20)$$

$$4\pi\delta_\perp^{ij}P^iP^j = P^iP^j\frac{(3r^ir^j - \delta^{ij}r^2)}{r^5} + \frac{8\pi}{3}\delta^3(r)P^2, \quad (3.21)$$

$$\left[p_1^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right] = Z\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - 2\left[\frac{1}{r^4}\right]_\epsilon + \frac{4}{3}\pi\delta^d(r)P^2 - P^iP^j\frac{(3r^ir^j - \delta^{ij}r^2)}{r^5}, \quad (3.22)$$

$$\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]=Z\left(\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}-2\left[\frac{1}{r^4}\right]_\epsilon-\frac{4}{3}\pi\delta^d(r)P^2+P^iP^j\frac{(3r^ir^j-\delta^{ij}r^2)}{r^5}, \tag{3.23}$$

$$p_1^2\left[\frac{1}{r}\right]_\epsilon p_2^2=\frac{1}{r}\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right)^2-\frac{2}{r^2}\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right)+\left[\frac{1}{r}\right]_\epsilon^3-\vec{P}\cdot\vec{p}\frac{1}{r}\vec{p}\cdot\vec{P}, \tag{3.24}$$

$$\vec{p}_1\cdot\vec{p}_2\left[\frac{1}{r}\right]_\epsilon\vec{p}_1\cdot\vec{p}_2=\frac{1}{r}\left(\frac{P^2}{2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r}-E\right)^2+\pi\delta^d(r)\left(\frac{1}{\epsilon}+2\right), \tag{3.25}$$

$$\vec{P}\cdot\vec{p}\frac{1}{r}\vec{p}\cdot\vec{P}=-\vec{p}_1\times\vec{p}_2\frac{1}{r}\vec{p}_1\times\vec{p}_2-\frac{P^4}{4r}+\frac{P^2}{r}\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r}\right)-2\pi\delta^3(r)P^2. \tag{3.26}$$

We are now ready to eliminate divergences from matrix elements of δH_i operators. In the following we make replacement $\sigma_1\sigma_2\to-d(d-1)$. To show this, we consider matrix elements of spin operators with the helium singlet wave function in d dimensions. All terms with a single-spin operator vanish. The spin-spin operators of the form $\sigma_1^{ij}\sigma_2^{ik}(\delta^{jk}/d-r^jr^k/r^2)$ vanish because of angular integration. Only operators of the form $\sigma_1^{ij}\sigma_2^{ij}Q$ fail to vanish, and we use a definition which was implicitly assumed in Ref. [5]. Namely, we postulate the existence of the charge conjugation operator C, such that

$$C^{-1}=C^T, \tag{3.27}$$

$$C\vec{\sigma}_2^TC^{-1}=-\vec{\sigma}_1, \tag{3.28}$$

and singlet states ψ_S are defined by

$$\langle\psi_S|Q_1\otimes Q_2|\psi_S\rangle=\frac{1}{2}\,\mathrm{Tr}[Q_1CQ_2^TC^{-1}]. \tag{3.29}$$

Using this definition one obtains

$$\langle\psi_S|Q\sigma_1^{ij}\sigma_2^{ij}|\psi_S\rangle=-d(d-1)\langle\psi_S|Q|\psi_S\rangle, \tag{3.30}$$

for an arbitrary operator Q.

All δE_i corrections are now transformed as follows. The first term $\delta E_0=\langle\delta H_0\rangle$ becomes

$$\delta E_0=\frac{1}{16}\langle p_1^6+p_2^6\rangle=\frac{1}{16}\langle(p_1^2+p_2^2)^3-3p_1^2p_2^2(p_1^2+p_2^2)\rangle=\frac{1}{16}\left\langle 4[(\nabla_1V)^2+(\nabla_2V)^2]+8(E-V)^3-6p_1^2(E-V)p_2^2+3\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right\rangle. \tag{3.31}$$

All singular operators in E_0 can be handled by Eqs. (3.14)–(3.26), and all the singularities are identified in the form of $\phi^2(0)/\epsilon$. Next the terms $\delta E_1-\delta E_8$ are transformed in a similar way:

$$\delta E_1=\frac{1}{128}\left\{-4[(\nabla_1V)^2+(\nabla_2V)^2]-2\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right\}-\frac{3}{32}\left\{2\left(E+\frac{Z-1}{r_2}\right)4\pi Z\delta^3(r_1)+2\left(E+\frac{Z-1}{r_1}\right)\times4\pi Z\delta^3(r_2)-2\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right)4\pi Z\delta^3(r)-p_2^24\pi Z\delta^3(r_1)-p_1^24\pi Z\delta^3(r_2)\right\},$$

$$\delta E_2=-\frac{\pi}{16}\nabla^2\delta^d(r)-\frac{\pi}{16}\delta_\perp^{ij}P^iP^j+\frac{\pi}{4}\delta_\perp^{ij}p^ip^j, \tag{3.32}$$

$$\delta E_3=-\frac{1}{16}\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right], \tag{3.33}$$

$$\delta E_4=p_1^i(E-V)\frac{1}{2r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)p_2^j-\frac{1}{2}\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right)4\pi\delta^3(r)-\frac{1}{2}\left[\frac{1}{2r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)\right]_\epsilon\nabla^i\nabla^j\left[\frac{1}{r}\right]_\epsilon, \tag{3.34}$$

$$\delta E_5=\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}-\frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon, \tag{3.35}$$

$$\delta E_6=\frac{1}{8}p_1^i\frac{1}{r^2}\left(\delta^{ij}+3\frac{r^ir^j}{r^2}\right)p_1^j+\frac{1}{8}p_2^i\frac{1}{r^2}\left(\delta^{ij}+3\frac{r^ir^j}{r^2}\right)p_2^j+\frac{d-1}{4}\left[\frac{1}{r^4}\right]_\epsilon, \tag{3.36}$$

$$\delta E_8=\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}-\frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon-\frac{(d-1)}{32}\left[p_1^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]-\frac{(d-1)}{32}\times\left[p_2^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]. \tag{3.37}$$

The calculation of the E_7 contribution is lengthier, and we split it into four parts, corresponding to Eq. (2.51):

$$\delta E_7 = \delta E_{7A} + \delta E_{7B} + \delta E_{7C} + \delta E_{7D}. \tag{3.38}$$

Each part contains singular operators which are handled similarly to those in Eqs. (3.14)–(3.26):

$$\delta E_{7A} = -\frac{(d-1)}{16}\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right], \tag{3.39}$$

$$\delta E_{7B} = -\left(Z\frac{r_1^i}{r_1^3} - \frac{r^i}{r^3}\right)\left(Z\frac{r_2^j}{r_2^3} + \frac{r^i}{r^3}\right)\frac{(r^i r^j - 3\delta^{ij}r^2)}{8r} - \frac{\pi}{4}\delta^d(r)\left(\frac{1}{\epsilon} - 5\right), \tag{3.40}$$

$$\delta E_{7C} = -\frac{Z}{8}p_2^k\frac{r_1^i}{r_1^3}\left(\delta^{jk}\frac{r^i}{r} - \delta^{ik}\frac{r^j}{r} - \delta^{ij}\frac{r^k}{r} - \frac{r^i r^j r^k}{r^3}\right)p_2^j + \frac{1}{8}p_2^j\frac{(\delta^{jk}r^2 - 3r^j r^k)}{r^4}p_2^k - \frac{Z}{8}p_1^k\frac{r_2^i}{r_2^3}\left(\delta^{jk}\frac{r^i}{r} - \delta^{ik}\frac{r^j}{r} - \delta^{ij}\frac{r^k}{r} - \frac{r^i r^j r^k}{r^3}\right)p_1^j + \frac{1}{8}p_1^j\frac{(\delta^{jk}r^2 - 3r^j r^k)}{r^4}p_1^k + \frac{1}{4r^4} + \frac{\pi}{4}\delta^d(r)\left(\frac{1}{\epsilon} - 7\right), \tag{3.41}$$

$$\delta E_{7D} = \frac{1}{8}\vec{p}_1\times\vec{p}_2\frac{1}{r}\vec{p}_1\times\vec{p}_2 - \frac{1}{8}\vec{p}_1\cdot\vec{p}_2\left[\frac{1}{r}\right]_\epsilon\vec{p}_1\cdot\vec{p}_2 + \frac{1}{8}p_1^k p_2^l\left(-\frac{\delta^{jl}r^i r^k}{r^3} - \frac{\delta^{ik}r^j r^l}{r^3} + 3\frac{r^i r^j r^k r^l}{r^5}\right)p_1^i p_2^j. \tag{3.42}$$

At this point we have completed the elimination of singularities from the effective Hamiltonian. It remains to consider, however, the second-order matrix element E_A:

$$E_A = \left\langle H_A\frac{1}{(E_0-H_0)'}H_A\right\rangle, \tag{3.43}$$

which requires subtractions of $1/\epsilon$ singularities. For this we use the transformation

$$H_A = H_A' + \{H_0 - E_0, Q\}, \tag{3.44}$$

$$Q = -\frac{1}{4}\left[\frac{Z}{r_1} + \frac{Z}{r_2}\right]_\epsilon + \frac{(d-1)}{4}\left[\frac{1}{r}\right]_\epsilon, \tag{3.45}$$

so that

$$E_A = E_A' + E_A'', \tag{3.46}$$

$$E_A' = \left\langle H_A'\frac{1}{(E_0-H_0)'}H_A'\right\rangle, \tag{3.47}$$

$$E_A'' = \langle Q(E_0-H_0)Q\rangle + 2\langle H_A\rangle\langle Q\rangle - \langle\{H_A,Q\}\rangle = X_1 + X_2 + X_3. \tag{3.48}$$

E_A' is finite in the limit $\epsilon\to 0$, and

$$H_A'|\phi\rangle = \left\{-\frac{1}{2}(E_0-V)^2 - p_1^i\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j + \frac{1}{4}\vec{\nabla}_1^2\vec{\nabla}_2^2 - \frac{Z}{4}\frac{\vec{r}_1}{r_1^3}\cdot\vec{\nabla}_1 - \frac{Z}{4}\frac{\vec{r}_1}{r_1^3}\cdot\vec{\nabla}_1\right\}|\phi\rangle, \tag{3.49}$$

where $\vec{\nabla}_1^2\vec{\nabla}_2^2$ is understood as a differentiation of ϕ on the right-hand side as a function [omitting $\delta^3(r)$]. What remains is the calculation of X_i terms. The first two are simple:

$$X_1 = \frac{1}{32}\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon + \frac{(d-1)^2}{16}\left[\frac{1}{r^4}\right]_\epsilon - \frac{Z}{8}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}, \tag{3.50}$$

$$X_2 = 2E^{(4)}\left\langle -\frac{1}{4}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{1}{2r}\right\rangle. \tag{3.51}$$

To calculate X_3 we split it again into four parts, correspondingly,

$$X_3 = -2\left\langle\phi\left|\left\{-\frac{p_1^4}{8} - \frac{p_2^4}{8} + \frac{\pi Z}{2}[\delta^d(r_1) + \delta^d(r_2)] - \frac{1}{2}p_1^i\left[\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right]_\epsilon p_2^j + \pi(d-2)\delta^d(r)\right\}\times\left\{-\frac{1}{4}\left[\frac{Z}{r_1} + \frac{Z}{r_2}\right]_\epsilon + \frac{(d-1)}{4}\left[\frac{1}{r}\right]_\epsilon\right\}\right|\phi\right\rangle = X_{3A} + X_{3B} + X_{3C} + X_{3D}, \tag{3.52}$$

and calculate each part separately:

$$X_{3A} = \frac{1}{4}\langle(p_1^4 + p_2^4)Q\rangle = \frac{1}{4}\left\langle(p_1^2+p_2^2)Q(p_1^2+p_2^2) + \frac{1}{2}[p_1^2+p_2^2,[p_1^2+p_2^2,Q]] - 2p_1^2Qp_2^2 - [p_1^2,[p_2^2,Q]]\right\rangle$$
$$= \frac{1}{4}\left(E + \left[\frac{Z}{r_1} + \frac{Z}{r_2}\right]_\epsilon - \left[\frac{1}{r}\right]_\epsilon\right)^2\left((d-1)\left[\frac{1}{r}\right]_\epsilon - \left[\frac{Z}{r_1} + \frac{Z}{r_2}\right]_\epsilon\right) - \frac{1}{8}\left(\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon + 2(d-1)\left[\frac{1}{r^4}\right]_\epsilon - 3Z\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right) + \frac{1}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2 - \frac{(d-1)}{8}p_1^2\left[\frac{1}{r}\right]_\epsilon p_2^2 - \frac{(d-1)}{16}\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right], \tag{3.53}$$

$$X_{3B} = Z(Z-2)\frac{\pi}{4}\delta^3(r_1)\frac{1}{r_2} + Z(Z-2)\frac{\pi}{4}\delta^3(r_2)\frac{1}{r_1}, \tag{3.54}$$

$$X_{3C} = -\frac{1}{4}p_1^i\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{2}{r}\right)\frac{1}{r}\left(\delta^{ij}+\frac{r^ir^j}{r^3}\right)p_2^j + \frac{(d-1)}{4}\left[\frac{1}{2r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)\right]_\epsilon \nabla^i\nabla^j\left[\frac{1}{r}\right]_\epsilon, \tag{3.55}$$

$$X_{3D} = \frac{\pi}{2}\delta^3(r)\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right). \tag{3.56}$$

The last term to be considered is H_H in Eq. (2.55). One transforms it into atomic units by the replacement in Eq. (3.2) and division by the factor in Eq. (3.4). As a result one obtains

$$H_H = \left(-\frac{1}{\epsilon} - 4\ln\alpha - \frac{39\zeta(3)}{\pi^2} + \frac{32}{\pi^2} - 6\ln(2) + \frac{7}{3}\right)\frac{\pi}{4}\delta^d(r) = H_H' - \left(\frac{1}{\epsilon}+4\ln\alpha\right)\frac{\pi}{4}\delta^d(r). \tag{3.57}$$

At this point we have separated out all singularities. They always have the form of $\phi^2(0)/\epsilon$ and finally cancel between themselves. The sum of all terms, which is the main result of this work, is

$$\begin{aligned}
E^{(6)} = {} & -\frac{E_0^3}{2} + \left[\left(-E_0+\frac{3}{2}p_2^2+\frac{1-2Z}{r_2}\right)\frac{Z\pi}{4}\delta^3(r_1)+(1\leftrightarrow 2)\right] + \left(1-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{P^2}{3}\right)\frac{\pi}{2}\delta^3(r) + \frac{E_0^2+2E^{(4)}}{4r} - \frac{E_0}{2r^2} + \frac{1}{4r^3} \\
& - \frac{E_0}{2r}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right) + \frac{E_0}{4}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)^2 - \frac{1}{4r^2}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right) - \frac{1}{4r}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)^2 + \frac{Z^2}{2r_1r_2}\left(E_0+\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r}\right) + \frac{Z}{32}\left(\frac{\vec r_1}{r_1^3}-\frac{\vec r_2}{r_2^3}\right)\cdot\frac{\vec r}{r^3} \\
& + \frac{Z}{4}\left(\frac{\vec r_1}{r_1^3}-\frac{\vec r_2}{r_2^3}\right)\cdot\frac{\vec r}{r^2} - \frac{Z^2}{8}\frac{r_1^i}{r_1^3}\frac{(r^ir^j-3\delta^{ij}r^2)}{r}\frac{r_2^j}{r_2^3} + \left[\frac{Z^2}{8}\frac{1}{r_1^2}\vec p_2^{\,2} + \frac{Z^2}{8}\vec p_1\frac{1}{r_1^2}\vec p_1 + \frac{1}{2}\vec p_1\frac{1}{r^2}\vec p_1 + (1\leftrightarrow 2)\right] + \frac{1}{4}p_1^i\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\frac{(r^ir^j+\delta^{ij}r^2)}{r^3}p_2^j \\
& - \frac{1}{32}P^i\frac{(3r^ir^j-\delta^{ij}r^2)}{r^5}P^j - \left[\frac{Z}{8}p_2^k\frac{r_1^i}{r_1^3}\left(\frac{\delta^{jk}r^i}{r}-\frac{\delta^{ik}r^j}{r}-\frac{\delta^{ij}r^k}{r}-\frac{r^ir^jr^k}{r^3}\right)p_2^j + (1\leftrightarrow 2)\right] - \frac{E_0}{8}p_1^2p_2^2 - \frac{1}{4}p_1^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)p_2^2 + \frac{1}{4}\vec p_1 \\
& \times\vec p_2\frac{1}{r}\vec p_1\times\vec p_2 + \frac{1}{8}p_1^kp_2^l\left(-\frac{\delta^{jl}r^ir^k}{r^3}-\frac{\delta^{ik}r^jr^l}{r^3}+3\frac{r^ir^jr^kr^l}{r^5}\right)p_1^ip_2^j + E_H' + E_A' + E_C + E_{R1} + E_{R2} - \ln(\alpha)\pi\delta^d(r),
\end{aligned} \tag{3.58}$$

where $E_H'=\langle H_H'\rangle$ from Eq. (3.57), E_A' is defined in Eq. (3.47), E_C in Eq. (4.12), E_{R1} and E_{R2} in Eqs. (2.56) and (2.57), correspondingly. In addition to various identities in Eqs. (3.19)–(3.26), we used two further equations

$$\left\langle\frac{Z}{r_1}+\frac{Z}{r_2}\right\rangle = \left\langle\frac{1}{r}\right\rangle - 2E_0, \tag{3.59}$$

$$\left\langle p_1^i\frac{(r^ir^i+\delta^{ij}r^2)}{r^3}p_2^j\right\rangle = -2E^{(4)} - \left(E_0+\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r}\right)^2 + \frac{p_1^2p_2^2}{2} + \pi Z[\delta^3(r_1)+\delta^3(r_2)] + 2\pi\delta^3(r) \tag{3.60}$$

to simplify final expression. The logarithmic term in Eq. (3.58) agrees with that obtained in Ref. [18]. The sum of "soft" operators [Eq. (3.58) without the last six terms] after $(1\leftrightarrow 2)$ simplification becomes

$$\begin{aligned}
E_Q = {} & -\frac{E_0^3}{2} - \frac{E_0Z}{8}Q_1 + \frac{1}{8}Q_2 - \frac{Z(2Z-1)}{8}Q_3 + \frac{3Z}{16}Q_4 - \frac{Z}{4}Q_5 + \frac{1}{24}Q_6 + \frac{E_0^2+2E^{(4)}}{4}Q_7 - \frac{E_0}{2}Q_8 + \frac{1}{4}Q_9 + \frac{E_0Z^2}{2}Q_{11} + E_0Z^2Q_{12} \\
& - E_0ZQ_{13} - Z^2Q_{14} + Z^3Q_{15} - \frac{Z^2}{2}Q_{16} - \frac{Z}{2}Q_{17} + \frac{Z}{16}Q_{18} + \frac{Z}{2}Q_{19} - \frac{Z^2}{8}Q_{20} + \frac{Z^2}{4}Q_{21} + \frac{Z^2}{4}Q_{21} + \frac{Z^2}{4}Q_{22} + Q_{23} + \frac{Z}{2}Q_{24} - \frac{1}{32}Q_{25} \\
& - \frac{Z}{4}Q_{26} - \frac{E_0}{8}Q_{27} - \frac{Z}{2}Q_{28} + \frac{1}{4}Q_{29} + \frac{1}{8}Q_{30},
\end{aligned} \tag{3.61}$$

where Q_i are defined in Table I.

TABLE I. Expectation values of operators entering $H^{(6)}$ for the $1S$ state, $\vec{r}=\vec{r}_1-\vec{r}_2$.

$Q_1=4\pi\delta^3(r_1)$	22.750 526
$Q_2=4\pi\delta^3(r)$	1.336 375
$Q_3=4\pi\delta^3(r_1)/r_2$	33.440 565
$Q_4=4\pi\delta^3(r_1)p_2^2$	49.160 046
$Q_5=4\pi\delta^3(r)/r_1$	5.019 714
$Q_6=4\pi\delta^3(r)P^2$	18.859 765
$Q_7=1/r$	0.945 818
$Q_8=1/r^2$	1.464 771
$Q_9=1/r^3$	0.989 274
$Q_{10}=1/r^4$	−3.336 383
$Q_{11}=1/r_1^2$	6.017 409
$Q_{12}=1/(r_1r_2)$	2.708 655
$Q_{13}=1/(r_1r)$	1.920 944
$Q_{14}=1/(r_1r_2r)$	4.167 175
$Q_{15}=1/(r_1^2r_2)$	9.172 094
$Q_{16}=1/(r_1^2r)$	8.003 454
$Q_{17}=1/(r_1r^2)$	3.788 791
$Q_{18}=(\vec{r}_1\cdot\vec{r})/(r_1^3r^3)$	3.270 472
$Q_{19}=(\vec{r}_1\cdot\vec{r})/(r_1^3r^2)$	1.827 027
$Q_{20}=r_1^ir_2^j(r^ir^j-3\delta^{ij}r^2)/(r_1^3r_2^3r)$	0.784 425
$Q_{21}=p_2^2/r_1^2$	14.111 960
$Q_{22}=\vec{p}_1/r_1^2\vec{p}_1$	21.833 598
$Q_{23}=\vec{p}_1/r^2\vec{p}_1$	4.571 652
$Q_{24}=p_1^i(r^ir^j+\delta^{ij}r^2)/(r_1r^3)p_2^j$	0.811 933
$Q_{25}=P^i(3r^ir^j-\delta^{ij}r^2)/r^5P^j$	−3.765 488
$Q_{26}=p_2^kr_1^i/r_1^3(\delta^{jk}r^i/r-\delta^{ik}r^j/r-\delta^{ij}r^k/r-r^ir^jr^k/r^3)p_2^j$	−0.266 894
$Q_{27}=p_1^2p_2^2$	7.133 710
$Q_{28}=p_1^2/r_1p_2^2$	37.010 642
$Q_{29}=\vec{p}_1\times\vec{p}_2/r\vec{p}_1\times\vec{p}_2$	4.004 703
$Q_{30}=p_1^kp_2^l(-\delta^{jl}r^ir^k/r^3-\delta^{ik}r^jr^l/r^3+3r^ir^jr^kr^l/r^5)p_1^ip_2^j$	−1.591 864

IV. NUMERICAL CALCULATIONS OF MATRIX ELEMENTS

The helium wave function is expanded in a basis set of exponential functions in the form of [19]

$$\phi(r_1,r_2,r)=\sum_{i=1}^{\mathcal{N}} v_i[e^{-\alpha_ir_1-\beta_ir_2-\gamma_ir}+(r_1\leftrightarrow r_2)], \quad (4.1)$$

where α_i, β_i, and γ_i are generated randomly with conditions

$$A_1<\alpha_i<A_2, \quad \beta_i+\gamma_i>\varepsilon, \quad (4.2)$$

$$B_1<\beta_i<B_2, \quad \alpha_i+\gamma_i>\varepsilon, \quad (4.3)$$

$$C_1<\gamma_i<C_2, \quad \alpha_i+\beta_i>\varepsilon. \quad (4.4)$$

In order to obtain a highly precise wave function following Korobov [19], we use a double set of the form (4.1). Each parameter A_i, B_i, C_i, and ε is determined by energy minimization, with the condition that $\varepsilon>0$, which is necessary for the normalizability of the wave function. The linear coefficients v_i in Eq. (4.1) form a vector v, which is a solution of the generalized eigenvalue problem

$$Hv=ENv, \quad (4.5)$$

where H is a matrix of the Hamiltonian in this basis set, N is a normalization (overlap) matrix, and E an eigenvalue, the energy of the state corresponding to v. For the solution of the eigenvalue problem with $\mathcal{N}=100,300,600,900,1200,1500$ we use LU decomposition in quadruple and sextuple precision. As a result we obtain the following nonrelativistic energies in a.u.:

$$E_0(1^1S_0)=-2.903\,724\,377\,034\,119\,592(6), \quad (4.6)$$

$$E_0(2^1S_0)=-2.145\,974\,046\,054\,417\,311(50). \quad (4.7)$$

These values agree with the more accurate result of Korobov [19] and Drake [20]. The calculation of matrix elements of nonrelativistic Hamiltonian can be performed with the use of one formula

$$\frac{1}{16\pi^2}\int d^3r_1\int d^3r_2\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1r_2r}=\frac{1}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}. \quad (4.8)$$

The result with any additional powers of r_i in the numerator can be obtained by differentiation with respect to the corresponding parameter α, β, or γ. The matrix elements of relativistic corrections involve inverse powers of r_1, r_2, and r. These can be obtained by integration with respect to corresponding parameter. This leads to the appearance of logarithmic and dilogarithmic functions—for example,

$$\frac{1}{16\pi^2}\int d^3r_1\int d^3r_2\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1r_2r^2}=\frac{1}{(\beta+\alpha)(\alpha+\beta)}\ln\left(\frac{\beta+\gamma}{\alpha+\gamma}\right), \quad (4.9)$$

$$\frac{1}{16\pi^2}\int d^3r_1\int d^3r_2\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1^2r_2r^2}=\frac{1}{2\beta}\left[\frac{\pi^2}{6}+\frac{1}{2}\ln^2\left(\frac{\alpha+\beta}{\beta+\gamma}\right)+\mathrm{Li}_2\left(1-\frac{\alpha+\gamma}{\alpha+\beta}\right)+\mathrm{Li}_2\left(1-\frac{\alpha+\gamma}{\beta+\gamma}\right)\right]. \quad (4.10)$$

All matrix elements involved in the $m\alpha^6$ correction (see Table I) can be expressed in terms of rational, logarithmic, and dilogarithmic functions, as above. The high quality of the wave function allows us to obtain precise matrix elements of $H^{(6)}$ operators, and the numerical results are presented in Table I. Some of these matrix elements have already been calculated in [21], and results in Table I are in agreement with them.

The calculation of second-order corrections E_A' and E_C is more complicated. The spin algebra in the second-order matrix element E_C is simplified with the help of

TABLE II. Contributions to $E^{(6)}$ for $1S$ and $2S$ states of the helium atom. E_{LG} is the logarithmic correction, last term in Eq. (3.58).

$m\alpha^6$	He$(1\,^1S)$	He$(2\,^1S)$	ΔE
E_Q	15.465 431	12.310 132	−3.155 299
E'_H	−0.278 403	−0.022 641	0.255 762
E'_A	−18.495 345(50)	−16.280 186(10)	2.215 159(50)
E_C	−0.392 621	−0.033 790	0.358 831
Subtotal	−3.700 937(50)	−4.026 485(10)	−0.325 547(50)
E_{R1}	141.924 288	100.971 873	−40.952 415
E_{R2}	1.144 012	0.890 559	−0.253 453
E_{LG}	1.643 823	0.133 682	−1.510 141
Total	141.011 185(50)	97.969 630(10)	−43.041 555(50)
$-E_D(\mathrm{He}^+)$	4.000 000	4.000 000	0.000 000
$-E_{R1}(\mathrm{He}^+)$	−97.971 914	−97.971 914	0.000 000
$-E_{R2}(\mathrm{He}^+)$	−0.873 699	−0.873 699	0.000 000
$E^{(6)}(\mathrm{He})$-$E^{(6)}(\mathrm{He}^+)$	46.165 572(50)	3.124 017(10)	−43.041 555(50)

$$|^1S_0\rangle\langle^1S_0| = |S_0\rangle\langle S_0|\left(1-\frac{\vec{s}^2}{2}\right), \tag{4.11}$$

where $\langle\vec{r}_1,\vec{r}_2|S_0\rangle$ is the wave function without spin and $\vec{s}=(\vec{\sigma}_1+\vec{\sigma}_2)/2$, so that

$$E_C = \left\langle S_0\left|\vec{C}\frac{1}{E_0-H_0}\vec{C}\right|S_0\right\rangle, \tag{4.12}$$

$$\vec{C} = \frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1-\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)+\frac{1}{4}\frac{\vec{r}}{r^3}\times(\vec{p}_1+\vec{p}_2). \tag{4.13}$$

The inversion of the operator E_0-H_0 in this expression is performed in a basis set of even parity functions with $l=1$ of the form

$$\vec{\phi}(r_1,r_2,r) = \sum_i v_i\vec{r}_1\times\vec{r}_2[e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r}+(r_1\leftrightarrow r_2)] \tag{4.14}$$

The values of parameters A_i, B_i, and C_i corresponding to $\vec{\phi}$ are obtained by minimization of E_C, and the results of these calculations are presented in Table II. The calculation of E'_A is similar to that of E_C, but additionally requires a subtraction of the reference state from the implicit sum over states. We obtain this by orthogonalization of $H'_A|\phi\rangle$ with respect to eigenstate with closest to 0 eigenvalue of $H-E$. This eigenvalue is not exactly equal to 0, because we use a basis set with different parameters, which are obtained by minimization of E'_A. The results are presented in Table II. Surprisingly, the total nonlogarithmic exchange contribution after subtraction of the He^+ value is very small—namely 0.299 063for the $1S$ state and −0.026 485 for the $2S$ state. This contribution is much smaller than the dominating one-loop contribution E_{R1} which is 43.952 374 and 2.999 959 correspondingly. It is similar for the triplet states $2\,^3S_1$ and $2\,^3P_1$ of helium and means that higher-order corrections can be well approximated by the one-loop self-energy contribution.

V. SUMMARY

We have derived the complete order-$m\alpha^6$ contribution to energy levels of singlet states of helium. It is expressed as the expectation value of the operators in Eq. (3.58). A similar, but not identical set of operators have been obtained previously by Yelkhovsky, Eq. (97) in [6], and the results obtained here are in slight disagreement (see Appendix C for details). The matrix elements of operators entering Eq. (3.58) for the ground state of the helium atom are presented in Table I, and a few of them are in disagreement with the results presented in Ref. [5]. Because of these discrepancies, the calculations presented here should be verified before definite conclusions can be made.

In this work we performed numerical calculations for the ground $1\,^1S_0$ and excited $2\,^1S_0$ states, and the results are presented in Table II. While the calculation of the E_Q operators was quite complicated, their contribution to $E^{(6)}$ is relatively small. The dominating contribution comes from the one-loop electron self-energy E_{R1} and is given by Dirac δ functions; see Eq. (2.56).

The summary of all known contributions to $1\,^1S_0$-$2\,^1S_0$ transition is presented in Table III. The nonrelativistic energy here, $E^{(2)}$, is the sum of μE_0 from Eqs. (4.6) and (4.7) with μ being the reduced mass and mass polarization corrections from Ref. [20]. The relativistic contribution $E^{(4)}$ is taken from Ref. [25] and includes nuclear recoil. The leading QED contribution $E^{(5)}$ also includes nuclear recoil [26], and we use Bethe logarithms as obtained by Drake and Goldman [27]. Our value for $E^{(5)}$ is greater by about 12 MHz from that of Korobov and Yelkhovsky (KY) [5], which is

TABLE III. Contributions to $1S$ and $2S$ ionization energies of the helium atom in MHz. Physical constants from [22], R_∞=1 097 3731.568 525(73) m^{-1}, α=1/137.035 999 11(46), $\lambda\!\!\!^-_e$=386.159 267 8(26) fm, m_α/m_e =7294.299 536 3(32), r_α=1.673 fm, c=299 792 458. The uncertainty for $E^{(7)}$ is due to its approximate calculation and is roughly estimated to be about half of $E^{(7)}$.

	$\nu(1\,^1S)$	$\nu(2\,^1S)$	$\Delta\nu(2\,^1S\text{-}1\,^1S)$
$E^{(2)}$	−5 945 262 288.61	−960 322 874.90	4 984 939 413.71
$E^{(4)}$	16 800.32	−11 974.80	−28 75.12
$E^{(5)}$	40 495.81	2 755.14	−37 740.68
$E^{(6)}$	861.24	58.28	−802.96
$E^{(7)}$	−72.(36)	−4.(2)	68.(34)
$E_{\rm FS}$	29.58	1.99	−27.59
Theory	−5 945 204 174.(36)	−960 332 038.(2)	4 984 872 136.(34)
V.K. and A.Y. [5]	−5 945 204 223.(42)		
Drake [20]	−5 945 204 223.(91)	−960 332 041.(25)	4 984 872 182.(91)
Expt. [24]	−5 945 204 356.(48)	−960 332 041.01(15)	4 984 872 315.(48)
Expt. [23]	−5 945 204 238.(45)		f

40 483.98(5) MHz, and we do not understand a reason for this discrepancy. We have not been able to find in the literature the result of Drake for $E^{(5)}$ as well as separate results for higher-order terms. However, the total result of Drake (see Table III) is in agreement with that of Ref. [5]. $E^{(6)}$ is obtained here, and our result is greater by about 25 MHz from the result in Ref. [5], which is 834.9(2). The source of this deviation is explained in Appendix C. $E^{(7)}$ includes all electron-nucleus terms of order $m\alpha^7$ which are known from the hydrogen Lamb shift [15] (one-, two-, and three-loop contributions) and are extended to helium in the standard way. Our value is larger by 12 MHz from the result of Ref. [5], −84(42), because we include all α^7 terms, not only the leading $\ln^2(\alpha)$. The current theoretical uncertainty comes mainly from the approximate treatment of these higher-order terms. The exact calculation of $E^{(7)}$ is at present very difficult, due to high complexity in the derivation of $H^{(7)}$, and thus limits the accuracy of theoretical predictions. Our final theoretical predictions are in moderate agreement with the measurement of Eikema *et al.* [23] and disagree significantly with the measurement by Bergeson *et al.* [24].

Having the exact formula for $m\alpha^6$ corrections for singlet and as well as triplet states [28], it is possible now to improve theoretical predictions for higher excited states of helium, as well as light heliumlike ions. The extension of this approach to three- and more-electron atoms or molecules is possible, but not all technical problems in calculating matrix elements in explicitly correlated basis set have been resolved yet.

ACKNOWLEDGMENT

I wish to acknowledge valuable comments from V. Korobov.

APPENDIX A: DIMENSIONALLY REGULARIZED QED OF BOUND STATES

The dimension of space is assumed to be $d=3-2\epsilon$. The surface area of d-dimensional unit sphere can be obtained by considering the following integral:

$$I=\int d^dk e^{-\vec{k}^2}. \tag{A1}$$

In Cartesian coordinates it is a product of d one-dimensional integrals,

$$I=\left[\int dk e^{-k^2}\right]^d=\pi^{d/2}, \tag{A2}$$

while in spherical coordinates it is

$$I=\int d\Omega_d\int_0^\infty dk k^{d-1}e^{-k^2}=\Omega_d\frac{1}{2}\Gamma(d/2). \tag{A3}$$

From comparison with Eqs. (A2) and (A3) one obtains

$$\Omega_d=\frac{2\pi^{d/2}}{\Gamma(d/2)}. \tag{A4}$$

The d-dimensional Laplacian is $\nabla^2=\partial^i\partial^i$. For spherically symmetric functions f and g,

$$\int d^dr\nabla^2(f)g=-\int d^dr\,\nabla(f)\cdot\nabla(g)=-\Omega_d\int dr r^{d-1}\partial_r f\partial_r g$$
$$=\Omega_d\int dr\partial_r(r^{d-1}\partial_r f)g=\int d^dr r^{1-d}\partial_r(r^{d-1}\partial_r f)g, \tag{A5}$$

the Laplacian takes the form

$$\nabla^2=r^{1-d}\partial_r r^{d-1}\partial_r. \tag{A6}$$

The photon propagator, and thus the Coulomb interaction, preserves its form in the momentum representation, while in the coordinate representation it is

$$\mathcal{V}(r) = \int \frac{d^d k}{(2\pi)^d} \frac{4\pi}{k^2} e^{i\vec{k}\cdot\vec{r}} = \pi^{\epsilon-1/2}\Gamma(1/2-\epsilon) r^{2\epsilon-1} \equiv \frac{C_1}{r^{1-2\epsilon}}. \tag{A7}$$

The alternative derivation of $\mathcal{V}(r)$ which omits the calculation of Fourier transform is the following. Consider the equation

$$\nabla^2 \mathcal{V}(r) = -4\pi\delta^d(r). \tag{A8}$$

If one assumes that $\mathcal{V}(r)$ is of the form $\mathcal{V}(r)=Cr^\gamma$, then, for $r\neq 0$,

$$r^{1-d}\partial_r r^{d-1}\partial_r(Cr^\gamma) = 0, \tag{A9}$$

and therefore $\gamma=2-d=2\epsilon-1$. The coefficient C is obtained by considering the integral with the trial function f:

$$\begin{aligned}4\pi f(0) &= -\int d^d r \nabla^2(\mathcal{V}) f = \int d^d r \nabla(\mathcal{V})\cdot\nabla(f)\\ &= \lim_{\varepsilon\to 0}\int_\varepsilon dr r^{d-1}\Omega_d \partial_r(\mathcal{V})\partial_r(f)\\ &= \lim_{\varepsilon\to 0}\left[r^{d-1}\Omega_d\partial_r(\mathcal{V})f\big|_{r=\varepsilon} - \int_\varepsilon dr \Omega_d \partial_r(r^{d-1}\partial_r(\mathcal{V}))f\right]\\ &= \lim_{\varepsilon\to 0}\Omega_d \varepsilon^{d-1}\partial_\varepsilon(C\varepsilon^{2-d})f(\varepsilon) = \Omega_d(2-d)Cf(0);\end{aligned} \tag{A10}$$

therefore,

$$C \equiv C_1 = \frac{4\pi}{(d-2)\Omega_d} = \pi^{\epsilon-1/2}\Gamma(1/2-\epsilon). \tag{A11}$$

We are now ready to consider quantum mechanics in d dimensions. The nonrelativistic Hamiltonian of hydrogenlike systems is

$$H_0 = \frac{\vec{p}^2}{2} - Z\frac{C_1}{r^{1-2\varepsilon}} \tag{A12}$$

and of heliumlike systems

$$H_0 = \frac{\vec{p}_1^{\,2}}{2} + \frac{\vec{p}_2^{\,2}}{2} - Z\frac{C_1}{r_1^{1-2\epsilon}} - Z\frac{C_1}{r_2^{1-2\epsilon}} + \frac{C_1}{r_{12}^{1-2\epsilon}}. \tag{A13}$$

The solution of stationary Schrödinger equation $H_0\phi=E_0\phi$ we denote by ϕ and will never refer to its explicit (and unknown) form in d dimensions. Instead, we will use only the generalized cusp condition to eliminate various singularities from matrix elements with relativistic operators. Namely, we expect that, for small $r\equiv r_{12}$,

$$\phi(r) \approx \phi(0)(1-Cr^\gamma), \tag{A14}$$

with some coefficient C and γ to be obtained from the two-electron Schrödinger equation around $r=0$:

$$[-\nabla^2 + \mathcal{V}(r)]\phi(0)(1-Cr^\gamma) \approx E\phi(0)(1-Cr^\gamma). \tag{A15}$$

From the cancellation of small r singularities of the left-hand side of the above equation, one obtains

$$\gamma = 1+2\epsilon, \tag{A16}$$

$$C \equiv C_2 = \frac{1}{4}\pi^{\epsilon-1/2}\Gamma(-1/2-\epsilon). \tag{A17}$$

Therefore, the two-electron wave function around $r_{12}=0$ behaves as

$$\phi(\vec{r}_1,\vec{r}_2) \approx \phi(r_{12}=0)(1-C_2 r_{12}^{1+2\epsilon}). \tag{A18}$$

Apart from the Coulomb potential $\mathcal{V}(r)$ in coordinate space, we need also other functions, which appear in the calculations of relativistic operators—namely,

$$\mathcal{V}_2(r) = \int \frac{d^d k}{(2\pi)^d}\frac{4\pi}{k^4}e^{i\vec{k}\cdot\vec{r}}, \tag{A19}$$

$$\mathcal{V}_3(r) = \int \frac{d^d k}{(2\pi)^d}\frac{4\pi}{k^6}e^{i\vec{k}\cdot\vec{r}}. \tag{A20}$$

They can be obtained from the differential equations

$$-\nabla^2\mathcal{V}_2(r) = \mathcal{V}(r), \tag{A21}$$

$$-\nabla^2\mathcal{V}_3(r) = \mathcal{V}_2(r), \tag{A22}$$

with the results

$$\mathcal{V}_2(r) = C_2 r^{1+2\epsilon}, \tag{A23}$$

$$\mathcal{V}_3(r) = C_3 r^{3+2\epsilon}, \tag{A24}$$

with C_2 defined in Eq. (A17) and

$$C_3 = \frac{1}{32}\pi^{\epsilon-1/2}\Gamma(-3/2-\epsilon). \tag{A25}$$

Using $\mathcal{V}_i$ we calculate various integrals involving the photon propagator in the Coulomb gauge—namely,

$$\begin{aligned}&\int \frac{d^d k}{(2\pi)^d}\frac{4\pi}{k^4}\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right)e^{i\vec{k}\cdot\vec{r}}\\ &= \delta^{ij}\mathcal{V}_2 + \partial^i\partial^j\mathcal{V}_3\\ &= \pi^{\epsilon-1/2}r^{-1+2\epsilon}\left[\frac{3}{16}\delta^{ij}\Gamma(-1/2-\epsilon)r^2 + \frac{1}{8}\Gamma(1/2-\epsilon)r^i r^j\right]\\ &\equiv \left[\frac{1}{8r}(r^i r^j - 3\delta^{ij}r^2)\right]_\epsilon,\end{aligned} \tag{A26}$$

$$\begin{aligned}&\int \frac{d^d k}{(2\pi)^d}\frac{4\pi}{k^2}\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right)e^{i\vec{k}\cdot\vec{r}}\\ &= \delta^{ij}\mathcal{V} + \partial^i\partial^j\mathcal{V}_2\\ &= \pi^{\epsilon-1/2}r^{-3+2\epsilon}\left[\frac{1}{2}\delta^{ij}\Gamma(1/2-\epsilon)r^2 + \Gamma(3/2-\epsilon)r^i r^j\right]\\ &\equiv \left[\frac{1}{2r^3}(\delta^{ij}r^2 + r^i r^j)\right]_\epsilon,\end{aligned} \tag{A27}$$

and

$$\int \frac{d^dk}{(2\pi)^d}4\pi\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)e^{i\vec{k}\cdot\vec{r}}$$
$$=\frac{(d-1)}{d}\delta^{ij}4\pi\delta^d(r)+\left(\partial^i\partial^j-\frac{\delta^{ij}}{d}\partial^2\right)\mathcal{V}$$
$$=\frac{(d-1)}{d}\delta^{ij}4\pi\delta^d(r)+\pi^{\epsilon-1/2}r^{-5+2\epsilon}$$
$$\times[-2\delta^{ij}\Gamma(3/2-\epsilon)r^2+4\Gamma(5/2-\epsilon)r^ir^j]$$
$$=\left[\frac{2}{3}\delta^{ij}4\pi\delta^3(r)+\frac{1}{r^5}(3r^ir^j-\delta^{ij}r^2)\right]_\epsilon$$
$$\equiv \delta_\perp^{ij}. \tag{A28}$$

APPENDIX B: FOLDY-WOUTHUYSEN TRANSFORMATION IN *d* DIMENSIONS

The Foldy-Wouthuysen (FW) transformation [2,29] is the nonrelativistic expansion of the Dirac Hamiltonian in an external electromagnetic field. Here we extend this transformation to the arbitrary dimension d of space. The Dirac Hamiltonian in the external electromagnetic field is

$$H=\vec{\alpha}\cdot\vec{\pi}+\beta m+eA^0, \tag{B1}$$

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

$$\alpha^i=\begin{pmatrix}0 & \sigma^i\\ \sigma^i & 0\end{pmatrix},\quad \beta=\begin{pmatrix}I & 0\\ 0 & -I\end{pmatrix}, \tag{B2}$$

and

$$\{\sigma^i,\sigma^j\}=2\delta^{ij}I. \tag{B3}$$

The FW transformation S [29] leads to a new Hamiltonian

$$H_{\rm FW}=e^{iS}(H-i\partial_t)e^{-iS}, \tag{B4}$$

which decouples the upper and lower components of the Dirac wave function up to a specified order in the $1/m$ expansion. Here we calculate FW Hamiltonian up to terms which contribute to the $m\alpha^6$ correction to the energy. We use a convenient form of the Foldy-Wouthuysen operator S, which can be written as

$$S=-\frac{i}{2m}\Bigg\{\beta\vec{\alpha}\cdot\vec{\pi}-\frac{1}{3m^2}\beta(\vec{\alpha}\cdot\vec{\pi})^3+\frac{1}{2m}[\vec{\alpha}\cdot\vec{\pi},eA^0-i\partial_t]$$
$$+\frac{\beta}{5m^4}(\vec{\alpha}\cdot\vec{\pi})^5-\frac{\beta e}{4m^2}\vec{\alpha}\cdot\dot{\vec{E}}+\frac{ie}{24m^3}[\vec{\alpha}\cdot\vec{\pi},[\vec{\alpha}\cdot\vec{\pi},\vec{\alpha}\cdot\vec{E}]]$$
$$-\frac{ie}{3m^3}\{(\vec{\alpha}\cdot\vec{\pi})^2,\vec{\alpha}\cdot\vec{E}\}\Bigg\}. \tag{B5}$$

The FW Hamiltonian is expanded in a power series in S,

$$H_{\rm FW}=\sum_{j=0}^{6}\mathcal{H}^{(j)}+\cdots, \tag{B6}$$

where

$$\mathcal{H}^{(0)}=H,$$
$$\mathcal{H}^{(1)}=[iS,\mathcal{H}^{(0)}-i\partial_t],$$
$$\mathcal{H}^{(j)}=\frac{1}{j}[iS,\mathcal{H}^{(j-1)}]\quad \text{for } j>1, \tag{B7}$$

and higher-order terms in this expansion, denoted by overdots, are neglected. The calculations of subsequent commutators is rather tedious but the result simple

$$H_{\rm FW}=eA^0+\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2m}-\frac{(\vec{\sigma}\cdot\vec{\pi})^4}{8m^3}+\frac{(\vec{\sigma}\cdot\vec{\pi})^6}{16m^5}$$
$$-\frac{ie}{8m^2}[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}]-\frac{e}{16m^3}\{\vec{\pi},\partial_t\vec{E}\}$$
$$-\frac{ie}{128m^4}[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}]]]$$
$$+\frac{ie}{16m^4}\{(\vec{\sigma}\cdot\vec{\pi})^2,[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}]\}. \tag{B8}$$

There is some arbitrariness in the operator S, which means that $H_{\rm FW}$ is not unique. The standard approach [29], which relies on subsequent use of FW transformations, differs from this one in $d=3$ by the transformation S with some additional even operator.

Our aim here is to obtain the Hamiltonian for further calculations of the $m\alpha^6$ contribution to the energy levels of an arbitrary light atom. For this one can neglect the vector potential $\vec{A}$ in all the terms having m^4 and m^5 in the denominator. Moreover, less obviously, one can neglect the term with $\vec{\sigma}\cdot\vec{A}\vec{\sigma}\cdot\dot{\vec{E}}$ and the $\vec{B}^2$ term. It is because they are of second order in electromagnetic fields which additionally contain derivatives and thus contribute only at higher orders. After these simplifications, $H_{\rm FW}$ takes the form

$$H_{\rm FW}=eA^0+\frac{\pi^2}{2m}-\frac{e}{4m}\sigma^{ij}B^{ij}-\frac{\pi^4}{8m^3}-\frac{e}{8m^2}(\vec{\nabla}\cdot\vec{E}$$
$$+\sigma^{ij}\{E^i,\pi^j\})+\frac{e}{16m^3}\{\sigma^{ij}B^{ij},p^2\}-\frac{e}{16m^3}\{\vec{p},\partial_t\vec{E}\}$$
$$+\frac{3e}{32m^4}\{\sigma^{ij}E^ip^j,p^2\}+\frac{e}{128m^4}[p^2,[p^2,A^0]]$$
$$-\frac{3e}{64m^4}\{p^2,\nabla^2A^0\}+\frac{p^6}{16m^5}, \tag{B9}$$

where

$$\sigma^{ij}=\frac{1}{2i}[\sigma^i,\sigma^j], \tag{B10}$$

$$B^{ij}=\partial^iA^j-\partial^jA^i, \tag{B11}$$

$$E^i=-\nabla^iA^0-\partial_tA^i. \tag{B12}$$

APPENDIX C: COMPARISON TO FORMER WORKS

A similar, but not identical set of operators in Eq. (3.58) has been obtained by Yelkhovsky, Eq. (97) in [6]. When his operators are transformed by using the three equations

$$\left\langle \frac{i}{r^3}\left(\frac{\vec{r}}{r}\cdot\vec{p}-\frac{1}{2}\right)\right\rangle = \frac{1}{4}\left\langle \vec{p}_1\frac{1}{r^2}\vec{p}_1+\vec{p}_2\frac{1}{r^2}\vec{p}_2-\frac{2}{r^2}\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right) + 4\pi\delta^3(r)\right\rangle, \tag{C1}$$

$$\left\langle \frac{i}{r_1^3}\left(\frac{\vec{r}_1}{r_1}\cdot\vec{p}_1+Z\right)\right\rangle = \frac{1}{2}\left\langle \vec{p}_1\frac{1}{r_1^2}\vec{p}_1-\frac{2}{r_1^2}\left(E+\frac{Z}{r_1}-\frac{1}{r}-\frac{p_1^2}{2}\right) - 4Z\pi\delta^3(r_1)\right\rangle, \tag{C2}$$

$$\frac{1}{8}p_1^k p_1^i\left(-\frac{\delta^{jl}r^ir^k}{r^3}-\frac{\delta^{ik}r^jr^l}{r^3}+3\frac{r^ir^jr^kr^l}{r^5}\right)p_2^l p_2^j = \frac{1}{8}p_1^k p_2^l\left(-\frac{\delta^{jl}r^ir^k}{r^3}-\frac{\delta^{ik}r^jr^l}{r^3}+3\frac{r^ir^jr^kr^l}{r^5}\right)p_1^i p_2^j - \frac{1}{8}P^i\frac{3r^ir^i-\delta^{ij}r^2}{r^5}P^j+\frac{\pi}{4}\delta^3(r)-\frac{1}{12}\pi\delta^3(r)P^2, \tag{C3}$$

then almost all operators agree with one exception. The difference between operators in Eq. (97) of Ref. [6] and that of ours, Eq. (3.58), is

$$\Delta = \frac{1}{32}\pi\delta^3(r)P^2. \tag{C4}$$

For this reason we checked the calculation in Ref. [6]. The derivation of initial operators was very similar to our former work in [17]. However, the electron-electron Coulomb interaction, according to Ref. [5], involves the term

$$\frac{7\pi\alpha}{32m^4}\{p_1^2+p_2^2,\delta(\vec{r})\}, \tag{C5}$$

while our calculations in [17] give

$$\frac{6\pi\alpha}{32m^4}\{p_1^2+p_2^2,\delta(\vec{r})\}-\frac{\alpha}{16m^4}\nabla^2\pi\delta(\vec{r}). \tag{C6}$$

The difference between Eqs. (C5) and (C6) for singlet S states is equal to Δ from Eq. (C4), and this term should be subtracted from Eq. (97) of Ref. [6]. Although in this work we use a different formalism, we obtain the same result (after using the Schrödinger equation) as in Ref. [17]; namely, the sum of our terms $V_C^{eN}+V_C^{ee}+\delta_C V$ differs from $\delta H_1+\delta H_2+\delta H_3$ by exactly the same term Δ.

Considering numerical matrix elements, we found that the results presented in Ref. [5] are not reliable. Most of them are accurate to only three digits; for example, the matrix element corresponding to Q_{28}, according to KY, is 36.983, while our result is 37.010642. Some of them are accurate only to the first digit; for example, for Q_{29} KY gives $4\times1.078=4.312$ and our result is 4.004703. Some of matrix elements in Ref. [5] contain misprints in their presentation; namely, they should include an additional 1/2 on the left-hand side, to agree with numerical values and to be consistent with Eq. (97) of Ref. [6]. Most importantly, some matrix elements from [5] are in error—for example,

$$\left\langle \frac{3i}{2r^3}\left(\frac{\vec{r}}{r}\cdot\vec{p}-\frac{1}{2}\right)\right\rangle. \tag{C7}$$

By using integration by parts we transform this matrix element to the form

$$\left\langle \frac{3i}{2r^3}\left(\frac{\vec{r}}{r}\cdot\vec{p}-\frac{1}{2}\right)\right\rangle = \frac{3}{4}\left\langle \frac{1}{r^4}-\frac{1}{r^3}-4\pi\delta(r)\right\rangle = -4.246525, \tag{C8}$$

which is in disagreement with the result of [5]—namely, −0.958. Alternatively, we use the identity in Eq. (3.19) and obtain the same numerical value as in Eq. (C8). Another example is Q_{26}, for which result of [5] is 2×4.749 and our result from Table I is −0.266 894. In conclusion, the numerical matrix elements of Ref. [5] should be verified.

[1] W. E. Caswell and G. P. Lepage, Phys. Lett. **167B**, 437 (1986).
[2] K. Pachucki, Phys. Rev. A **71**, 012503 (2005).
[3] K. Pachucki, Phys. Rev. Lett. **97**, 013002 (2006).
[4] G. W. F. Drake, Can. J. Phys. **80**, 1195 (2002).
[5] V. I. Korobov and A. Yelkhovsky, Phys. Rev. Lett. **87**, 193003 (2001).
[6] A. Yelkhovsky, Phys. Rev. A **64**, 062104 (2001).
[7] K. Pachucki, Phys. Rev. Lett. **84**, 4561 (2000).
[8] K. Pachucki, J. Phys. B **35**, 3087 (2002).
[9] Z.-C. Yan and G. W. F. Drake, Phys. Rev. Lett. **91**, 113004 (2003).
[10] K. Pachucki and J. Komasa, Phys. Rev. Lett. **92**, 213001 (2004); Phys. Rev. A **73**, 052502 (2006).
[11] R. Sánchez *et al.*, Phys. Rev. Lett. **96**, 033002 (2006).
[12] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics Of One-And Two-Electron Atoms* (Plenum, New York, 1977).
[13] J. R. Sapirstein, in *Handbook of Atomic, Molecular, and Optical Physics*, edited by G. W. F. Drake (Springer, Berlin, 2005).
[14] K. Pachucki, J. Phys. B **31**, 5123 (1998).
[15] M. I. Eides, H. Grotch, and V. A. Shelyuto, Phys. Rep. **342**, 63 (2001).
[16] A. Czarnecki, K. Melnikov, and A. Yelkhovsky, Phys. Rev. A **59**, 4316 (1999).
[17] K. Pachucki, J. Phys. B **31**, 3547 (1998).

[18] G. W. F. Drake, I. B. Khriplovich, A. I. Milstein, and A. S. Yelkhovsky, Phys. Rev. A **48**, R15 (1993).
[19] V. I. Korobov, Phys. Rev. A **61**, 064503 (2000); **66**, 024501 (2002).
[20] G. W. F. Drake, in *Handbook of Atomic, Molecular, and Optical Physics*, edited by G. W. F. Drake (Springer, Berlin, 2005).
[21] G. W. F. Drake, Nucl. Instrum. Methods Phys. Res. B **31**, 7 (1988).
[22] P. J. Mohr and B. N. Taylor, Rev. Mod. Phys. **77**, 1 (2005).
[23] K. S. E. Eikema, W. Ubachs, W. Vassen, and W. Hogervorst, Phys. Rev. A **55**, 1866 (1997).
[24] S. D. Bergeson *et al.*, Phys. Rev. Lett. **80**, 3475 (1998).
[25] G. W. F. Drake and W. C. Martin, Can. J. Phys. **76**, 679 (1998).
[26] K. Pachucki and J. Sapirstein, J. Phys. B **33**, 455 (2000).
[27] G. W. F. Drake and S. P. Goldman, Can. J. Phys. **77**, 835 (1999).
[28] K. Pachucki, J. Phys. B **31**, 2489 (1998).
[29] C. Itzykson and J. B. Zuber, *Quantum Field Theory* (McGraw-Hill, New York, 1990).