$O(m\alpha^6)$ corrections to energy levels of positronium with nonvanishing orbital angular momentum

Jacek Zatorski*

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

(Received 24 July 2008; published 4 September 2008)

A detailed calculation of the $O(m\alpha^6)$ corrections to the energy levels of positronium for the orbital angular momentum number $l>0$ is presented. The formulas obtained are in agreement with the known results for the particular case of $l=1$. The complete analytical formulas to $O(m\alpha^6)$ are given for an arbitrary $l>0$ state, as well as numerical values of the energy levels $3\,{}^{2S+1}D_J$.

DOI: 10.1103/PhysRevA.78.032103 PACS number(s): 12.20.Ds, 31.15.xp, 31.30.jy, 36.10.Dr

I. INTRODUCTION

Positronium is an unstable bound system consisting of an electron and a positron. In the nonrelativistic limit its energy is given by

$$E_0 = -\frac{m\alpha^2}{4n^2}, \tag{1}$$

which results from the nonrelativistic Schrödinger equation with a Coulomb potential. However, in order to meet the accuracy of the experiments, the theory has to account for relativistic effects as well as for those coming from quantum electrodynamics (QED).

For positronium the most precisely measured transitions are the hyperfine splitting of the ground state [1,2], the $1S$-$2S$ interval [3,4], and the $2S$-$2P$ transitions [5–9]. At the same time, most of the theoretical efforts have been devoted to calculation of the energy of S and P states. For a recent comparison of the theoretical and the experimental results, see, for example, Ref. [10]. For a general review on QED bound-state calculations see, for example, Ref. [11]. The complete energy spectrum of positronium up to $O(m\alpha^5)$ can be found in Ref. [12]. The energy levels for S states with $m\alpha^6$ accuracy were obtained in Refs. [13,14] and with the same accuracy for P states in Ref. [15] (corrected in Ref. [14]).

We present an analytical calculation of the $O(m\alpha^6)$ corrections to the spectrum of positronium for states with arbitrary angular momentum number $l>0$. For P states our formulas are in agreement with those from Ref. [15] (corrected in Ref. [14]). The corrections for states with $l>1$ are also obtained here. Since the presented method allows for a systematic treatment of two-body systems consisting of components that have comparable masses it will also be useful in the case of antiprotonic atoms, which are of great interest now. For a recent review on antiprotonic atoms, see, for example, Ref. [16].

The rest of this paper is organized as follows. In Sec. II we outline the method of calculation. Section III contains details of the calculation of the effective Hamiltonian. Section IV is devoted to the presentation of a perturbative calculation of the corrections to the energy levels. In Sec. V we present our $O(m\alpha^6)$ analytical formulas, a complete analytical formula for the $l>0$ energy levels to $O(m\alpha^5)$, and the numerical values of D state energy levels to $O(m\alpha^6)$.

II. FRAMEWORK OF THE CALCULATION

In the first stage of the calculation we obtain an effective Hamiltonian for electron-positron system of $O(m\alpha^6)$. Let us briefly recall the formal method of derivation of an effective Hamiltonian. We follow the path shown in Refs. [17,18]. In the first step the many-body Lagrangian is constructed from the Foldy-Wouthuysen (FW) single-particle Hamiltonian (the FWH) (in our case; the FWHs for an electron and a positron). The use of the FWH instead of the Dirac Hamiltonian and, consequently, the use of the Schrödinger-Pauli wave function instead of the Dirac one, helps to control orders in which various photon-exchange processes contribute to the energy levels. In the next step the equal-time retarded Green function of the system is considered (similar to the one used in Ref. [19]). The Fourier transform of this Green function in the time variable $(t'-t)$ allows one to define an effective Hamiltonian as

$$G(E) \equiv \frac{1}{E-H_0-\Sigma(E)} \equiv \frac{1}{E-H_{\rm eff}}, \tag{2}$$

where $\Sigma(E)$ is a two-particle self-energy operator, which can be described in terms of various photon-exchange processes. A correction to the energy level is a pole of the $G(E)$ function; therefore it can be expressed as (see Ref. [11])

$$\delta E = E - E_0 = \langle\phi|\Sigma(E_0)|\phi\rangle + \langle\phi|\Sigma(E_0)\frac{1}{(E_0-H_0)'}\Sigma(E_0)|\phi\rangle + \langle\phi|\Sigma'(E_0)|\phi\rangle\langle\phi|\Sigma(E_0)|\phi\rangle + \cdots, \tag{3}$$

where $|\phi\rangle$ is an eigenstate of H_0. The last term in Eq. (3) contributes at orders higher than $O(m\alpha^6)$ so it is not considered in this paper. The relevant contributions are calculated with the help of QED perturbation theory.

In our calculation we treat a positron as an electron with opposite charge. There are no contributions of photon-annihilation processes to energy levels at $O(m\alpha^6)$ for the states with $l>0$. The calculations of contributions due to one-photon-annihilation virtual processes can be found in Refs. [20] [at $O(m\alpha^6)$] and [21] [at $O(m\alpha^6\ln\alpha)$]. In addition, in Appendix C we present a simple derivation of an

*jacek.zatorski@fuw.edu.pl

effective potential operator at $O(m\alpha^6)$ arising because of relativistic corrections to leading-order one-photon-annihilation amplitude. As far as annihilation processes involving more that one photon are concerned, a power counting argument shows that for $l>0$ they contribute at orders higher than $O(m\alpha^6)$.

The corrections to the energy levels are calculated with the help of the ordinary quantum-mechanical perturbation theory, where the solutions of the Schrödinger equation with the Coulomb potential are the unperturbed states. We use an effective $O(m\alpha^6)$ Hamiltonian to calculate corrections in the first order of perturbation theory, whereas the Breit-Pauli Hamiltonian [Eq. (85)] gives rise to $O(m\alpha^6)$ corrections in the second order of perturbation theory.

III. CALCULATION OF THE EFFECTIVE HAMILTONIAN

A. Foldy-Wouthuysen Hamiltonian

We start with the Foldy-Wouthuysen transformation [22] of the Dirac Hamiltonian in an external electromagnetic field,

$$H = \vec{\alpha}\cdot\vec{\pi} + \beta m + eA^0, \tag{4}$$

where $\vec{\pi}=\vec{p}-e\vec{A}$. The FW transformation F gives a new Hamiltonian

$$H_{\rm FW} = e^{iF}(H - i\partial_t)e^{-iF}, \tag{5}$$

which decouples the upper and lower components of the Dirac wave function. Below, we use the result from Ref. [17], namely, we take the FW Hamiltonian up to $O(m\alpha^6)$ for an electron,

$$\begin{aligned} H_{\rm FW}^{(-)} &= eA^0 + \frac{1}{2m}(\pi^2 - 2e\vec{s}\cdot\vec{B}) \\ &- \frac{1}{8m^3}(\pi^4 - 2e\vec{s}\cdot\vec{B}\pi^2 - 2\pi^2 e\vec{s}\cdot\vec{B}) \\ &- \frac{1}{8m^2}[e\vec{\nabla}\cdot\vec{E} + 2e\vec{s}\cdot(\vec{E}\times\vec{\pi} - \vec{\pi}\times\vec{E})] \\ &- \frac{e}{4m^3}(\vec{s}\cdot\vec{p}\vec{s}\cdot\vec{E} + \vec{s}\cdot\vec{E}\vec{s}\cdot\vec{p}) - \frac{3}{16m^4}[p^2\vec{\nabla}(eA^0)\times\vec{p}\cdot\vec{s} \\ &+ \vec{\nabla}(eA^0)\times\vec{p}\cdot\vec{s}p^2] + \frac{1}{128m^4}[p^2,[p^2,eA^0]] \\ &- \frac{3}{64m^4}[p^2\nabla^2(eA^0) + \nabla^2(eA^0)p^2] + \frac{1}{16m^5}p^6, \end{aligned} \tag{6}$$

where $\vec{s}=\vec{\sigma}/2$ and σ_i is the Pauli matrix. $H_{\rm FW}^{(+)}$ for a positron is obtained simply by changing the sign of the electric charge $e\to -e$ in the above expression. Different parts of $H_{\rm FW}^{(\pm)}$ carry different orders of the constant α and in the following calculation we select the appropriate terms to get the effective operators of $O(m\alpha^6)$.

B. Construction of the effective Hamiltonian

We consider the following many-body Lagrangian density:

$$\mathcal{L} = \phi^\star(i\partial_t - H_{\rm FW}^{(-)})\phi + \psi^\star(i\partial_t - H_{\rm FW}^{(+)})\psi + \mathcal{L}_{\rm EM}, \tag{7}$$

where the symbols ϕ and ψ refer to the fields of the electron and positron, respectively. $\mathcal{L}_{\rm EM}$ is the Lagrangian of the electromagnetic field. With the help of Eq. (3) we construct an effective operator δH that satisfies the condition

$$\langle\phi|\delta H|\phi\rangle = \langle\phi|\Sigma(E_0)|\phi\rangle, \tag{8}$$

and δH does not depend on the state $|\phi\rangle$. The typical contribution has the form of a one-photon exchange between electron and positron, that is,

$$\begin{aligned} \langle\phi|\Sigma(E_0)|\phi\rangle = &- 2e^2\int\frac{d^4k}{(2\pi)^4 i}G_{\mu\nu}(k) \\ &\times\Bigg(\Bigg\langle\phi\Bigg|J_1^\mu(k)e^{i\vec{k}\cdot\vec{r}_1}\frac{1}{E_0 - H_0 - k^0 + i\epsilon}J_2^\nu \\ &\times(-k)e^{-i\vec{k}\cdot\vec{r}_2}\Bigg|\phi\Bigg\rangle \\ &+\Bigg\langle\phi\Bigg|J_2^\mu(k)e^{i\vec{k}\cdot\vec{r}_2}\frac{1}{E_0 - H_0 - k^0 + i\epsilon}J_1^\nu \\ &\times(-k)e^{-i\vec{k}\cdot\vec{r}_1}\Bigg|\phi\Bigg\rangle\Bigg). \end{aligned} \tag{9}$$

The factor of 2 is present in front of the above integral since typically currents J_1 and J_2 come from different terms in the FWH and in such cases one should also take into account a contribution with reversed currents. Additionally, the last term on the right-hand side (RHS) of Eq. (9) accounts for another possible ordering of the currents.

Modified rules for the interaction vertices result from the definition of the J_a^μ currents. Namely, this current is defined as a coefficient that couples to the annihilation part of $A^\mu \propto \epsilon_\lambda^\mu e^{i\vec{k}\cdot\vec{r}-ik^0t}\hat{a}_\lambda(\vec{k})$+H.c. in the Lagrangian [Eq. (7)]. For example, the current operator $J^0(\vec{k})$ has an expansion

$$j^0(\vec{k}) = 1 + \frac{i}{2m}\vec{s}(\vec{k}\times\vec{p}) - \frac{1}{8m^2}\vec{k}^2 + \cdots, \tag{10}$$

where the first coefficient comes from the first term in $H_{\rm FW}$ in Eq. (6), the other two come from the fourth term in $H_{\rm FW}$, and the ellipsis indicates higher-order terms. We emphasize that the electric charges of particles are omitted here as they have already been included in front of the integral in Eq. (9). Similarly,

$$\vec{j}(\vec{k}) = \frac{\vec{p}}{m} + \frac{i}{m}\vec{s}\times\vec{k}, \tag{11}$$

where we do not take into account the terms coming from the two-photon-exchange processes, i.e., the terms that are quadratic in fields. These are to be treated separately.

We work in the Coulomb gauge, in which the photon propagator takes the form

$$G_{\mu\nu}(k) = \begin{cases} -\dfrac{1}{\vec{k}^2}, & \mu=\nu=0, \\ \dfrac{-1}{k_0^2-\vec{k}^2+i\epsilon}\left(\delta_{ij}-\dfrac{k_ik_j}{\vec{k}^2}\right), & \mu=i,\nu=j. \end{cases} \tag{12}$$

Many contributions will be calculated in the nonretardation approximation which is realized by putting $k^0=0$ in both the photon propagator and $J(k)$. In this case, the spectral integral of $1/(E_0-H_0-k^0+i\epsilon)$ can be performed by means of Sokhotsky's formula, that is,

$$\frac{1}{x\pm x_0+i\epsilon} = \mp i\pi\delta(x-x_0)+\mathrm{PV}\left(\frac{1}{x-x_0}\right), \tag{13}$$

where PV is the Cauchy principal value functional, i.e., it acts on a test function $f(x)$ as follows

$$\mathrm{PV}\left(\frac{1}{x-x_0}\right)f = \lim_{\epsilon\to 0^+}\left(\int_{-\infty}^{x_0-\epsilon}\frac{f(x)}{x-x_0}dx+\int_{x_0+\epsilon}^{\infty}\frac{f(x)}{x-x_0}dx\right). \tag{14}$$

In Eq. (13) we substitute $x=-k^0$, $x_0=\Delta E=H_0-E_0$, and obtain

$$\int\frac{dk^0}{2\pi i}\frac{1}{-\Delta E-k^0+i\epsilon}\to-\frac{1}{2}. \tag{15}$$

This result is a consequence of the observation that in the case of the above integral the PV functional from Sokhotsky's formula vanishes as there is no k^0 in the numerator. By means of substitution (15), the amplitude (9) in the nonretardation approximation reads

$$\langle\phi|\Sigma(E_0)|\phi\rangle = e^2\int\frac{d^3k}{(2\pi)^3}G_{\mu\nu}(0,\vec{k})\langle\phi|J_1^{\mu}(k)e^{i\vec{k}\cdot\vec{r}_1} \times J_2^{\nu}(-k)e^{-i\vec{k}\cdot\vec{r}_2}|\phi\rangle+(1\leftrightarrow 2), \tag{16}$$

where the symbol $(1\leftrightarrow 2)$ stands for a term which is the same as the preceding one except for a reversed order of particle indices.

In the final stage of calculation, we use the center-of-mass reference frame (CMRF). All operators are to be rewritten in terms of the electron-positron relative position operator and the appropriate momentum operator. We introduce the relative position vector $\vec{r}$,

$$\vec{r}=\vec{r}_1-\vec{r}_2, \tag{17}$$

where $\vec{r}_1$ and $\vec{r}_2$ refer to the positions of the electron and positron, respectively. The appropriate momentum vector reads

$$\vec{p}=\vec{p}_1=-\vec{p}_2. \tag{18}$$

Additionally, we introduce the total spin operator $\vec{S}$,

$$\vec{S}=\vec{s}^{(1)}+\vec{s}^{(2)}, \tag{19}$$

where $\vec{s}^{(a)}$, where $a=1,2$, is an individual particle spin operator.

C. Calculation of the effective operators

The $O(m\alpha^6)$ Hamiltonian ($H^{(6)}$) will be presented as the sum

$$H^{(6)}=\sum_{i=0,9}\delta H_i. \tag{20}$$

We start with the kinetic energy correction which comes from the last term in $H_{\mathrm{FW}}^{(-)}$ and $H_{\mathrm{FW}}^{(+)}$ in Eq. (6),

$$\delta H_0=\frac{p_1^6}{16m^5}+\frac{p_2^6}{16m^5}=\frac{p^6}{8m^5}. \tag{21}$$

It is already an effective operator since it does not contain a photon field. Expectation values of all the effective operators will be calculated in the next section.

δH_1 is the contribution coming from the sixth, seventh, and eighth terms in $H_{\mathrm{FW}}^{(-)}$ (and $H_{\mathrm{FW}}^{(+)}$), i.e.,

$$H_{\mathrm{FW},1}^{(-)}=H_{\mathrm{FW},1A}+H_{\mathrm{FW},1B}+H_{\mathrm{FW},1C}, \tag{22}$$

where:

$$H_{\mathrm{FW},1A}=-\frac{3}{16m^4}[p^2\vec{\nabla}(eA^0)\times\vec{p}\cdot\vec{s}+\vec{\nabla}(eA^0)\times\vec{p}\cdot\vec{s}p^2],$$

$$H_{\mathrm{FW},1B}=\frac{1}{128m^4}[p^2,[p^2,eA^0]],$$

$$H_{\mathrm{FW},1C}=-\frac{3}{64m^4}[p^2\nabla^2(eA^0)+\nabla^2(eA^0)]. \tag{23}$$

Let us construct a one-photon-exchange amplitude of the form of Eq. (16). We start with the first operator in Eq. (23). The appropriate contribution to the current reads

$$J_{1A}^0(\vec{k})=\frac{3}{16m^4}i[p^2(\vec{k}\times\vec{p})\cdot\vec{s}+(\vec{k}\times\vec{p})\cdot\vec{s}p^2]. \tag{24}$$

As will become clear soon, to obtain an effective operator of $O(m\alpha^6)$ it is sufficient to substitute only one current, in Eq. (16), with the help of Eq. (24). For the second current we substitute the lowest-order expansion [see Eq. (10)], that is, $J^0(\vec{k})=1$. Therefore, according to Eq. (16), the effective operator reads

$$\begin{aligned}\delta H_1^A &= e^2\frac{3}{16m^4}\int\frac{d^3k}{(2\pi)^3}G_{00}(\vec{k})[ip_1^2(\vec{k}\times\vec{p}_1)\cdot\vec{s}_1 \\ &\quad +i(\vec{k}\times\vec{p}_1)\cdot\vec{s}_1p_1^2]e^{i\vec{k}\cdot\vec{r}} \\ &\quad +e^2\frac{3}{16m^4}\int\frac{d^3k}{(2\pi)^3}G_{00}(\vec{k})e^{i\vec{k}\cdot\vec{r}_2}[ip_2^2(\vec{k}\times\vec{p}_2)\cdot\vec{s}_2 \\ &\quad +i(\vec{k}\times\vec{p}_2)\cdot\vec{s}_2p_2^2]e^{-i\vec{k}\cdot\vec{r}_1}.\end{aligned} \tag{25}$$

Now, in the second row we commute $e^{i\vec{k}\cdot\vec{r}_2}$ to the left-hand side (LHS) and change the sign of the resulting position vector $\vec{r}$. Next, we express the sum of the spin operators in terms of the total spin operator $\vec{S}$. Additionally, we substitute the momentum and position operators of the electron and positron with the momentum and position operators in the CMRF [see Eq. (18)]. In this way we obtain

$$\delta H_1^A = -e^2\frac{3}{16m^4}\int\frac{d^3k}{(2\pi)^3}\frac{1}{\vec{k}^2}[ip^2(\vec{k}\times\vec{p})\cdot\vec{S} + i(\vec{k}\times\vec{p})\cdot\vec{S}p^2]e^{i\vec{k}\cdot\vec{r}}. \tag{26}$$

In the next step we perform the integral with the help of the relation

$$\frac{e^2}{i}\int\frac{d^3k}{(2\pi)^3}\frac{\vec{k}}{\vec{k}^2}e^{i\vec{k}\cdot\vec{r}} = -\frac{e^2}{4\pi}\vec{\nabla}\left(\frac{1}{r}\right) = \vec{\nabla}V(r), \tag{27}$$

where V is the nonrelativistic Coulomb potential

$$V = -\frac{\alpha}{r}. \tag{28}$$

We also introduce the static electric field

$$e\vec{\mathcal{E}} = -\vec{\nabla}_1 V = \vec{\nabla}_2 V = \alpha\frac{\vec{r}}{r^3}. \tag{29}$$

After integration the effective operator H_1^A can be expressed as

$$\delta H_1^A = -\frac{3}{16m^4}\vec{S}\cdot(p^2 e\vec{\mathcal{E}}\times\vec{p} + e\vec{\mathcal{E}}\times\vec{p}p^2). \tag{30}$$

Since the operators $\vec{p}$ and $1/r$ are of $O(m\alpha)$ when acting on $|\phi\rangle$, we can see that δH_1^A is, indeed, of $O(m\alpha^6)$. Let us notice now that δH_1^A could be obtained from $H_{\mathrm{FW},1A}$ in Eq. (23) by the substitution $eA^0\to V$. Moreover, it can be seen that a nonretardation contribution of the form shown in Eq. (16) that involves only the A^0 fields (also when there is an operator acting on A^0) can be obtained simply by the substitution $eA^0\to V$. In particular, δH_1^B and δH_1^C can be calculated in this way. Hence

$$\delta H_1 = -\frac{3}{16m^4}\vec{S}\cdot(p^2 e\vec{\mathcal{E}}\times\vec{p} + e\vec{\mathcal{E}}\times\vec{p}p^2) + \frac{1}{64m^4}[p^2,[p^2,V]] - \frac{3}{32m^4}(p^2\nabla^2 V + \nabla^2 V p^2). \tag{31}$$

The next effective operator (δH_2) arises when both particles interact through the fourth term in $H_{\mathrm{FW}}^{(-)}$ in Eq. (6), that is,

$$H_{\mathrm{FW},2}^{(-)} = -\frac{1}{8m^2}[e\vec{\nabla}\cdot\vec{E} + 2e\vec{s}(\vec{E}\times\vec{p} - \vec{p}\times\vec{E})] \tag{32}$$

for an electron, and similarly for a positron ($e\to -e$). We recall that $\vec{E}=-\vec{\nabla}A_0-\partial_0\vec{A}$ and write the relevant contribution to the current as

$$J_2^0 = -\frac{1}{8m^2}[\vec{k}^2 - 2\vec{s}(i\vec{k}\times\vec{p} - i\vec{p}\times\vec{k})]. \tag{33}$$

The effective operator can be calculated in the nonretardation approximation:

$$\delta H_2 = -\alpha\int\frac{d^3k}{(2\pi)^3}\frac{1}{k^2}\frac{4\pi}{64m^4}(k^2 - 4i\vec{s}_2\cdot\vec{p}\times\vec{k})e^{i\vec{k}\cdot\vec{r}} \times(k^2 + 4i\vec{s}_1\cdot\vec{p}\times\vec{k}). \tag{34}$$

One can integrate the above expression with the help of formula (27). The result is

$$\delta H_2 = \frac{\alpha}{m^4}\frac{\pi}{16}\nabla^2\delta^3(\vec{r}) + \frac{\alpha}{m^4}\frac{i\pi}{4}\vec{S}\cdot[\vec{p}\times\delta^3(\vec{r})\vec{p}] + \frac{\alpha}{m^4}\frac{1}{4}(\vec{s}_2\times\vec{p})^i\left[\frac{\delta_{ij}}{3}4\pi\delta^3(\vec{r}) + \frac{1}{r^3}\left(\delta^{ij} - 3\frac{r^i r^j}{r^2}\right)\right] \times(\vec{s}_1\times\vec{p})^j. \tag{35}$$

The δH_3 operator is due to a process in which one particle interacts by the fifth term in Eq. (6), which for an electron is (and correspondingly for a positron)

$$H_{\mathrm{FW},3}^{(-)} = -\frac{e}{4m^3}(\vec{s}\cdot\vec{p}\vec{s}\cdot\dot{\vec{E}} + \vec{s}\cdot\dot{\vec{E}}\vec{s}\cdot\vec{p}), \tag{36}$$

while a second particle interacts through the term eA^0. The appropriate contribution to the current reads

$$J_3^0 = \frac{1}{4m^3}(\vec{s}\cdot\vec{p}\vec{s}\cdot\vec{k}k^0 + \vec{s}\cdot\vec{k}k^0\vec{s}\cdot\vec{p}). \tag{37}$$

The operator δH_3 should be calculated including the retardation effect. We return to the one-photon-exchange contribution [Eq. (9)] and write

$$\begin{aligned}\delta H_3 = \frac{e^2}{4m^3}\int\frac{d^4k}{i\vec{k}^2(2\pi)^4} &\times\Bigg((\vec{s}_1\cdot\vec{p}_1\vec{s}_1\cdot\vec{k}e^{i\vec{k}\cdot\vec{r}_1} + e^{i\vec{k}\cdot\vec{r}_1}\vec{s}_1\cdot\vec{k}\vec{s}_1\cdot\vec{p}_1)\\ &\times\frac{k^0}{E_0 - H_0 - k^0 + i\epsilon}e^{-i\vec{k}\cdot\vec{r}_2}\\ &- e^{i\vec{k}\cdot\vec{r}_2}\frac{k^0}{E_0 - H_0 - k^0 + i\epsilon}(\vec{s}_1\cdot\vec{p}_1\vec{s}_1\cdot\vec{k}e^{-i\vec{k}\cdot\vec{r}_1}\\ &+ e^{-i\vec{k}\cdot\vec{r}_1}\vec{s}_1\cdot\vec{k}\vec{s}_1\cdot\vec{p}_1)\Bigg) + (1\leftrightarrow 2).\end{aligned} \tag{38}$$

In order to integrate over the variable k^0, we perform a Hermitian symmetrization $\delta H_3\to\frac{1}{2}(\delta H_3+\delta H_3^\dagger)$ and then $(\vec{k}\leftrightarrow-\vec{k})$ symmetrization to $\int dk^3$. After applying this procedure, we can proceed with the help of the Cauchy theorem and obtain

$$\int\frac{dk^0}{2\pi i}\left(\frac{k^0}{-\Delta E - k^0 + i\epsilon} - \frac{k^0}{-\Delta E - k^0 - i\epsilon}\right) = \Delta E = H_0 - E_0. \tag{39}$$

Therefore

$$\delta H_3 = \frac{e^2}{8m^3}\int \frac{d^4k}{\vec{k}^2(2\pi)^3}\times\{(\vec{s}_1\cdot\vec{p}_1\vec{s}_1\cdot\vec{k}e^{i\vec{k}\cdot\vec{r}_1}+e^{i\vec{k}\cdot\vec{r}_1}\vec{s}_1\cdot\vec{k}\vec{s}_1\cdot\vec{p}_1)\times(H_0-E_0)e^{-i\vec{k}\cdot\vec{r}_2}+e^{i\vec{k}\cdot\vec{r}_2}(H_0-E_0)(\vec{s}_1\cdot\vec{p}_1\vec{s}_1\cdot\vec{k}e^{-i\vec{k}\cdot\vec{r}_1}+e^{-i\vec{k}\cdot\vec{r}_1}\vec{s}_1\cdot\vec{k}\vec{s}_1\cdot\vec{p}_1)\}+(1\leftrightarrow 2). \tag{40}$$

After commuting the operator (H_0-E_0) with $e^{-i\vec{k}\cdot\vec{r}_i}$ and simplification of the double-spin operators, δH_3 reads

$$\delta H_3 = \frac{\alpha}{32m^4}\int\frac{d^4k}{(2\pi)^3}\frac{4\pi}{\vec{k}^2}[p_1^2,[p_2^2,e^{-i\vec{k}\cdot\vec{r}}]]+(1\leftrightarrow 2). \tag{41}$$

Finally, the above operator is expressed in the CMRF as

$$\delta H_3 = \frac{\alpha}{16m^4}\left[p^2,\left[p^2,\frac{1}{r}\right]\right]. \tag{42}$$

The operator δH_4 is obtained when one particle interacts through the second term in Eq. (6), namely,

$$H^{(-)}_{\mathrm{FW},4A} = -\frac{e}{m}\vec{p}\cdot\vec{A}-\frac{e}{m}\vec{s}\cdot\vec{B}. \tag{43}$$

We recall the relation $\vec{B}=\vec{\nabla}\times\vec{A}$ and see that the contribution to the current reads

$$\vec{J}_{4A} = -\frac{1}{m}\vec{p}-\frac{i}{m}\vec{s}\times\vec{k}. \tag{44}$$

A second particle interacts by the relativistic corrections from the third term,

$$H^{(-)}_{\mathrm{FW},4B} = -\frac{1}{8m^3}(\pi^4-2e\vec{s}\cdot\vec{B}\pi^2-4\pi^2e\vec{s}\cdot\vec{B}) \to \frac{e}{4m^3}(p^2\vec{p}\cdot\vec{A}+p^2\vec{s}\cdot\vec{B})+\frac{e}{4m^3}(\vec{p}\cdot\vec{A}p^2+\vec{s}\cdot\vec{B}p^2). \tag{45}$$

The first expression in parentheses in the second row gives the current

$$\vec{J}_{4B1} = \frac{1}{4m^3}p^2\vec{p}+\frac{i}{4m^3}p^2\vec{s}\times\vec{k}. \tag{46}$$

An almost identical contribution comes from the second expression in parentheses in Eq. (45). The operator δH_4 can be treated in the nonretardation approximation; therefore

$$\delta H_4 = -e^2\int\frac{d^3k}{(2\pi)^3}G_{ij}(0,\vec{k})\left[\left(\frac{1}{m}\vec{p}_1+\frac{i}{m}\vec{s}_1\times\vec{k}\right)e^{i\vec{k}\cdot\vec{r}_1}\times\left(\frac{1}{4m^3}p_2^2\vec{p}_2-\frac{i}{4m^3}p_2^2\vec{s}_2\times\vec{k}\right)e^{-i\vec{k}\cdot\vec{r}_2}+\left(\frac{1}{m}\vec{p}_1+\frac{i}{m}\vec{s}_1\times\vec{k}\right)e^{i\vec{k}\cdot\vec{r}_1}\left(\frac{1}{4m^3}p_2^2e^{-i\vec{k}\cdot\vec{r}_2}\vec{p}_2-\frac{i}{4m^3}e^{-i\vec{k}\cdot\vec{r}_2}p_2^2\vec{s}_2\times\vec{k}\right)\right]+(1\leftrightarrow 2). \tag{47}$$

One can integrate the last expression with the help of the formula

$$\tilde{G}_{\mu\nu}(\vec{r}) = \int\frac{d^3k}{(2\pi)^3}G_{\mu\nu}(0,\vec{k})e^{-i\vec{k}\cdot\vec{r}} = \frac{1}{4\pi}\begin{cases}-\dfrac{1}{r}, & \mu=\nu=0,\\[2ex] \dfrac{1}{2r}\left(\delta_{ij}+\dfrac{r_ir_j}{r^2}\right), & \mu=i,\ \nu=j,\end{cases} \tag{48}$$

where $\tilde{G}_{\mu\nu}(\vec{r})$ is the position representation of a photon propagator. It is convenient to introduce the static vector potentials [17]

$$e\mathcal{A}_1^i = \frac{\alpha}{2r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)\frac{p_j}{m}-\frac{\alpha}{m}\frac{(\vec{s}_2\times\vec{r})^i}{r^3},$$

$$e\mathcal{A}_2^i = -\frac{\alpha}{2r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)\frac{p_j}{m}+\frac{\alpha}{m}\frac{(\vec{s}_1\times\vec{r})^i}{r^3}. \tag{49}$$

These static potentials arise when an integral of the following form is performed:

$$e\mathcal{A}^i_{1,2} = -e^2\int\frac{d^3k}{(2\pi)^3}G^{ij}(0,\vec{k})\left(\frac{1}{m}p_{2,1,j}\pm\frac{i}{m}(\vec{s}_{2,1}\times\vec{k})_j\right)e^{i\vec{k}\cdot\vec{r}}, \tag{50}$$

where the upper signs on the LHS of the above equations refer to the field $e\mathcal{A}_1^i$. Finally, we obtain

$$\delta H_4 = \frac{e}{4}\sum_{a=1,2}[p_a^2\vec{p}_a\vec{\mathcal{A}}_a+\vec{p}_a\vec{\mathcal{A}}_ap_a^2+p_a^2\vec{s}_a(\vec{\nabla}_a\times\vec{\mathcal{A}}_a)+\vec{s}_a(\vec{\nabla}_a\times\vec{\mathcal{A}}_a)]. \tag{51}$$

The next operator (δH_5) is the first example of a contribution of a two-photon-exchange process. More specifically, it arises when one particle interacts twice through the term $H^{(-)}_{\mathrm{FW},4A}$ [see Eq. (43)] and the other particle interacts through the term

$$H_{\mathrm{FW},5} = \frac{e^2}{2m}\vec{A}^2. \tag{52}$$

Generally, a contribution involving two-photon exchange has the following form:

$$\langle\phi|\Sigma(E_0)|\phi\rangle = 4e^4\int\int\frac{d^4k}{(2\pi)^4i}\frac{d^4u}{(2\pi)^4i}G_{\mu\nu}(k)G_{\alpha\beta}(u)\times\left\langle\phi\left|J_1^\mu(k)e^{i\vec{k}\cdot\vec{r}_1}\frac{1}{E_0-H_0-k^0+i\epsilon}J_2^\nu(-k)\times e^{-i\vec{k}\cdot\vec{r}_2}J_2^\alpha(u)e^{i\vec{u}\cdot\vec{r}_2}\frac{1}{E_0-H_0-u^0+i\epsilon}\times J_1^\beta(-u)e^{-i\vec{u}\cdot\vec{r}_1}\right|\phi\right\rangle+(1\leftrightarrow 2), \tag{53}$$

where the factor of 4 in front of the above integral accounts for equivalent amplitudes that also contribute. In the case of

δH_5 one current, say $\vec{J}_1$, is given by Eq. (44). The second current comes from a single $\vec{A}$ field operator in Eq. (52). The effective operator δH_5 can be calculated in the nonretardation approximation; therefore we exploit Eq. (15) to integrate over k^0 and u^0. We obtain

$$\delta H_5 = e^4 \int\int \frac{d^3k}{(2\pi)^3}\frac{d^3u}{(2\pi)^3} G_{ij}(0,\vec{k})G_{mn}(0,\vec{u}) \times J_1^i(k)e^{i\vec{k}\cdot\vec{r}_1}J_2^j(-k)e^{-i\vec{k}\cdot\vec{r}_2}J_2^m(u)e^{i\vec{u}\cdot\vec{r}_2}J_1^n(-u)e^{-i\vec{u}\cdot\vec{r}_1} + (1\leftrightarrow 2). \quad (54)$$

The above expression is a product of two integrals, where each of them has the form of the integral in Eq. (50). Again it follows that, in order to get an effective operator, one can simply substitute fields $\vec{A}_a$ with static potentials from Eq. (49). Hence,

$$\delta H_5 = \sum_{a=1,2}\frac{e^2}{2}\vec{\mathcal{A}}_a^2. \quad (55)$$

The operator δH_6 is another example of a two-photon-exchange contribution. In this case one particle couples to the term

$$H_{\mathrm{FW},6} = \frac{e^2}{4m^2}\vec{s}(\vec{E}\times\vec{A} - \vec{A}\times\vec{E}), \quad (56)$$

which is a part of the fourth term of the FW Hamiltonian in Eq. (6). The other particle couples once to the term $H^{(-)}_{\mathrm{FW},4A}$ [see Eq. (43)] and once to eA^0. We can use the nonretardation approximation for Eq. (53), which means that we can simply substitute fields with their static forms. The result is

$$\delta H_6 = \sum_{a=1,2}\frac{e^2}{4m^2}\vec{s}_a(\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a - \vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a). \quad (57)$$

The next term (δH_7) is due to a process when each particle is coupled to the $H_{\mathrm{FW},4A}$ term [see Eq. (43)]. This is one-photon exchange with retardation. One can see that only the transverse part of the photon propagator is involved in the calculation; therefore

$$\delta H_7 = e^2\int\frac{d^4k}{(2\pi)^4 i}\frac{1}{k_0^2-\vec{k}^2+i\epsilon}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)\times\left(J_1^i(k)e^{i\vec{k}\cdot\vec{r}_1}\frac{1}{E_0-H_0-k^0+i\epsilon}J_2^j(-k)e^{-i\vec{k}\cdot\vec{r}_2} + J_2^i(k)e^{i\vec{k}\cdot\vec{r}_2}\frac{1}{E_0-H_0-k^0+i\epsilon}J_1^j(-k)e^{-i\vec{k}\cdot\vec{r}_1}\right). \quad (58)$$

First, we will deal with the $\int k^0$ integral. Although the above currents J_1, J_2 do not contain any powers of k^0 we consider a more general situation, that is, we consider the integral

$$\int\frac{dk^0}{(2\pi)i}\frac{1}{k_0^2-\vec{k}^2+i\epsilon}\frac{f(k^0)}{E_0-H_0-k^0+i\epsilon} = \int\frac{dk^0}{(2\pi)i}\frac{1}{2k^0}\left(\frac{1}{k^0-(k-i\epsilon)}+\frac{1}{k^0+(k-i\epsilon)}\right)\times\frac{f(k^0)}{E_0-H_0-k^0+i\epsilon}, \quad (59)$$

where $f(k^0)$ may contain at most one power of k^0 and $k=|\vec{k}|$. In order to perform integration we notice that in the $\mathrm{Im}\,k^0<0$ complex half plane the function of interest has only one pole, which is at the point $k^0=k-i\epsilon$. We encircle this half plane with a half circle of radius $R\to\infty$. With the help of simple power counting, one can see that the integral over this half circle vanishes. Finally, we can use the Cauchy theorem to tackle the integral in Eq. (59),

$$\int\frac{dk^0}{(2\pi)i}\frac{1}{k_0^2-\vec{k}^2+i\epsilon}\frac{f(k^0)}{E_0-H_0-k^0+i\epsilon} = \frac{1}{2k}\frac{f(k)}{E_0-H_0-k}. \quad (60)$$

By virtue of the above relation δH_7 reads

$$\delta H_7 = e^2\int\frac{d^3k}{(2\pi)^3}\frac{1}{2k}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)\left(J_1^i(\vec{k})e^{i\vec{k}\cdot\vec{r}_1}\frac{1}{E_0-H_0-k}\times J_2^j(-\vec{k})e^{-i\vec{k}\cdot\vec{r}_2} + J_2^i(\vec{k})e^{i\vec{k}\cdot\vec{r}_2}\frac{1}{E_0-H_0-k}J_1^j(-\vec{k})e^{-i\vec{k}\cdot\vec{r}_1}\right). \quad (61)$$

Next, we proceed with the retardation expansion, that is, we expand

$$\frac{1}{E_0-H_0-k} = -\frac{1}{k}+\frac{H_0-E_0}{k^2}-\frac{(H_0-E_0)^2}{k^3}+\cdots \quad (62)$$

and identify the third term as the one that gives corrections of $O(m\alpha^6)$; however, with one remark. Namely, one has to subtract the divergent term arising (see the δH_7^A operator below). We substitute the appropriate currents into Eq. (61), perform the nonretardation expansion, and obtain

$$\delta H_7 = \frac{e^2}{m^2}\int\frac{d^3k}{(2\pi)^3}\frac{1}{2k^4}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)(\vec{p}_1+i\vec{s}_1\times\vec{k})e^{i\vec{k}\cdot\vec{r}_1}\times(H_0-E_0)^2(\vec{p}_2-i\vec{s}_2\times\vec{k})e^{-i\vec{k}\cdot\vec{r}_2}+(1\leftrightarrow 2). \quad (63)$$

For the sake of clarity we split this expression into three parts with no-spin, single-spin, and double-spin terms, respectively:

$$\delta H_7 = \delta H_7^A + \delta H_7^B + \delta H_7^C. \quad (64)$$

The nonspin part reads

$$\delta H_7^A = \frac{e^2}{m^2}\int \frac{d^3k}{(2\pi)^3}\frac{1}{2k^4}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right) \times p_1^i[e^{i\vec{k}\cdot\vec{r}_1}(H_0-E_0)^2e^{-i\vec{k}\cdot\vec{r}_2}-(H_0-E_0)^2]p_2^j+(1\leftrightarrow 2), \tag{65}$$

where we have subtracted lower-order terms responsible for infrared divergence (see Ref. [17]). To obtain the effective operator we use the commutator identity from Ref. [17],

$$\begin{aligned} e^{i\vec{k}\cdot\vec{r}_a}(H_0-E_0)^2e^{-i\vec{k}\cdot\vec{r}_b}-(H_0-E_0)^2 &= (H_0-E_0)(e^{i\vec{k}\cdot(\vec{r}_a-\vec{r}_b)}-1)(H_0-E_0)+(H_0-E_0) \\ &\times\left[\frac{p_b^2}{2m},e^{i\vec{k}(\vec{r}_a-\vec{r}_b)}-1\right]+\left[e^{i\vec{k}(\vec{r}_a-\vec{r}_b)}-1,\frac{p_a^2}{2m}\right](H_0-E_0) \\ &+\left[\frac{p_b^2}{2m},\left[e^{i\vec{k}(\vec{r}_a-\vec{r}_b)}-1,\frac{p_a^2}{2m}\right]\right], \end{aligned} \tag{66}$$

and the formula

$$\int d^3k\frac{4\pi}{k^4}\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)(e^{i\vec{k}\cdot\vec{r}}-1)=\frac{1}{8r}(r^ir^j-3\delta^{ij}r^2). \tag{67}$$

We can express the δH_7^A operator in terms of the operators in the CMRF,

$$\begin{aligned} \delta H_7^A = -\frac{\alpha}{8m^2}\Bigg([p^i,V]\frac{r^ir^j-3\delta_{ij}r^2}{r}[V,p^j]-[p^i,V] &\times\left[\frac{p^2}{2m},\frac{r^ir^j-3\delta_{ij}r^2}{r}\right]p^j-p^i\left[\frac{r^ir^j-3\delta_{ij}r^2}{r},\frac{p^2}{2m}\right][V,p^j] \\ &+p^i\left[\frac{p^2}{2m},\left[\frac{r^ir^j-3\delta_{ij}r^2}{r},\frac{p^2}{2m}\right]\right]p^j\Bigg). \end{aligned} \tag{68}$$

The single-spin part is given by the expression

$$\begin{aligned} \delta H_7^B = \frac{ie^2}{4m^2}\int\frac{d^3k}{(2\pi)^3}\frac{1}{k^4}[e^{i\vec{k}\cdot\vec{r}_1}(H_0-E_0)^2e^{-i\vec{k}\cdot\vec{r}_2}(\vec{s}_1\times\vec{k})\vec{p}_2 \\ -\vec{p}_1(\vec{s}_2\times\vec{k})e^{i\vec{k}\cdot\vec{r}_1}(H_0-E_0)^2e^{-i\vec{k}\cdot\vec{r}_2}]+(1\leftrightarrow 2). \end{aligned} \tag{69}$$

In order to integrate the above expression over $\vec{k}$, we use Eq. (66) and the integral

$$\int\frac{d^3k}{2\pi^2}\frac{\vec{k}}{k^4}e^{i\vec{k}\cdot\vec{r}}=\frac{i}{2}\frac{\vec{r}}{r}. \tag{70}$$

In the CMRF δH_7^B reads

$$\begin{aligned} \delta H_7^B = \frac{\alpha}{8m^2}\Bigg\{\left[\left(\vec{S}\times\frac{\vec{r}}{r}\right)^i,p^2\right][V,p_i]+[p_i,V]\left[p^2,\left(\vec{S}\times\frac{\vec{r}}{r}\right)^i\right] \\ +\left[\frac{p^2}{2},\left[\left(\vec{S}\times\frac{\vec{r}}{r}\right)^i,p^2\right]\right]p_i+p_i\left[\frac{p^2}{2},\left[\left(\vec{S}\times\frac{\vec{r}}{r}\right)^i,p^2\right]\right]\Bigg\}. \end{aligned} \tag{71}$$

The double-spin part is

$$\delta H_7^C = e^2\int\frac{d^3k}{(2\pi)^32k^4}\frac{(\vec{s}_1\times\vec{k})(\vec{s}_2\times\vec{k})}{m^2}e^{i\vec{k}\cdot\vec{r}_1}(H_0-E_0)^2e^{-i\vec{k}\cdot\vec{r}_2} +(1\leftrightarrow 2). \tag{72}$$

With the help of Eq. (66) one gets

$$\delta H_7^C = -\frac{\alpha}{4m^4}\left[p^2,\left[p^2,\vec{s}_1\vec{s}_2\frac{2}{3r}+s_1^is_2^j\frac{1}{2r}\left(\frac{r_ir_j}{r^2}-\frac{\delta_{ij}}{3}\right)\right]\right]. \tag{73}$$

The next retardation correction (δH_8) arises when one particle couples to the term in Eq. (43) and the second particle couples to the term

$$\delta H_{\mathrm{FW},8} = \frac{e}{4m^2}\vec{s}(\vec{E}\times\vec{p}-\vec{p}\times\vec{E}). \tag{74}$$

Only the transverse part of the photon propagator is involved here; therefore the operator reads

$$\begin{aligned} \delta H_8 = \Bigg[\frac{e^2}{4m^3}\int\frac{d^4k}{(2\pi)^4i}\frac{1}{k_0^2-\vec{k}^2+i\epsilon}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)(-ik_0) \\ \times(e^{i\vec{k}\vec{r}_1}\vec{p}_1\times\vec{s}_1+\vec{p}_1\times\vec{s}_1e^{i\vec{k}\cdot\vec{r}_1})^i\frac{1}{E_0-H_0-k_0+i\epsilon} \\ \times(\vec{p}_2-i\vec{s}_2\times\vec{k})^je^{-i\vec{k}\cdot\vec{r}_2}+\mathrm{H.c.}\Bigg]+(1\leftrightarrow 2). \end{aligned} \tag{75}$$

One can exploit Eq. (60) to perform the integral over k^0 and obtain

$$\begin{aligned} \delta H_8 = \Bigg[-\frac{ie^2}{8m^3}\int\frac{d^3k}{(2\pi)^3}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)\times(e^{i\vec{k}\vec{r}_1}\vec{p}_1\times\vec{s}_1+\vec{p}_1 \\ \times\vec{s}_1e^{i\vec{k}\cdot\vec{r}_1})^i\frac{1}{E_0-H_0-k}(\vec{p}_2-i\vec{s}_2\times\vec{k})^je^{-i\vec{k}\cdot\vec{r}_2}+\mathrm{H.c.}\Bigg] \\ +(1\leftrightarrow 2). \end{aligned} \tag{76}$$

Now, we proceed with the retardation expansion in Eq. (62). In the present case we substitute $1/(E_0-H_0-k)\to(H_0-E_0)/k^2$ and commute (H_0-E_0) to the left. The result is

$$\begin{aligned} \delta H_8 = \Bigg\{-\frac{ie^2}{8m^3}\int\frac{d^3k}{(2\pi)^3k^2}\left(\delta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)\times\Bigg[e^{i\vec{k}\vec{r}_1}\vec{p}_1\times\vec{s}_1+\vec{p}_1 \\ \times\vec{s}_1e^{i\vec{k}\cdot\vec{r}_1},\frac{p_1^2}{2m}+V\Bigg]^i(\vec{p}_2-i\vec{s}_2\times\vec{k})^je^{-i\vec{k}\cdot\vec{r}_2}+\mathrm{H.c.}\Bigg\} \\ +(1\leftrightarrow 2). \end{aligned} \tag{77}$$

With the help of Eq. (50) one can recognize the static magnetic field in the above integral. Additionally, the term with the commutator of V produces static electric field $\vec{\mathcal{E}}$. Therefore

$$\delta H_8 = \sum_{a=1,2} \frac{e^2}{4m^2}\vec{s}_a(\vec{\mathcal{E}}_a \times \vec{\mathcal{A}}_a - \vec{\mathcal{A}}_a \times \vec{\mathcal{E}}_a) + \frac{ie}{8}[\vec{\mathcal{A}}_a(\vec{p}_a \times \vec{s}_a) + (\vec{p}_a \times \vec{s}_a)\vec{\mathcal{A}}_a, p_a^2]. \tag{78}$$

δH_9 is the sum of one- and two-loop corrections,

$$\delta H_9 = H_{L1} + H_{L2}, \tag{79}$$

which requires a separate treatment. We take this correction from Ref. [17] and adopt it for the positronium. For the states with $l>0$ the operator H_{L1} vanishes and we can write

$$\delta H_9 = H_{L2} = -\frac{\alpha^3}{\pi^2 m^2}\frac{s_2^i s_1^j}{r^3}\left(\delta^{ij} - 3\frac{r^i r^j}{r^2}\right)[2a^{(2)} + (a^{(1)})^2] + \frac{2\alpha^3}{\pi^2 m^2 r^3}\vec{S}(\vec{r}\times\vec{p})a^{(2)}, \tag{80}$$

where:

$$\kappa = \frac{\alpha}{\pi}a^{(1)} + \left(\frac{\alpha}{\pi}\right)^2 a^{(2)} + \cdots, \tag{81}$$

$$a^{(1)} = \frac{1}{2}, \tag{82}$$

$$a^{(2)} = \frac{3}{4}\zeta(3) - \frac{\pi^2}{2}\ln(2) + \frac{\pi^2}{12} + \frac{197}{144}, \tag{83}$$

κ is the anomaly of the electron's magnetic moment, and $\zeta(z)$ is the Riemann zeta function.

IV. CORRECTIONS TO THE ENERGY LEVELS

In this section we present the calculation of the correction to the energy levels ($E^{(6)}$). We use the ordinary quantum-mechanical perturbation theory. The total perturbed Hamiltonian reads

$$H = H_0 + H^{(4)} + H^{(5)} + H^{(6)} + \cdots. \tag{84}$$

Let us consider the basis consisting of the states $\{|n,j,l,s,j_z\rangle\}$. The unperturbed Hamiltonian H_0 is degenerate with respect to the quantum numbers (j,l,s,j_z). According to the general theory, if one want to use these states in perturbation calculus then one should check whether the perturbed Hamiltonian is diagonal in that basis. In order to show that this is the case, first let us consider the operator $H^{(4)}$ in the first order of perturbation theory. For states with $l>0$ the Breit-Pauli Hamiltonian reads (see, e.g., Ref. [25], Sec. 84)

$$H^{(4)} = -\frac{p^4}{4m^3} - \frac{\alpha}{2m^2 r}[p^2 + \vec{n}\cdot(\vec{n}\cdot\vec{p})\vec{p}] + \frac{3\alpha}{2m^2 r^3}\vec{L}\cdot\vec{S} + \frac{3\alpha}{2m^2 r^3}\left((\vec{S}\cdot\vec{n})^2 - \frac{1}{3}\vec{S}^2\right). \tag{85}$$

It contains the spin-orbital term $(\vec{S}\cdot\vec{n})^2$ which has nonzero matrix elements between the states for which the difference in the quantum number l is $|\Delta l|=0,2$. However, with the help of the results presented in Appendix B and Eq. (180), one can show that after all

$$\left\langle n,j,l,s,j_z\left|\frac{1}{r^3}\left((\vec{S}\vec{n})^2 - \frac{1}{3}\vec{S}^2\right)\right|n,j,l\pm 2,s,j_z\right\rangle = 0. \tag{86}$$

Moreover, $H^{(4)}$ removes the degeneracy with respect to the number l. Owing to this fact, there is no need to solve the secular equation in the case of the $H^{(6)}$ operator, which contains some nondiagonal terms with respect to the number l. According to the ordinary perturbation theory we can write

$$E^{(6)} = \langle\phi|H^{(6)}|\phi\rangle + \langle\phi|H^{(4)}\frac{1}{(E_0 - H_0)'}H^{(4)}|\phi\rangle. \tag{87}$$

We recall the notation $|\phi\rangle = |n,j,l,s,j_z\rangle$ and add the remark that owing to symmetry properties the energy corrections do not depend on the number j_z. In the following section we proceed with the first-order perturbation theory using the effective Hamiltonian derived in the last section. For simplicity, below we put $m=1$ and $\alpha=1$.

A. First-order corrections

Let us start with $\delta E_0 = \langle\phi|H_0|\phi\rangle$, where H_0 is given by Eq. (21). We use the relations

$$p^2 = H_0 + \frac{1}{r}, \tag{88}$$

$$H_0|\phi\rangle = E_0|\phi\rangle, \tag{89}$$

$$\left\langle\frac{1}{r}H_0\frac{1}{r}\right\rangle = E_0\left\langle\frac{1}{r^2}\right\rangle + \left\langle\frac{1}{r^4}\right\rangle, \tag{90}$$

and get

$$\delta E_0 = E_0^3 + 3E_0^2\left\langle\frac{1}{r}\right\rangle + 3E_0\left\langle\frac{1}{r^2}\right\rangle + \left\langle\frac{1}{r^3}\right\rangle + \left\langle\frac{1}{r^4}\right\rangle. \tag{91}$$

In the above formula and below, the expectation values are calculated for the state $|\phi\rangle$. In Appendix A we present the expectation values for various operators, starting with $1/r^k$.

The next correction is given by $\delta E_1 = \langle H_1\rangle$ with H_1 from Eq. (31). First, we rewrite this effective operator in terms of more familiar operators. We use a definition of the orbital angular momentum operator $\vec{L}=\vec{r}\times\vec{p}$ and the fact that $\nabla^2(1/r) = -4\pi\delta^3(\vec{r})$. In this way we get

$$\delta H_1 = -\frac{3}{32}(p^2\vec{S}\vec{L} + \vec{S}\vec{L}p^2) + \frac{1}{64}(p^4V + Vp^4 - 2p^2Vp^2) - \frac{12\pi}{32}[p^2\delta^{(3)}(\vec{r}) + \delta^{(3)}(\vec{r})p^2]. \tag{92}$$

Let us notice that the last term on the RHS of the above equation vanishes for the states with $l>0$. By virtue of the relations (88)–(90), we may write

$$\delta E_1 = -\frac{3}{8}\left(E_0\left\langle\frac{1}{r^3}\right\rangle\vec{S}\cdot\vec{L} + \left\langle\frac{1}{r^4}\right\rangle\vec{S}\cdot\vec{L} - \frac{1}{32}\left\langle\frac{1}{r^4}\right\rangle\right). \tag{93}$$

In the rest of this paper we use the following notation: $\vec{S}\cdot\vec{L} = \frac{1}{2}[j(j+1)-l(l+1)-s(s+1)]$, $\vec{L}^2 = l(l+1)$, and $\vec{S}^2 = s(s+1)$, where j,l,s are the appropriate quantum numbers.

The next correction comes from the operator δH_2 in Eq. (35). For the states with $l>0$ this operator can be written as

$$\delta H_2 = \frac{\pi}{8}\vec{p}\delta^3(\vec{r})\vec{p} + \frac{i\pi}{4}\vec{S}\cdot[\vec{p}\times\delta^3(\vec{r})\vec{p}] + \frac{1}{4}(\vec{s}_2\times\vec{p})^i\left[\frac{\delta_{ij}}{3}4\pi\delta^3(\vec{r}) + \frac{1}{r^3}\left(\delta^{ij} - 3\frac{r^i r^j}{r^2}\right)\right](\vec{s}_1\times\vec{p})^j. \tag{94}$$

Now, let us notice that the terms with Dirac δ function and two $\vec{p}$ operators vanishes for the states with $l>1$. Because of this fact the analytical formulas for $l=1$ and for $l>1$ are different. For the case $l=1$ we calculate E_2 in a different manner, namely, we use the identity

$$\langle\psi|H|\psi\rangle = \mathrm{Tr}(H|\psi\rangle\langle\psi|) \tag{95}$$

and a set of identities for P states from Ref. [23]:

$$|{}^3P_0\rangle\langle{}^3P_0| = |P^i\rangle\langle P^j|\left(\frac{1}{2}\delta_{ij}\vec{S}^2 - S_iS_j\right),$$

$$\frac{1}{3}\sum_{j_z}|{}^3P_1,j_z\rangle\langle{}^3P_1,j_z| = |P^i\rangle\langle P^j|\frac{1}{2}S_iS_j,$$

$$\frac{1}{5}\sum_{j_z}|{}^3P_2,j_z\rangle\langle{}^3P_2,j_z| = |P^i\rangle\langle P^j|\frac{1}{10}(2\delta_{ij}\vec{S}^2 - 3S_iS_j + 2S_jS_i),$$

$$\frac{1}{3}\sum_{j_z}|{}^1P_1,j_z\rangle\langle{}^1P_1,j_z| = |P^i\rangle\langle P^j|\delta_{ij}\left(1 - \frac{1}{2}\vec{S}^2\right), \tag{96}$$

where

$$\langle\vec{r}|P^i\rangle = \frac{r^i}{r}R_{n1}(r), \tag{97}$$

and R_{nl} is the radial part of the $\langle\vec{r}|\phi\rangle$ wave function. In order to tackle the terms containing the Dirac δ function we exploit the formula

$$\langle P_j|p_k\delta^{(3)}(\vec{r})p_l|P_i\rangle = \frac{\delta_{jk}\delta_{il}}{72}\frac{(n-1)(n+1)}{4\pi n^5}. \tag{98}$$

Then we use a symbolic computer program [24] to trace over spin variables, differentiate, and integrate over $\vec{r}$ variables. The formulas for P states are

$$\delta E_2(n\,{}^1P_1) = -\frac{1}{1920n^5} + \frac{1}{1280n^3},$$

$$\delta E_2(n\,{}^3P_0) = -\frac{7}{960n^5} + \frac{9}{1280n^3},$$

$$\delta E_2(n\,{}^3P_1) = -\frac{1}{256n^5} + \frac{1}{256n^3},$$

$$\delta E_2(n\,{}^3P_2) = \frac{19}{19\,200n^5} - \frac{7}{6400n^3}. \tag{99}$$

Now, we will calculate E_2 for states with $l>1$. As mentioned before, in this case all the terms containing the Dirac δ function vanish and δH_2 reduces to

$$\delta H_2 = \frac{1}{4}(\vec{s}_2\times\vec{p})^i\frac{1}{r^3}\left(\delta^{ij} - 3\frac{r^ir^j}{r^2}\right)(\vec{s}_1\times\vec{p})^j = \frac{1}{4}\epsilon_{iab}\epsilon_{jcd}s_2^a s_1^c p^b\frac{1}{r^3}\left(\delta^{ij} - 3\frac{r^ir^j}{r^2}\right)p^d. \tag{100}$$

Similar terms containing a double-spin operator occur frequently throughout this paper. In order to tackle them, we exchange the s_1,s_2 operators for the total spin operator $\vec{S}$. This can be done with the help of the observation that, if the expectation value $\langle s_1^i s_2^j T_{ij}\rangle$ satisfies the condition $\langle s_1^i s_2^j T_{ij}\rangle = \langle s_1^i s_2^j T_{ji}\rangle$ and T_{ij} is a spin-independent operator, then

$$\langle s_1^i s_2^j T_{ij}\rangle = \left\langle\frac{1}{2}\left(S^iS^j - \frac{1}{2}\delta^{ij} - \frac{i}{2}\epsilon^{ijk}S_k\right)T_{ij}\right\rangle = \frac{1}{2}\langle S^iS^jT_{ij}\rangle - \frac{1}{4}\langle\mathrm{Tr}(T)\rangle. \tag{101}$$

We have obtained an expression containing a double-total-spin operator, which can be handled by means of the general theory concerning tensor corrections [26,27] (see Appendix B). In the case of δH_2 we recognize

$$T_{ac} = \frac{1}{4}\epsilon_{iab}\epsilon_{jcd}p^b\frac{1}{r^3}\left(\delta^{ij} - 3\frac{r^ir^j}{r^2}\right)p^d. \tag{102}$$

After some algebra the following result is obtained (for $l>1$):

$$\delta E_2 = \frac{1}{16}\left\langle\frac{1}{r^5}\right\rangle[3\vec{L}^2 + 4\vec{S}^2 - 6 - 3\vec{S}\cdot\vec{L} - 6(\vec{S}\cdot\vec{L})^2 - 15\xi(j,l,s)] + \frac{1}{24}\left\langle\frac{1}{r^4}\right\rangle[2\vec{S}^2 - 3 - 3\xi(j,l,s)] + \frac{E_0}{24}\left\langle\frac{1}{r^3}\right\rangle[2\vec{S}^2 - 3 - 3\xi(j,l,s)], \tag{103}$$

where we have introduced the symbol

$$\xi(j,l,s) = \frac{1}{3}\frac{2\vec{L}^2\vec{S}^2 - 3\vec{S}\cdot\vec{L}(1 + 2\vec{S}\cdot\vec{L})}{4\vec{L}^2 - 3}, \tag{104}$$

which origin is shown in Appendix B. Let us notice that, even though the expectation value of the operator $1/r^5$ is divergent for the states with $l<2$, the correction δE_2 for $l=1$ still can be obtained from Eq. (103). In order to do that, first, one should reduce the factors $(l-1)$ in δE_2 and then substitute $l=1$. Similar situations appear for the other effective operators.

The next correction is

$$\delta E_3 = \frac{1}{16}\left\langle\left[p^2,\left[p^2,\frac{1}{r}\right]\right]\right\rangle. \tag{105}$$

By the virtue of relations (88)–(90) we obtain

$$\delta E_3 = \frac{1}{8}\left\langle\frac{1}{r^4}\right\rangle. \tag{106}$$

The next correction is δE_4. First, we put the δH_4 operator from Eq. (51) in a different form. Namely, we split it into four terms:

$$\delta H_4 = \delta H_4^{(1)} + \delta H_4^{(2)} + \delta H_4^{(3)} + \delta H_4^{(4)}, \tag{107}$$

where

$$\delta H_4^{(1)} = \frac{1}{4}p^2 p_i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_j + \frac{1}{4}p_i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_j p^2, \tag{108}$$

$$\delta H_4^{(2)} = -\frac{1}{2}p^2 p_i(\vec{S}\times\vec{A}_{\rm II})^i - \frac{1}{2}p_i(\vec{S}\times\vec{A}_{\rm II})^i p^2, \tag{109}$$

$$\delta H_4^{(3)} = \frac{1}{4}p^2\vec{S}\cdot(\vec{\nabla}\times\vec{A}_{\rm I}) + \frac{1}{4}\vec{S}\cdot(\vec{\nabla}\times\vec{A}_{\rm I})p^2, \tag{110}$$

$$\begin{aligned} H_4^{(4)} = &-\frac{1}{2}p^2\{\vec{s}_1[\vec{\nabla}\times(\vec{s}_2\times\vec{A}_{\rm II})] + \vec{s}_2[\vec{\nabla}\times(\vec{s}_1\times\vec{A}_{\rm II})]\} \\ &-\frac{1}{2}\{\vec{s}_1[\vec{\nabla}\times(\vec{s}_2\times\vec{A}_{\rm II})] + \vec{s}_2[\vec{\nabla}\times(\vec{s}_1\times\vec{A}_{\rm II})]\}p^2. \end{aligned} \tag{111}$$

Here we have split the static magnetic field from Eq. (50) into

$$A_1^i = A_{\rm I}^i - 2(\vec{s}_2\times\vec{A}_{\rm II})^i, \tag{112}$$

$$A_2^i = -A_{\rm I}^i + 2(\vec{s}_1\times\vec{A}_{\rm II})^i, \tag{113}$$

where:

$$A_{\rm I}^i = \frac{\alpha}{2r}\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)\frac{p_j}{m}, \tag{114}$$

$$A_{\rm II}^i = \frac{\alpha}{2m}\frac{r^i}{r^3}. \tag{115}$$

In order to calculate $\langle H_4^{(1)}\rangle$ one can commute operators until the momentum operators form either $(r^i/r)p_i=\partial_r$ or p^2 operators. The result is

$$\begin{aligned}\langle H_4^{(1)}\rangle = &\frac{1}{2}E_0^2\left\langle\frac{1}{r}\right\rangle + E_0\left\langle\frac{1}{r^2}\right\rangle - \frac{1}{2}E_0\left\langle\frac{1}{r}\partial_r^2\right\rangle + \frac{1}{2}\left\langle\frac{1}{r^3}\right\rangle \\ &+ \frac{1}{8}\left\langle\frac{1}{r^4}\right\rangle - \frac{1}{2}\left\langle\frac{1}{r^2}\partial_r^2\right\rangle - \frac{1}{4}\left\langle\frac{1}{r^3}\partial_r\right\rangle.\end{aligned} \tag{116}$$

The appropriate expectation values can be found in Appendix A. The operator $\delta H_4^{(2)}$ can be written as

$$\delta H_4^{(2)} = -\frac{1}{4}p^2 p^i\frac{(\vec{S}\times r)^i}{r^3} - \frac{1}{4}p^i\frac{(\vec{S}\times r)^i}{r^3}p^2; \tag{117}$$

therefore

$$\begin{aligned}\langle\delta H_4^{(2)}\rangle &= -\frac{1}{4}\left\langle p^2\frac{\vec{L}\cdot\vec{S}}{r^3}\right\rangle - \frac{1}{4}\left\langle\frac{\vec{L}\cdot\vec{S}}{r^3}p^2\right\rangle \\ &= -\frac{E_0}{2}\left\langle\frac{1}{r^3}\right\rangle\vec{L}\cdot\vec{S} - \frac{1}{2}\left\langle\frac{1}{r^4}\right\rangle\vec{L}\cdot\vec{S}.\end{aligned} \tag{118}$$

Similarly,

$$\langle\delta H_4^{(3)}\rangle = -\frac{E_0}{2}\left\langle\frac{1}{r^3}\right\rangle\vec{L}\cdot\vec{S} - \frac{1}{2}\left\langle\frac{1}{r^4}\right\rangle\vec{L}\cdot\vec{S} = \langle\delta H_4^{(2)}\rangle. \tag{119}$$

In the first step of the calculation of $\langle\delta H_4^{(4)}\rangle$ we use the formula given by Eq. (101). Then with the help of relation (88) the operator $\delta H_4^{(4)}$ can be written as

$$\delta H_4^{(4)} = \frac{1}{2}\left(E_0 + \frac{1}{r}\right)\left(\delta_{ij} - \frac{3r_i r_j}{r^2}\right)\frac{S^i S^j}{r^3}. \tag{120}$$

According to the theory of tensor corrections (see Appendix B) we obtain

$$\delta H_4^{(4)} = -\frac{3}{2}E_0\left\langle\frac{1}{r^3}\right\rangle\xi(j,l,s) - \frac{3}{2}\left\langle\frac{1}{r^4}\right\rangle\xi(j,l,s). \tag{121}$$

Finally, δE_4 reads

$$\begin{aligned}\delta E_4 = &\left(\frac{1}{2} - \frac{1}{2}\vec{L}^2\right)\left\langle\frac{1}{r^4}\right\rangle + \left(1 - \frac{1}{2}\vec{L}^2 E_0\right)\left\langle\frac{1}{r^3}\right\rangle + 2E_0\left\langle\frac{1}{r^2}\right\rangle \\ &+ E_0^2\left\langle\frac{1}{r}\right\rangle - \left(E_0\left\langle\frac{1}{r^3}\right\rangle + \left\langle\frac{1}{r^4}\right\rangle\right)\left(\vec{L}\cdot\vec{S} + \frac{3}{2}\xi(j,l,s)\right).\end{aligned} \tag{122}$$

The next correction to the Hamiltonian [Eq. (55)] reads

$$\begin{aligned}\delta H_5 = \sum_a \frac{e^2}{2}A_a^2 = &\frac{1}{2}[A_{\rm I}^i - 2(\vec{s}_2\times\vec{A}_{\rm II})^i]^2 \\ &+ \frac{1}{2}[-A_{\rm I}^i + 2(\vec{s}_1\times\vec{A}_{\rm II})^i]^2.\end{aligned} \tag{123}$$

It can be expressed in terms of operators $\vec{A}_{\rm I}$ and $\vec{A}_{\rm II}$ defined by Eq. (112):

$$\begin{aligned}\delta H_5 = &\vec{A}_{\rm I}\vec{A}_{\rm I} - \vec{A}_{\rm I}(\vec{S}\times\vec{A}_{\rm II}) - (\vec{S}\times\vec{A}_{\rm II})\vec{A}_{\rm I} + 2(\vec{s}_1\times\vec{A}_{\rm II})(\vec{s}_1\times\vec{A}_{\rm II}) \\ &+ 2(\vec{s}_2\times\vec{A}_{\rm II})(\vec{s}_2\times\vec{A}_{\rm II}).\end{aligned} \tag{124}$$

Calculation of this correction is similar to what we have done before; therefore we skip the details and present the result:

$$\delta E_5 = E_0\left\langle\frac{1}{r^2}\right\rangle + \left\langle\frac{1}{r^3}\right\rangle + \left(\frac{3}{4}\vec{L}^2 - \frac{1}{2}\vec{L}\cdot\vec{S} + \frac{3}{2}\right)\left\langle\frac{1}{r^4}\right\rangle. \tag{125}$$

The next operator can be written as

$$\delta H_6 = \sum_{a=1,2} \frac{e^2}{2}\vec{A}_a^2 = \delta H_6^{(1)} + \delta H_6^{(2)}, \tag{126}$$

where

$$\delta H_6^{(1)} = \frac{1}{4}\vec{S}\left(\vec{A}_{\mathrm{I}} \times \frac{\vec{r}}{r^3} - \frac{\vec{r}}{r^3} \times \vec{A}_{\mathrm{I}}\right), \tag{127}$$

$$\delta H_6^{(2)} = \vec{s}_1\left(\frac{\vec{r}}{r^3} \times (\vec{s}_2 \times \vec{A}_{\mathrm{II}})\right) + \vec{s}_2\left(\frac{\vec{r}}{r^3} \times (\vec{s}_1 \times \vec{A}_{\mathrm{II}})\right). \tag{128}$$

The operator $H_6^{(1)}$ can be treated in a similar way as $H_4^{(2)}$, whereas a double-spin operator $H_6^{(2)}$ can be calculated by means of Eq. (101). The total δE_6 reads

$$\delta E_6 = -\frac{\vec{L}\cdot\vec{S}}{4}\left\langle\frac{1}{r^4}\right\rangle - \frac{1}{2}\left\langle\frac{1}{r^4}\right\rangle + \frac{\vec{S}^2}{3}\left\langle\frac{1}{r^4}\right\rangle - \frac{1}{2}\xi(j,l,s)\left\langle\frac{1}{r^4}\right\rangle. \tag{129}$$

The operator $\delta H_7^{(A)}$ from Eq. (68) can be treated in a similar fashion as $\delta H_4^{(1)}$ from Eq. (107); namely, one can commute operators until they form either of the operators $(r^i/r)p_i = \partial_r$ or p^2. After this rather tedious procedure we obtain

$$\begin{aligned}\delta E_7^{(A)} = &-\left\langle\frac{1}{r}\right\rangle\frac{E_0^2}{4} - \left\langle\frac{1}{r^2}\right\rangle E_0 + \left\langle\frac{1}{r^3}\right\rangle\left(\frac{E_0}{4}\vec{L}^2 - \frac{E_0}{4} - \frac{1}{2}\right)\\ &+\left\langle\frac{1}{r^4}\right\rangle\left(\frac{3}{2}\vec{L}^2 - \frac{7}{8}\right) - \left\langle\frac{1}{r^5}\right\rangle\frac{3}{2}\left(1 + \frac{1}{4}\vec{L}^2(l-1)(l+2)\right)\\ &-\frac{1}{4}\left\langle\frac{1}{r^2}\partial_r^2\right\rangle + \frac{1}{4}\left\langle\frac{1}{r^3}\partial_r\right\rangle - \frac{3}{4}\left\langle\frac{1}{r^3}\partial_r^2\right\rangle + \frac{3}{2}\left\langle\frac{1}{r^4}\partial_r\right\rangle\\ &-\frac{E_0}{4}\left\langle\frac{1}{r}\partial_r^2\right\rangle,\end{aligned} \tag{130}$$

where all necessary expectation values are presented in Appendix A.

The single-spin part $\delta H_7^{(B)}$ [Eq. (71)] can be treated with the help of the relations

$$\left[\vec{S}\times\frac{\vec{r}}{r},p^2\right][V,\vec{p}] = 2\frac{\vec{S}\cdot\vec{L}}{r^4},$$

$$[\vec{p},V]\left[p^2,\vec{S}\times\frac{\vec{r}}{r}\right] = 2\frac{\vec{S}\cdot\vec{L}}{r^4}, \tag{131}$$

and the result is

$$\langle\delta H_7^B\rangle = \frac{\vec{S}\cdot\vec{L}}{4}\left\langle\frac{1}{r^4}\right\rangle. \tag{132}$$

Now, we turn to the double-spin part, which is

$$\delta H_7^C = -\frac{1}{4}\left[p^2,\left[p^2,\vec{s}_1\vec{s}_2\frac{2}{3r} + s_1^i s_2^j\frac{1}{2r}\left(\frac{r_i r_j}{r^2} - \frac{\delta_{ij}}{3}\right)\right]\right]. \tag{133}$$

By virtue of relation (88), the above correction can be written as

$$\begin{aligned}\langle\delta H_7^C\rangle = &-\frac{\vec{s}_1\cdot\vec{s}_2}{3}\left\langle\frac{1}{r^4}\right\rangle - \frac{1}{16}\left\langle s_1^i s_2^j\left[\frac{1}{r},\left[p^2,\frac{1}{2r}\right.\right.\right.\\ &\left.\left.\left.\times\left(\frac{r_i r_j}{r^2} - \frac{\delta_{ij}}{3}\right)\right]\right]\right\rangle,\end{aligned} \tag{134}$$

where

$$\vec{s}_1\cdot\vec{s}_2 = \frac{1}{2}\left(\vec{S}^2 - \frac{3}{2}\right). \tag{135}$$

The second term on the RHS of Eq. (134) can be treated with the help of Eq. (101) and basic commutator identities, yielding

$$\delta E_7^C = \left\langle\frac{1}{r^4}\right\rangle\left(\frac{1}{4} - \frac{\vec{S}^2}{6} - \frac{1}{8}\xi(j,l,s)\right). \tag{136}$$

In the case of the next correction, δE_8, we notice that the appropriate operator [see Eq. (78)] can be written as

$$\begin{aligned}\delta H_8 = \sum_{a=1,2}&\left(\frac{1}{4}\vec{s}_a(\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a - \vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a) + \frac{i}{8}[\vec{\mathcal{A}}_a(\vec{p}_a\times\vec{s}_a)\right.\\ &\left.+(\vec{p}_a\times\vec{s}_a)\vec{\mathcal{A}}_a,p_a^2]\right) = \delta H_5 + \delta H_8^{(2)},\end{aligned} \tag{137}$$

where

$$\delta H_8^{(2)} = \sum_{a=1,2}\frac{i}{8}[\vec{\mathcal{A}}_a\cdot(\vec{p}_a\times\vec{s}_a) + (\vec{p}_a\times\vec{s}_a)\cdot\vec{\mathcal{A}}_a,p_a^2]. \tag{138}$$

The expectation value of δH_8 is similar to expressions we have calculated before; therefore we just write the total result, which is

$$\delta E_8 = \delta E_5 + \left\langle\frac{1}{r^4}\right\rangle\left(\frac{1}{4} - \frac{\vec{L}\cdot\vec{S}}{8} + \frac{1}{4}\xi(j,l,s) - \frac{\vec{S}^2}{6}\right), \tag{139}$$

where δE_5 is given by Eq. (125).

We write here only those parts of δH_9 [see Eq. (79)] that contribute to the states with $l>0$. Therefore

$$\begin{aligned}\delta H_9 = &-\frac{1}{\pi^2}\frac{s_2^i s_1^j}{r^3}\left(\delta^{ij} - 3\frac{r^i r^j}{r^2}\right)[2a^{(2)} + (a^{(1)})^2]\\ &+\frac{2}{\pi^2 r^3}\vec{S}\cdot(\vec{r}\times\vec{p})a^{(2)}.\end{aligned} \tag{140}$$

As before, for the single-spin part one can use the relation $\vec{L}=\vec{r}\times\vec{p}$ and for the double-spin part one uses Eq. (101). In this way one obtains

$$\delta E_9 = \left\langle \frac{1}{r^3} \right\rangle \left(2a_2 \frac{\vec{S}\cdot\vec{L}}{\pi^2} + (2a_2 + a_1^2)\xi(j,l,s)\frac{3}{2\pi^2} \right), \tag{141}$$

which is the last correction coming from the first order of perturbation theory.

B. Second-order corrections

Now, we turn to the second-order corrections, that is, we calculate corrections of the form

$$\delta E^{(6)} = \left\langle \phi \left| H^{(4)} \frac{1}{(E_0 - H_0)'} H^{(4)} \right| \phi \right\rangle. \tag{142}$$

The Breit Hamiltonian for $l>0$ [see Eq. (85)] can be expressed as

$$H^{(4)} = -\frac{1}{4}H_0^2 + \sum_{i=1}^{5} R_i, \tag{143}$$

where:

$$R_1 = -\frac{5}{4}\frac{1}{r^2}, \tag{144}$$

$$R_2 = -\frac{3}{4}\frac{1}{r}H_0, \tag{145}$$

$$R_3 = -\frac{3}{4}H_0\frac{1}{r}, \tag{146}$$

$$R_4 = \frac{1}{2r^3}(\vec{L}^2 + 3\vec{L}\cdot\vec{S} - \vec{S}^2), \tag{147}$$

$$R_5 = \frac{3}{2r^3}(\vec{S}\cdot\vec{n})^2. \tag{148}$$

The term with operator H_0^2 vanishes in the second order of perturbative calculation so it does not occur below. We also introduce the reduced Green function

$$G = \frac{1}{(E_n - H_0)'} = \sum_{k\neq n,j,l,s,j_z} \frac{|k,j,l,s,j_z\rangle\langle k,j,l,s,j_z|}{E_n - E_k}. \tag{149}$$

The sum of the corrections coming from second order of perturbation theory can be written as

$$\delta E^{(6)} = \sum_{i<j} R_{ij} + \sum_i R_{ii}, \tag{150}$$

where

$$R_{ij} = \langle R_i G R_j + R_j G R_i \rangle, \quad i \neq j, \tag{151}$$

$$R_{ii} = \langle R_i G R_i \rangle. \tag{152}$$

Let us start the calculation with R_{11}:

$$R_{11} = \left(\frac{5}{4}\right)^2 \left\langle \frac{1}{r^2} G \frac{1}{r^2} \right\rangle = \left(\frac{5}{4}\right)^2 \delta E_{22}, \tag{153}$$

where

$$\delta E_{nm} = \begin{cases} \left\langle \dfrac{1}{r^n} G \dfrac{1}{r^m} + \dfrac{1}{r^m} G \dfrac{1}{r^n} \right\rangle, & n \neq m = 1,2,3, \\ \left\langle \dfrac{1}{r^n} G \dfrac{1}{r^n} \right\rangle, & n = 1,2,3. \end{cases} \tag{154}$$

The values of δE_{nm} are calculated in Appendix A.

Since the calculation of the next term is typical for the second-order corrections, we present it at length so later we can proceed faster:

$$\begin{aligned} R_{12} &= \frac{15}{16}\left\langle \frac{1}{r^2}G\frac{1}{r}H_0 + \frac{1}{r}H_0 G \frac{1}{r^2} \right\rangle \\ &= \frac{15}{16}\left(E_0 \left\langle \frac{1}{r^2}G\frac{1}{r} \right\rangle + \left\langle \frac{1}{r}(H_0 - E_0 + E_0) G \frac{1}{r^2} \right\rangle \right) \\ &= \frac{15}{16}\left(E_0 \left\langle \frac{1}{r^2}G\frac{1}{r} + \frac{1}{r}G\frac{1}{r^2} \right\rangle + \left\langle \frac{1}{r}(|\phi\rangle\langle\phi| - \mathbb{1})\frac{1}{r^2} \right\rangle \right) \\ &= \frac{15}{16}\left(E_0 \delta E_{12} + \left\langle \frac{1}{r} \right\rangle \left\langle \frac{1}{r^2} \right\rangle - \left\langle \frac{1}{r^3} \right\rangle \right), \end{aligned} \tag{155}$$

where we have used the following identity:

$$(H_0 - E_0)G = |\phi\rangle\langle\phi| - \mathbb{1}. \tag{156}$$

Several corrections can be obtained in a similar way; therefore we drop the details and list the results:

$$R_{13} = R_{12}, \tag{157}$$

$$R_{14} = -\frac{5}{8}(\vec{L}^2 + 3\vec{L}\cdot\vec{S} - \vec{S}^2)\delta E_{23}, \tag{158}$$

$$R_{22} = \left(\frac{3}{4}\right)^2 E_0 \left(E_0 \delta E_{11} + \left\langle \frac{1}{r} \right\rangle^2 - \left\langle \frac{1}{r^2} \right\rangle \right), \tag{159}$$

$$R_{23} = \left(\frac{3}{4}\right)^2 \left(2E_0^2 \delta E_{11} + 2E_0 \left\langle \frac{1}{r} \right\rangle^2 - 2E_0 \left\langle \frac{1}{r^2} \right\rangle - \left\langle \frac{1}{r^4} \right\rangle \right), \tag{160}$$

$$R_{24} = \frac{3}{4}(\vec{L}^2 + 3\vec{L}\cdot\vec{S} - \vec{S}^2)\left(E_0 \delta E_{13} + \left\langle \frac{1}{r} \right\rangle \left\langle \frac{1}{r^3} \right\rangle - \left\langle \frac{1}{r^4} \right\rangle \right), \tag{161}$$

$$R_{33} = \left(\frac{3}{4}\right)^2 \left\langle H_0 \frac{1}{r} G H_0 \frac{1}{r} \right\rangle = R_{22}, \tag{162}$$

$$R_{34} = R_{24}, \tag{163}$$

$$R_{44} = \frac{1}{4}\delta E_{33}(\vec{L}^2 + 3\vec{L}\cdot\vec{S} - \vec{S}^2)^2. \tag{164}$$

We turn now to the terms that contain R_5. Let us start with

$$R_{15} = -\frac{15}{8}\left\langle \frac{1}{r^2} G \frac{(\vec{S}\cdot\vec{n})^2}{r^3} + \frac{(\vec{S}\cdot\vec{n})^2}{r^3} G \frac{1}{r^2} \right\rangle. \quad (165)$$

In the first step, we expand the operator G in the amplitude

$$\left\langle \frac{1}{r^2} G \frac{(\vec{S}\cdot\vec{n})^2}{r^3} \right\rangle = \left\langle \frac{1}{r^2} \sum_{k\neq n, j', l', s', j_z'} \frac{|k,j',l',s',j_z'\rangle\langle k,j',l',s',j_z'|}{E_n - E_k} \frac{(\vec{S}\cdot\vec{n})^2}{r^3} \right\rangle. \quad (166)$$

The matrix element of the operator $(\vec{S}\cdot\vec{n})^2$ does not vanish only for the states for which the difference in the quantum number l is $|\Delta l| = 0, 2$. Additionally, operator $(\vec{S}\cdot\vec{n})^2$ is diagonal in the numbers j, s, and j_z; therefore

$$\left\langle \frac{1}{r^2} G \frac{(\vec{S}\cdot\vec{n})^2}{r^3} \right\rangle = \left\langle \frac{1}{r^2} G \frac{1}{r^3} \right\rangle \langle \phi_l | (\vec{S}\cdot\vec{n})^2 | \phi_l \rangle, \quad (167)$$

where $|\phi_l\rangle$ is the spin-orbital part of the state, that is, $|\phi_l\rangle = |j,l,s,j_z\rangle$ and the numbers j, s, j_z are fixed. In order to calculate the spin-orbital part of the above expression we invoke the result derived in Appendix B:

$$\langle T_{ij} s^i s^j \rangle = \langle n,l | f(r) | n,l \rangle \xi(j,l,s), \quad (168)$$

where T_{ij} is a symmetric and traceless tensor. We can see that

$$\langle \phi_l | (\vec{S}\cdot\vec{n})^2 | \phi_l \rangle = \left\langle \phi_l \left| \left(n_i n_j - \frac{1}{3}\delta_{ij} \right) S^i S^j \right| \phi_l \right\rangle + \frac{1}{3}\vec{S}^2; \quad (169)$$

hence

$$\langle (\vec{S}\cdot\vec{n})^2 \rangle \equiv \langle \phi_l | (\vec{S}\cdot\vec{n})^2 | \phi_l \rangle = \xi(j,l,s) + \frac{1}{3}\vec{S}^2. \quad (170)$$

Finally,

$$R_{15} = -\frac{15}{8}\delta E_{23} \langle (\vec{S}\cdot\vec{n})^2 \rangle. \quad (171)$$

We also write the corrections which can be easily obtained in a similar way:

$$R_{25} = -\frac{9}{8}\langle (\vec{S}\cdot\vec{n})^2 \rangle \left(E_0 \delta E_{13} + \left\langle \frac{1}{r} \right\rangle \left\langle \frac{1}{r^3} \right\rangle - \left\langle \frac{1}{r^4} \right\rangle \right), \quad (172)$$

$$R_{35} = R_{25}, \quad (173)$$

$$R_{45} = \frac{3}{2}(\vec{L}^2 + 3\vec{L}\cdot\vec{S} - \vec{S}^2)\delta E_{33} \langle (\vec{S}\cdot\vec{n})^2 \rangle. \quad (174)$$

The next correction needs a separate treatment. In the first step we split it as below:

$$R_{55} = \left(\frac{3}{2}\right)^2 \left\langle \frac{(\vec{S}\cdot\vec{n})^2}{r^3} G \frac{(\vec{S}\cdot\vec{n})^2}{r^3} \right\rangle = A_1 + A_2 + A_3, \quad (175)$$

where

$$A_1 = \left\langle n,l \left| \frac{1}{r^3} \sum_{k\neq n} \frac{|k,l\rangle\langle k,l|}{E_n - E_k} \frac{1}{r^3} \right| n,l \right\rangle |\langle \phi_l | (\vec{S}\cdot\vec{n})^2 | \phi_l \rangle|^2,$$

$$A_2 = \left\langle n,l \left| \frac{1}{r^3} \sum_{k\neq n} \frac{|k,l+2\rangle\langle k,l+2|}{E_n - E_k} \frac{1}{r^3} \right| n,l \right\rangle \times |\langle \phi_l | (\vec{S}\cdot\vec{n})^2 | \phi_{l+2} \rangle|^2,$$

$$A_3 = \left\langle n,l \left| \frac{1}{r^3} \sum_{k\neq n} \frac{|k,l-2\rangle\langle k,l-2|}{E_n - E_k} \frac{1}{r^3} \right| n,l \right\rangle \times |\langle \phi_l | (\vec{S}\cdot\vec{n})^2 | \phi_{l-2} \rangle|^2. \quad (176)$$

Next, we calculate the necessary radial expectation values. We already have one [see Eq. (A21)], namely,

$$\left\langle n,l \left| \frac{1}{r^3} \sum_{k\neq n} \frac{|k,l\rangle\langle k,l|}{E_n - E_k} \frac{1}{r^3} \right| n,l \right\rangle = \delta E_{33}. \quad (177)$$

The next radial term reads

$$G_{L,L+2} = \left\langle n,l \left| \frac{1}{r^3} \sum_{k\neq n} \frac{|k,l+2\rangle\langle k,l+2|}{E_n - E_k} \frac{1}{r^3} \right| n,l \right\rangle = \left\langle n,l \left| \frac{1}{r^3} \frac{1}{(E_0 - H_{l+2})'} \frac{1}{r^3} \right| n,l \right\rangle, \quad (178)$$

where H_l is the radial part of the Hamiltonian, that is,

$$H_l = -\frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} - \frac{1}{r}. \quad (179)$$

In order to obtain $G_{L,L+2}$ we will generalize the trick from Ref. [15] to an arbitrary number l. In the first step, we represent the operator $1/r^3$ in the special forms

$$\frac{1}{r^3} = H_l \hat{\alpha} - \hat{\alpha} H_{l+2},$$

$$\frac{1}{r^3} = \hat{\beta} H_l - H_{l+2} \hat{\beta}, \quad (180)$$

where H_l is the radial part of the Hamiltonian [see Eq. (180)] and

$$\hat{\alpha} = a_1 D_r + \frac{b_1}{r} + c_1,$$

$$\hat{\beta} = -a_1 D_r + \frac{b_1}{r} + c_1, \quad (181)$$

where $D_r = 1/r + \partial_r$. The coefficients above are

$$a_1 = -\frac{1}{6(2 + 3l + l^2)},$$

$$b_1 = -\frac{3+2l}{6(2+3l+l^2)},$$

$$c_1 = -\frac{1}{12(6+13l+9l^2+2l^3)}. \tag{182}$$

In the next step, we substitute decomposition (180) into Eq. (178) and obtain

$$G_{L,L+2} = \left\langle (H_l\hat{\alpha} - \hat{\alpha}H_{l+2})\frac{1}{(E_0-H_{l+2})'}(\hat{\beta}H_l - H_{l+2}\hat{\beta})\right\rangle$$
$$= E_0\langle\hat{\alpha}\hat{\beta}\rangle - \langle\hat{\alpha}H_{l+2}\hat{\beta}\rangle, \tag{183}$$

where we have used the identity

$$\frac{E_0-H_{l+2}}{(E_0-H_{l+2})'} = \mathbb{1} - |n,l+2\rangle\langle n,l+2|. \tag{184}$$

After some algebra we get

$$\langle\hat{\alpha}\hat{\beta}\rangle = c_1^2 + a_1^2E_0 + (a_1^2+2b_1c_1)\left\langle\frac{1}{r}\right\rangle - \vec{L}^2a_1^2\left\langle\frac{1}{r^2}\right\rangle$$
$$- a_1b_1\left\langle\frac{1}{r^2}\right\rangle + b_1^2\left\langle\frac{1}{r^2}\right\rangle \tag{185}$$

and

$$\langle\hat{\alpha}H_{l+2}\hat{\beta}\rangle$$
$$= c_1^2E_0 + a_1^2E_0^2 + (a_1^2E_0 + 2b_1c_1E_0)\left\langle\frac{1}{r}\right\rangle$$
$$+ (a_1c_1 + c_1^2\Delta_l - \vec{L}^2a_1^2E_0 - a_1b_1E_0 + b_1^2E_0 + a_1^2\Delta_lE_0)$$
$$\times\left\langle\frac{1}{r^2}\right\rangle + [-a_1^2 + 2a_1b_1 + a_1^2\Delta_l + 2b_1c_1\Delta_l - 2a_1c_1$$
$$\times(\vec{L}^2+\Delta_l)]\left\langle\frac{1}{r^3}\right\rangle + [3(2+l)(3+l)a_1^2 - 4(2+l)$$
$$\times(3+l)a_1b_1 + b_1^2 - \vec{L}^2a_1^2\Delta_l + a_1b_1\Delta_l + b_1^2\Delta_l]\left\langle\frac{1}{r^4}\right\rangle, \tag{186}$$

where $\Delta_l=(l+2)(l+3)-l(l+1)$.

The last radial element is obtained in a similar way:

$$G_{L,L-2} = \left\langle (H_l\hat{\delta} - \hat{\delta}H_{l-2})\frac{1}{(E_0-H_{l-2})'}(\hat{\gamma}H_l - H_{l-2}\hat{\gamma})\right\rangle$$
$$= E_0\langle\hat{\delta}\hat{\gamma}\rangle - \langle\hat{\delta}H_{l-2}\hat{\gamma}\rangle. \tag{187}$$

This time the decomposition of $1/r^3$ reads

$$\frac{1}{r^3} = H_l\hat{\delta} - \hat{\delta}H_{l-2},$$

$$\frac{1}{r^3} = \hat{\gamma}H_l - H_{l-2}\hat{\gamma}, \tag{188}$$

where

$$\hat{\delta} = a_2D_r + \frac{b_2}{r} + c_2,$$

$$\hat{\gamma} = -a_2D_r + \frac{b_2}{r} + c_2, \tag{189}$$

and the coefficients are

$$a_2 = -\frac{1}{6(l-1)l},$$

$$b_2 = -\frac{1-2l}{6(l-1)l},$$

$$c_2 = -\frac{1}{12l(1-3l+2l^2)}. \tag{190}$$

If we additionally substitute $\Delta_l \to \tilde{\Delta}_l = -l(l+1)+(l-2)(l-1)$ then we can use the previous results and write

$$\langle\hat{\delta}\hat{\gamma}\rangle = c_2^2 + a_2^2E_0 + (a_2^2+2b_2c_2)\left\langle\frac{1}{r}\right\rangle - \vec{L}^2a_2^2\left\langle\frac{1}{r^2}\right\rangle$$
$$- a_2b_2\left\langle\frac{1}{r^2}\right\rangle + b_2^2\left\langle\frac{1}{r^2}\right\rangle \tag{191}$$

and

$$\langle\hat{\delta}H_{l-2}\hat{\gamma}\rangle = c_2^2E_0 + a_2^2E_0^2 + (a_2^2E_0 + 2b_2c_2E_0)\left\langle\frac{1}{r}\right\rangle$$
$$+ (a_2c_2 + c_2^2\tilde{\Delta}_l - \vec{L}^2a_2^2E_0 - a_2b_2E_0 + b_2^2E_0 + a_2^2\tilde{\Delta}_lE_0)$$
$$\times\left\langle\frac{1}{r^2}\right\rangle + [-a_2^2 + 2a_2b_2 + a_2^2\tilde{\Delta}_l + 2b_2c_2\tilde{\Delta}_l$$
$$- 2a_2c_2(\vec{L}^2+\tilde{\Delta}_l)]\left\langle\frac{1}{r^3}\right\rangle + [3(l-2)(l-1)a_2^2$$
$$- 4(l-2)(l-1)a_2b_2 + b_2^2 - \vec{L}^2a_2^2\tilde{\Delta}_l + a_2b_2\tilde{\Delta}_l$$
$$+ b_2^2\tilde{\Delta}_l]\left\langle\frac{1}{r^4}\right\rangle. \tag{192}$$

Now, we turn to matrix elements of the operator $(\vec{S}\cdot\vec{n})^2$ [see Eq. (176)]

$$\xi_{L+2}(j,l,s) = \langle\phi_l|(\vec{S}\cdot\vec{n})^2|\phi_{l+2}\rangle$$
$$= \left\langle \phi_l \left| \left(n_in_j - \frac{1}{3}\delta_{ij}\right)\left(s_is_j - \frac{\vec{S}^2}{3}\delta_{ij}\right)\right| \phi_{l+2}\right\rangle. \tag{193}$$

As before, we calculate this expression with the help of the theory recalled in Appendix B. We use the formula

$$\langle n,l,s,j,j_z|(T^{(1)}(2)\cdot T^{(2)}(2))_{00}|n,l+2,s,j,j_z\rangle$$
$$= (-1)^{s+l+j}W_{6j}(j,s,l;2,l+2,s)\cdot\langle n,l\|T^{(1)}(2)\|n,l+2\rangle\langle s\|T^{(2)}$$
$$\times(2)\|s\rangle, \tag{194}$$

where the notation is the same as in the Appendix. The new quantity here is the reduced matrix element

$$\langle n,l\|T^{(1)}(2)\|n,l+2\rangle = \sqrt{\frac{2+3l+l^2}{3+2l}} \tag{195}$$

and the specific value of the Wigner 6-j symbol (see Ref. [26])

$$W_{6j}(j,s,l-2;2,l,s) = (-1)^w\sqrt{\frac{6w(w+1)(w-2j-1)(w-2j)(w-2s-1)(w-2s)(w-2l+1)(w-2l+2)}{2l(-3+2l)(-2+2l)(2l-1)(1+2l)2s(1+2s)(2+2s)(3+2s)(2s-1)}}, \tag{196}$$

where $w=j+l+s$. After some reduction the following formula is obtained:

$$\xi_{L+2}(j,l,s) = \frac{1}{4}\sqrt{\frac{(-j+l-s)(1-j+l-s)(1+j+l-s)(2+j+l-s)}{(3+2l)^2(5+12l+4l^2)}} \times \sqrt{(1-j+l+s)(2-j+l+s)(2+j+l+s)(3+j+l+s)}. \tag{197}$$

The next necessary matrix element is

$$\xi_{L-2}(j,l,s) = \left\langle \phi_l \left| \left(n_i n_j - \frac{1}{3}\delta_{ij}\right)\left(s_i s_j - \frac{\vec{S}^2}{3}\delta_{ij}\right) \right| \phi_{l-2} \right\rangle = \xi_{L+2}(j,l-2,s). \tag{198}$$

The last equation follows from the Hermiticity of the appropriate operator. Finally, we can write

$$R_{55} = \delta E_{33}\left[\xi(j,l,s) + \frac{1}{3}\vec{S}^2\right] + G_{L,L+2}\xi_{L+2}(j,l,s) + G_{L,L-2}\xi_{L-2}(j,l,s). \tag{199}$$

We have now all of the corrections so we can write the total value of the $O(m\alpha^6)$ correction to the energy levels.

V. RESULTS AND SUMMARY

First, we present the energy levels up to $O(m\alpha^5)$ from Ref. [12]. Next, we write our formulas for the $O(m\alpha^6)$ corrections to the energy levels. Finally, we present the numerical values for the D-state energy levels to $O(m\alpha^6)$.

A. Analytical formulas

The general formula $E^{(5)}(n,j,l,s)$ is split into four cases. For readability, we use L to denote the quantum number of the orbital angular momentum (instead of l). For $L>0$,

$$E^{(5)}(n,L,L,0) = -\frac{m\alpha^2}{4n^2} + \frac{m\alpha^4}{8}\left(\frac{11}{8n^4} - \frac{4}{(1+2L)n^3}\right) - \frac{2m\alpha^5}{3\pi n^3}\left(\frac{7}{16L(L+1)(2L+1)} + \ln[k_0(n,L)]\right), \tag{200}$$

$$E^{(5)}(n,L-1,L,1) = -\frac{m\alpha^2}{4n^2} + \frac{m\alpha^4}{8}\left(\frac{11}{8n^4} - \frac{2(4L^2+L-1)}{L(1+2L)(2L-1)n^3}\right) - \frac{2m\alpha^5}{3\pi n^3}\left(\frac{-12L^2-23L+10}{16L(1+L)(1-2L)(1+2L)} + \ln[k_0(n,L)]\right), \tag{201}$$

$$E^{(5)}(n,L,L,1) = -\frac{m\alpha^2}{4n^2} + \frac{m\alpha^4}{8}\left(\frac{11}{8n^4} - \frac{2(1+2L+2L^2)}{L(1+L)(1+2L)n^3}\right) - \frac{2m\alpha^5}{3\pi n^3}\left(\frac{10}{16L(1+L)(1+2L)} + \ln[k_0(n,L)]\right), \tag{202}$$

$$E^{(5)}(n,L+1,L,1) = -\frac{m\alpha^2}{4n^2} + \frac{m\alpha^4}{8}\left(\frac{11}{8n^4} - \frac{2(1+2L+2L^2)}{L(1+L)(1+2L)n^3}\right) - \frac{2m\alpha^5}{3\pi n^3}\left(\frac{-12L^2-L+21}{16L(1+L)(1+2L)(3+2L)} + \ln[k_0(n,L)]\right), \tag{203}$$

where $\ln[k_0(n,L)]$ is the Bethe logarithm.

Now, we present the $O(m\alpha^6)$ corrections to the energy levels. First, we write the results for the P states. They are presented separately due to the presence of terms in δH_2 [see Eq. (94)] that do not vanish for $L=1$ and vanish for $L>1$, as mentioned before. The formulas are

$$\delta E^{(6)}(n\ ^1P_1) = m\alpha^6\left(-\frac{69}{512n^6} + \frac{23}{120n^5} - \frac{1}{12n^4} + \frac{163}{4320n^3}\right),$$

$$\delta E^{(6)}(n\,^3P_0) = m\alpha^6\left(-\frac{69}{512n^6}+\frac{119}{240n^5}-\frac{1}{3n^4}-\frac{833}{4320n^3}-\frac{a_1^2+6a_2}{24\pi^2n^3}\right),$$

$$\delta E^{(6)}(n\,^3P_1) = m\alpha^6\left(-\frac{69}{512n^6}+\frac{77}{320n^5}-\frac{25}{192n^4}+\frac{553}{17\,280n^3}+\frac{a_1^2-2a_2}{48\pi^2n^3}\right),$$

$$\delta E^{(6)}(n\,^3P_2) = m\alpha^6\left(-\frac{69}{512n^6}+\frac{559}{4800n^5}-\frac{169}{4800n^4}+\frac{17\,977}{432\,000n^3}+\frac{-a_1^2+18a_2}{240\pi^2n^3}\right), \tag{204}$$

where a_1 and a_2 are defined in Eqs. (82) and (83). These results are in agreement with those from [15] (corrected in Ref. [14]).

Below we present formulas for $L>1$. For the states with $S=0$ and $J=L$ the correction reads

$$\delta E^{(6)}(n,L,L,0) = m\alpha^6\left(\frac{f_1}{n^3}+\frac{g_1}{n^4}+\frac{h_1}{n^5}-\frac{69}{512n^6}\right), \tag{205}$$

where

$$f_1 = \frac{3+48L+64L^2+32L^3+16L^4}{16L(1+L)(2L-1)(1+2L)^3(3+2L)}, \tag{206}$$

$$g_1 = -\frac{3}{4(1+2L)^2}, \tag{207}$$

$$h_1 = \frac{20L^2+20L-17}{8(2L-1)(1+2L)(3+2L)}. \tag{208}$$

For the states with $S=1$ and $J=L-1$ the correction reads

$$\delta E^{(6)}(n,L-1,L,1) = m\alpha^6\left(\frac{f_2}{n^3}+\frac{1}{n^3}\frac{a_1^2+2a_2(4L-1)}{8L(1-4L^2)\pi^2}+\frac{g_2}{n^4}+\frac{h_2}{n^5}-\frac{69}{512n^6}\right), \tag{209}$$

where

$$f_2 = (15-5L-235L^2+242L^3+1537L^4-581L^5-3926L^6-2020L^7-40L^8-144L^9+416L^{10}+448L^{11}+128L^{12})/[80L^3(1+L)(3+2L)(4L^2-1)^3], \tag{210}$$

$$g_2 = -\frac{3-6L-21L^2+24L^3+48L^4}{16L^2(2L-1)^2(1+2L)^2}, \tag{211}$$

$$h_2 = \frac{495-1137L-1496L^2+3500L^3+2400L^4-128L^5-64L^6}{480(1-2L)^2L(1+2L)(3+2L)}. \tag{212}$$

For the states with $S=1$ and $J=L$ the correction reads

$$\delta E^{(6)}(n,L,L,1) = m\alpha^6\left(\frac{f_3}{n^3}+\frac{1}{n^3}\frac{a_1^2-2a_2}{8L(1+L)(1+2L)\pi^2}+\frac{g_3}{n^4}+\frac{h_3}{n^5}-\frac{69}{512n^6}\right), \tag{213}$$

where

$$f_3 = (15+85L+140L^2+107L^3+112L^4+261L^5+459L^6+506L^7+488L^8+384L^9+176L^{10}+32L^{11})/\times[80L^3(1+L)^3(1+2L)^3(3+2L)(2L-1)], \tag{214}$$

$$g_3 = -\frac{3+12L+24L^2+24L^3+12L^4}{16L^2(L+1)^2(1+2L)^2}, \tag{215}$$

$$h_3 = -\frac{495+348L-860L^2-2360L^3-1120L^4+32L^5}{480L(L+1)(1+2L)(3+2L)(2L-1)}. \tag{216}$$

For the states with $S=1$ and $J=L+1$ the correction reads

$$\delta E^{(6)}(n,L+1,L,1) = m\alpha^6\left(\frac{f_4}{n^3}-\frac{1}{n^3}\frac{a_1^2-2a_2(5+4L)}{8(1+L)(1+2L)(3+2L)\pi^2}+\frac{g_4}{n^4}+\frac{h_4}{n^5}-\frac{69}{512n^6}\right), \tag{217}$$

where

$$f_4 = (-45 + 190L + 4247L^2 + 18398L^3 + 36114L^4 + 36559L^5 + 17474L^6 - 1300L^7 - 8776L^8 - 7824L^9 - 3936L^{10} - 1088L^{11} - 128L^{12})/[80L(1+L)^3(2L-1)(1+2L)^3(3+2L)^3], \tag{218}$$

$$g_4 = -\frac{12 + 84L + 195L^2 + 168L^3 + 48L^4}{16(1+L)^2(1+2L)^2(3+2L)^2}, \tag{219}$$

$$h_4 = \frac{-900 - 2571L + 2556L^2 + 6260L^3 + 2720L^4 + 256L^5 + 64L^6}{480(1+L)(2L-1)(1+2L)(3+2L)^2}. \tag{220}$$

B. Numerical results

Table I presents numerical values of the corrections to the energies of positronium $3\,^{2S+1}D_J$ levels. For the numerical evaluations we use the CODATA 2006 recommended values of the fundamental constants [28], i.e., $R_\infty = 10\,973\,731.568\,527(73) m^{-1}$, $\alpha = 1/137.035\,999\,679(94)$, and $c = 299\,792\,458$. The value of the Bethe logarithm is taken from Ref. [29], $\ln[k_0(3,2)] = -0.005\,232\,148\,140\,883$. Our estimation of $O(m\alpha^7)$ correction is based on the leading logarithmic term for the hydrogen atom found in Ref. [30]. In the case of positronium it reads

$$\delta E^{(7)} = \frac{\alpha^7}{\pi}\frac{4}{3}\ln\left(\frac{\alpha^2}{2}\right)\left\langle\frac{1}{r^4}\right\rangle. \tag{221}$$

Numerical evaluation of the above correction for the $3\,D$ states gives $\delta E^{(7)} \approx 20(10)$ Hz. The uncertainty of the $O(m\alpha^7)$ correction is assumed to be half of the $\delta E^{(7)}$ and its value is negligible as compared with the total theoretical uncertainty $\Delta\Sigma$. The latter is due to an uncertainty of the Rydberg constant.

C. Summary

We have obtained the complete analytical formulas for the $O(m\alpha^6)$ corrections to the positronium spectrum of states with $L > 0$. For the P states, formulas (204) are in agreement with those from Ref. [15] (corrected in Ref. [14]).

The method we have used in this paper is well suited for derivation of QED effective Hamiltonians for atomic systems consisting of two constituents of comparable masses. In particular, it seems that a high accuracy can be achieved for the energy levels of the antiproton-nucleus system, but with two remarks. First, a system should be in a state with orbital angular momentum high enough to neglect non-QED interactions. Second, some additional effort is needed to treat the large anomalous magnetic moments of proton and antiproton as well as to account for the vacuum polarization. The latter is negligible for light systems, e.g., positronium, but may be important for the antiproton-nucleus system.

ACKNOWLEDGMENTS

I would like to thank Krzysztof Pachucki for support, much useful advice concerning calculations, and comments on the manuscript. I also would like to thank Oliver Eyton-Williams for reading the manuscript.

APPENDIX A: EXPECTATION VALUES

1. First-order perturbation theory expectation values

In this appendix we list the expectation values that occur throughout this paper. For simplicity we put $m=1$ and $\alpha=1$. Let us start with the expectation values that can be found, for the case of the hydrogen atom, in Ref. [31]:

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{2n^2}, \tag{A1}$$

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{1}{4}\frac{1}{\left(l+\frac{1}{2}\right)n^3}, \tag{A2}$$

TABLE I. Contribution to the energies of positronium $3\,^{2S+1}D_J$ levels (in MHz). $\delta E^{(n)}$ is a contribution of $O(m\alpha^n)$. The last row presents the total theoretical uncertainty $\Delta\Sigma$.

	$3\,^1D_2$	$3\,^3D_1$	$3\,^3D_2$	$3\,^3D_3$
E_0	−182 768 997.797 8	−182 768 997.797 8	−182 768 997.797 8	−182 768 997.797 8
$\delta E^{(4)}$	−554.223 0	−1 094.928 4	−662.364 1	−245.248 5
$\delta E^{(5)}$	−0.187 9	0.278 6	−0.313 5	−1.067 2
$\delta E^{(6)}$	0.001 4	0.016 3	0.008 6	−0.012 9
Σ	−182 769 552.207 3	−182 770 093.791 9	−182 769 660.474 0	−182 769 242.766 3
$\Delta\Sigma$	0.001 2	0.001 2	0.001 2	0.001 2

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{8} \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)n^3}, \tag{A3}$$

$$\left\langle \frac{1}{r^4} \right\rangle = \frac{1}{32} \frac{-l(1+l)+3n^2}{\left(l-\frac{1}{2}\right)l\left(l+\frac{1}{2}\right)(l+1)\left(l+\frac{3}{2}\right)n^5}, \tag{A4}$$

$$\left\langle \frac{1}{r^5} \right\rangle = \frac{1}{8} \frac{1-3l(1+l)+5n^2}{(l-1)l(l+1)(l+2)(2l-1)(2l+1)(3+2l)n^5}. \tag{A5}$$

Next, we list the expectation values containing the ∂_r operator for the states with $l>0$:

$$\left\langle \frac{1}{r^2}\partial_r \right\rangle = 0, \tag{A6}$$

$$\left\langle \frac{1}{r^3}\partial_r \right\rangle = \frac{1}{64} \frac{-l(1+l)+3n^2}{\left(l-\frac{1}{2}\right)l\left(l+\frac{1}{2}\right)(l+1)\left(l+\frac{3}{2}\right)n^5}, \tag{A7}$$

$$\left\langle \frac{1}{r^4}\partial_r \right\rangle = \frac{1}{8} \frac{1-3l(1+l)+5n^2}{(l-1)l(l+1)(l+2)(2l-1)(2l+1)(3+2l)n^5} + \frac{1}{2} \left.\frac{R^2}{r^2}\right|_{r=0}, \tag{A8}$$

$$\left\langle \frac{1}{r}\partial_r^2 \right\rangle = \frac{1+2l-2n}{8(1+2l)n^4}, \tag{A9}$$

$$\left\langle \frac{1}{r^2}\partial_r^2 \right\rangle = \frac{-1+2l+2l^2-2n^2}{8(-3-2l+12l^2+8l^3)n^5}, \tag{A10}$$

$$\left\langle \frac{1}{r^3}\partial_r^2 \right\rangle = \frac{-1+2l+2l^2-2n^2}{16l(-3-5l+10l^2+20l^3+8l^4)n^5}. \tag{A11}$$

One can derive the above formulas by performing appropriate integration by parts and with the help of the radial Hamiltonian [see Eq. (179)]. In addition, we use the following relation which holds for $l=1$:

$$\left.\frac{R_{nl}^2}{r^2}\right|_{r=0} = \frac{1}{72n^3} - \frac{1}{72n^5}. \tag{A12}$$

For $l>1$ the RHS of the above equation vanishes.

2. Second-order perturbation theory expectation values

Below we derive the values of δE_{nm} [see Eq. (154)], which occur frequently in the second order of perturbation theory. We use here the trick from Ref. [15], namely, we consider the Hamiltonian with the Kramers potential,

$$H_K = -\frac{p^2}{m} - \frac{\alpha}{r} + \frac{\beta}{r^2}, \tag{A13}$$

which has the eigenvalues

$$E_K(\alpha,\beta) = -\frac{2m\alpha^2}{2[2k+l+\sqrt{8m\beta/2h^2+(2l+1)^2}]^2}, \tag{A14}$$

where the following relation between quantum numbers holds: $(k+l+1)=n$ and n is the principal quantum number. Now, we observe that δE_{nm} for $n,m=1,2$ can be obtained as the appropriate perturbation corrections to the Hamiltonian H_0, that is,

$$\delta E_{11} = \left(\frac{\partial^2}{\partial\alpha^2}E_K(\alpha,\beta)\right)_{\alpha=1,\beta=0} = -\frac{1}{4n^2}, \tag{A15}$$

$$\delta E_{12} = \delta E_{21} = \left(\frac{\partial^2}{\partial\alpha\partial\beta}E_K(\alpha,\beta)\right)_{\alpha=1,\beta=0} = -\frac{1}{2(1+2l)n^3}, \tag{A16}$$

$$\delta E_{22} = \left(\frac{\partial^2}{\partial\beta^2}E_K(\alpha,\beta)\right)_{\alpha=1,\beta=0} = -\frac{1}{8}\left(\frac{6}{(1+2l)^2n^4} + \frac{4}{(1+2l)^3n^3}\right). \tag{A17}$$

Next, we calculate δE_{13}, δE_{23}, and δE_{33}. First, we represent $1/r^3$ as

$$\frac{1}{r^3} = \frac{1}{2\vec{L}^2}\left(\frac{1}{r^2} - [D_r, H_0]\right), \tag{A18}$$

where $D_r = 1/r + \partial_r$, and use the relation $p^2 = -D_r^2 + \vec{L}^2/r^2$. Now, we perform the calculation of δE_{13} in detail so the next cases can proceed faster:

$$\begin{aligned}\delta E_{13} &= \left\langle \frac{1}{r}G\frac{1}{r^3} + \frac{1}{r^3}G\frac{1}{r} \right\rangle \\ &= \left\langle \frac{1}{r}G\frac{1}{2\vec{L}^2}\left(\frac{1}{r^2} - [D_r,H_0]\right) + \text{H.c.} \right\rangle \\ &= \frac{1}{2\vec{L}^2}\left(\delta E_{12} - \left\langle \frac{1}{r}G[D_r, H_0 - E_0] \right\rangle - \left\langle [D_r, H_0 - E_0]G\frac{1}{r} \right\rangle\right) \\ &= \frac{1}{2\vec{L}^2}\left(\delta E_{12} - \left\langle \frac{1}{r}(\mathrm{I} - |\phi\rangle\langle\phi|)D_r \right\rangle + \left\langle D_r(\mathrm{I} - |\phi\rangle\langle\phi|)\frac{1}{r} \right\rangle\right) \\ &= \frac{1}{2\vec{L}^2}\left(\delta E_{12} + \left\langle \left[D_r, \frac{1}{r}\right] \right\rangle\right) = -\frac{1}{n^3}\frac{3}{4l(1+l)(1+2l)}.\end{aligned} \tag{A19}$$

In a similar way one obtains

$$\delta E_{23} = -\frac{1}{n^3}\frac{1+6l+6l^2}{4l^2(1+l)^2(1+2l)^3} - \frac{1}{n^4}\frac{3}{4l(1+l)(1+2l)^2} \quad \text{(A20)}$$

and

$$\delta E_{33} = \frac{1}{n^3}\frac{3+5l-55l^2-120l^3-60l^4}{16l^3(1+l)^2(1+2l)^3(-3+l+8l^2+4l^3)} - \frac{1}{n^4}\frac{3}{16l^2(1+l)^2(1+2l)^2} + \frac{1}{n^5}\frac{3}{128\left(l-\frac{1}{2}\right)l\left(\frac{1}{2}+l\right)(1+l)\left(\frac{3}{2}+l\right)}. \quad \text{(A21)}$$

APPENDIX B: MATRIX ELEMENTS OF TENSOR OPERATORS

Let us recall here the theory of matrix elements of the form

$$A = \langle T_{ij} S^i S^j \rangle, \quad \text{(B1)}$$

where T_{ij} is a symmetric and traceless tensor which does not contain any spin operators. We adopt the general theory of tensor corrections [26,27]. The crucial formula is

$$\langle n_1', n_2', l', s', j | [T^{(1)}(k)\cdot T^{(2)}(k)]_{00} | n_1, n_2, l, s, j\rangle = (-1)^{\max(s',s)+\min(l',l)+j} W_{6j}(j,s',l';k,l,s)\cdot\langle n_1', l' \| T^{(1)}(k) \| n_1, l\rangle \langle n_2', s' \| T^{(2)}(k) \| n_2, s\rangle, \quad \text{(B2)}$$

where

(1) $T^{(i)}(k)$ denotes a spherical tensor of order k;

(2) $[T^{(1)}(k)\cdot T^{(2)}(k)]_{00} = \Sigma_{q=-k}^{k} T^{(1)}(k,q)\cdot T^{(2)*}(k,q)$ denotes a scalar product of spherical tensors, and the number $q \in \{-k,\ldots,k\}$ enumerates the components of a spherical tensor;

(3) $W_{6j}(j,s',l';k,l,s)$ is the Wigner $6j$ symbol;

(4) the quantity $\langle n', j' \| T(k) \| n, j\rangle$ denotes the reduced matrix element of tensor T, where j is the total angular momentum number in the sector where the operator T acts and n denotes other quantum numbers.

The components of the spherical tensor appear in the following relation with T_{ij}:

$$T(2,0) = -\sqrt{\frac{3}{2}}T_{33},$$

$$T(2,\pm 1) = \pm(T_{13} \pm iT_{23}),$$

$$T(2,\pm 2) = -\frac{1}{2}(T_{11} - T_{22} \pm 2iT_{12}), \quad \text{(B3)}$$

and one can write the equality between contractions of the tensors

$$[T^{(1)}(k)\cdot T^{(2)}(k)]_{00} = T_{ij}^{(1)}\cdot T^{(2)ij}. \quad \text{(B4)}$$

We are interested in finding appropriate formulas for the case of $k=2$. In full, the appropriate Wigner $6j$ symbol reads

$$W_{6j}(j,s,l;2,l,s) = \frac{(-1)^{j+s+l}2[6\vec{L}\cdot\vec{S}(2\vec{L}\cdot\vec{S}+1) - 4\vec{S}^2\vec{L}^2]}{[(2s-1)2s(2s+1)(2s+2)(2s+3)(2l-1)2l(2l+1)(2l+2)(2l+3)]^{1/2}} \quad \text{(B5)}$$

and the reduced matrix element can be computed from the equation

$$\langle \alpha', j', m' | T(k,q) | \alpha, j, m\rangle = i^k (-1)^{\max(j',j)-m'} W_{3j}(j',k,j;-m',q,m)\langle \alpha', j', \| T(k) \| \alpha, j\rangle, \quad \text{(B6)}$$

where $W_{3j}(j',k,j;-m',q,m)$ denotes the Wigner $3j$ symbol. It is sufficient to compute the LHS of the above equation for one specific value of the quantum number m and then one immediately obtains $\langle \alpha', j', \| T(k) \| \alpha, j\rangle$ for arbitrary m. In our case the proper Wigner $3j$ symbol equals

$$W_{3j}(j,2,j;-m,0,m) = \frac{(-1)^{l-m}\{2[3m^2 - j(j+1)]\}}{[(2j+3)(2j+2)(2j+1)2j(2j-1)]^{1/2}}. \quad \text{(B7)}$$

Let us use this theory and compute an important example which occurs several times in the calculation. That is, we consider the correction

$$\left\langle n,j,l,s \middle| f(r)\left(n_i n_j - \frac{1}{3}\delta_{ij}\right) S^i S^j \middle| n,j,l,s \right\rangle = \left\langle n,j,l,s \middle| f(r)\left(n_i n_j - \frac{1}{3}\delta_{ij}\right)\left(S^i S^j - \frac{1}{3}\delta^{ij}\vec{S}^2\right) \middle| n,j,l,s \right\rangle, \quad \text{(B8)}$$

where $n_i = r_i/r$ and $f(r)$ is a function of distance r alone. We identify the tensors

$$T_{ij}^{(1)} = f(r)\left(n_i n_j - \frac{1}{3}\delta_{ij}\right),$$

$$T_{ij}^{(2)} = \left(S^i S^j - \frac{1}{3}\delta^{ij}\vec{S}^2 \right) \tag{B9}$$

and obtain the reduced matrix elements of the appropriate spherical tensors,

$$\langle n,l\|T^{(1)}(2)\|n,l\rangle = -\frac{1}{3}\sqrt{\frac{3}{2}}\sqrt{\frac{(2l+2)(2l+1)2l}{(2l+3)(2l-1)}}\langle n,l|f(r)|n,l\rangle, \tag{B10}$$

$$\langle n,s\|T^{(2)}(2)\|n,s\rangle = \frac{1}{6}\sqrt{\frac{3}{2}}\sqrt{(2s+3)(2s+2)(2s+1)2s(2s-1)}. \tag{B11}$$

Now, we collect all the pieces together in Eq. (B2) and get the result

$$\langle n,j,l,s|T_{ij}s^i s^j|n,j,l,s\rangle = \langle n,l|f(r)|n,l\rangle \xi(j,l,s), \tag{B12}$$

where

$$\xi(j,l,s) = \frac{1}{3}\frac{2\vec{L}^2\vec{S}^2 - 3\vec{S}\cdot\vec{L}(1+2\vec{S}\cdot\vec{L})}{4\vec{L}^2-3}. \tag{B13}$$

APPENDIX C: ONE-PHOTON-ANNIHILATION EFFECTIVE POTENTIAL

In this appendix we present the derivation of an effective potential operator at $O(m\alpha^6)$ arising owing to relativistic corrections to the leading-order one-photon-annihilation virtual process amplitude. Our calculations are based on a method described in Sec. 83 of Ref. [25]. We use natural units $c=1$ and $\hbar=1$. Let us start with the electron-positron annihilation amplitude, i.e.,

$$M = e^2[\bar{v}(p_+)\gamma^\mu u(p_-)]G_{\mu\nu}(p_+ + p_-)[\bar{u}(p'_-)\gamma^\nu v(p'_+)], \tag{C1}$$

where $p_\pm$ are the momentum four-vectors attributed to the positron and electron, respectively. The bispinors u and v are, respectively, positive- and negative-energy solutions of the free Dirac equation in momentum representation. We use bispinors that satisfy the standard normalization $\bar{u}(p)u(p)=1$, which differs from the normalization used in Ref. [25]. We are going to construct an effective nonrelativistic potential operator which reproduces annihilation amplitude (C1). For the calculations we choose the Feynman gauge in which the photon propagator is

$$G_{\mu\nu}(k) = \frac{g_{\mu\nu}}{k^2 + i\epsilon} = \frac{g_{\mu\nu}}{\omega^2 - \vec{k}^2 + i\epsilon}, \tag{C2}$$

where

$$\vec{k} = \vec{p}_+ + \vec{p}_- = \vec{p}\,'_+ + \vec{p}\,'_-, \tag{C3}$$

$\omega^2=(\epsilon_+ + \epsilon_-)^2$, and $\epsilon_\pm$ is the energy of the positron and electron, respectively. The dispersion relation for a free particle is

$$\epsilon = m\sqrt{1+\left(\frac{\vec{p}}{m}\right)^2} = m + \frac{\vec{p}^2}{2m} + \cdots. \tag{C4}$$

We work in the CMRF, in which by definition $\vec{k}=\vec{0}$. Consequently, in this reference frame a nonrelativistic expansion of a photon propagator can be written

$$G_{\mu\nu}(k) = \frac{g_{\mu\nu}}{4m^2} - \frac{g_{\mu\nu}}{16m^4}(2\vec{p}_-^{\,2} + 2\vec{p}\,'^2_+) + \cdots. \tag{C5}$$

As we want to construct a nonrelativistic effective operator that acts on Pauli spinors, we need an appropriate nonrelativistic expansion of the Dirac bispinors. The appropriate formulas within desired accuracy read

$$u(p) = \begin{pmatrix} [1-\vec{p}^2/(8m^2)]w \\ (\vec{\sigma}\vec{p}/2m)w \end{pmatrix} \tag{C6}$$

and

$$v(p) = \begin{pmatrix} (\vec{\sigma}\vec{p}/2m)w' \\ [1-\vec{p}^2/(8m^2)]w' \end{pmatrix}, \tag{C7}$$

where two-component spinors satisfy the normalization $w^\dagger w = w'^\dagger w' = 1$.

Now we calculate the Coulomb part of the amplitude (C1). Since we work in the CMRF it is easy to see that

$$\bar{v}(p_+)\gamma^0 u(p_-) = \frac{1}{2m}(w^\dagger\vec{\sigma}\cdot\vec{p}_+ w_- + w^\dagger\vec{\sigma}\cdot\vec{p}_- w_-) = \frac{w^\dagger\vec{\sigma}\cdot\vec{k}w_-}{2m} = 0. \tag{C8}$$

As a consequence of this result, the Coulomb part of the amplitude (C1) vanishes. In order to calculate the transverse part of the annihilation amplitude we need the following contractions:

$$\bar{v}(p_+)\gamma^j u(p_-) = w^\dagger\sigma^j w_- + \frac{1}{4m^2}w^\dagger(\vec{p}_+\vec{\sigma})\sigma^j(\vec{p}_-\vec{\sigma})w_- - \frac{p_+^2}{8m^2}(w^\dagger\sigma^j w_-) - \frac{p_-^2}{8m^2}(w^\dagger\sigma^j w_-) \tag{C9}$$

and

$$\bar{u}(p'_-)\gamma^j v(p'_+) = w_-'^\dagger\sigma^j w' + \frac{1}{4m^2}w_-'^\dagger(\vec{p}\,'_-\cdot\vec{\sigma})\sigma^j(\vec{p}\,'_+\cdot\vec{\sigma})w' - \frac{p_-'^2}{8m^2}(w_-'^\dagger\sigma^j w') - \frac{p_+'^2}{8m^2}(w_-'^\dagger\sigma^j w'). \tag{C10}$$

The first terms on the RHS of Eqs. (C9) and (C10) lead to corrections of lower order; therefore we neglect them in further calculation. If we substitute Eqs. (C5), (C9), and (C10) in the amplitude (C1) we obtain

$$\begin{aligned} M^{(2)} = \frac{e^2}{16m^4}\{&3(w^\dagger\vec{\sigma}w_-)[\vec{p}_-^{\,2} + \vec{p}_+'^{\,2}](w_-'^\dagger\vec{\sigma}w') + (w^\dagger\sigma^i w_-) \\ &\times[w_-'^\dagger(\vec{p}\,'_+\vec{\sigma})\sigma_i(\vec{p}\,'_+\vec{\sigma})w'] + [w^\dagger(\vec{p}_-\vec{\sigma})\sigma^i(\vec{p}_-\vec{\sigma})w_-] \\ &\times(w_-'^\dagger\sigma_i w')\} = M_A^{(2)} + M_B^{(2)} + M_C^{(2)}. \end{aligned} \tag{C11}$$

In order to extract an effective operator we need to express the amplitude (C11) in terms of the electron and positron spinors w_-, w'_- and w_+, w'_+, respectively. Moreover, in the amplitude, the spinors of different particles should not be contracted. Let us start with the term

$$M_A^{(2)} = \frac{3e^2}{16m^4}(w^\dagger \vec{\sigma} w_-)(\vec{p}_-^2 + \vec{p}_+'^2)(w_-'^\dagger \vec{\sigma} w'). \tag{C12}$$

First, we separate spinors of different types with the help of the completeness relation for the Pauli matrices,

$$\vec{\sigma}_{\alpha\beta}\cdot\vec{\sigma}_{\delta\gamma} = -\frac{1}{2}\vec{\sigma}_{\alpha\gamma}\cdot\vec{\sigma}_{\delta\beta} + \frac{3}{2}\delta_{\alpha\gamma}\delta_{\delta\beta}. \tag{C13}$$

Second, we introduce the positron's bispinors. The charge-conjugated wave function reads

$$\psi^c = C\bar{\psi}^T, \tag{C14}$$

where in the standard representation the matrix C is

$$C = i\gamma^2\gamma^0 = \begin{pmatrix} 0 & -i\sigma^2 \\ -i\sigma^2 & 0 \end{pmatrix}. \tag{C15}$$

It follows that the charge-conjugated two-component spinor reads

$$w_+ = -i\sigma^2 w^{\dagger T}. \tag{C16}$$

In addition, the following relations hold:

$$w^\dagger = -iw_+^T\sigma^2,$$

$$w = i\sigma^2 w_+^{\dagger T}. \tag{C17}$$

With the help of the relations (C17) it is easy to check that

$$(w^\dagger w') = (w_+'^\dagger w_+),$$

$$(w^\dagger \sigma^i w') = -(w_+'^\dagger \sigma^i w_+). \tag{C18}$$

By a virtue of relations (C13) and (C18) we obtain

$$M_A^{(2)} = (w_-'^\dagger w_+'^\dagger)\left(\frac{3e^2}{32m^4}(3 + \vec{\sigma}_+\cdot\vec{\sigma}_-)\right)(\vec{p}_-^2 + \vec{p}_+'^2)(w_- w_+). \tag{C19}$$

After elementary reductions of the products of Pauli matrices, we can write

$$M_B^{(2)} = \frac{e^2}{16m^4}[2(w^\dagger\sigma^i w_-)(w_-'^\dagger \sigma^j w')p'_{+i}p'_{+j} - (w^\dagger\vec{\sigma}w_-)\cdot(w_-'^\dagger\vec{\sigma}w')\vec{p}_+'^2]. \tag{C20}$$

In order to put the spinors in Eq. (C20) in the desired order, we need a relation more general than (C13). It can be checked that

$$(w^\dagger\vec{\sigma}\cdot\vec{a}w_-)(w_-'^\dagger\vec{\sigma}\cdot\vec{a}w') = \frac{1}{2}(w_+^\dagger w_+')(w_-^\dagger w_-')\vec{a}^2 + \frac{1}{2}\vec{a}^2(w_+^\dagger\vec{\sigma}w_+')\cdot(w_-^\dagger\vec{\sigma}w_-') - (w_+^\dagger\sigma^i w_+')(w_-^\dagger\sigma^j w_-')a_i a_j, \tag{C21}$$

provided that the vector $\vec{a}$ commutes with $\vec{\sigma}$. With the help of identity (C21) we can write $M_B^{(2)}$ in the desired form,

$$M_B^{(2)} = \frac{e^2}{16m^4}(w_-'^\dagger w_+'^\dagger)\left(\frac{1}{2}(3 + \vec{\sigma}_+\cdot\vec{\sigma}_-)\cdot\vec{p}_+'^2 - \sigma^i\sigma^j p'_{+i}p'_{+j}\right)\times(w_- w_+), \tag{C22}$$

where $\vec{\sigma} = \vec{\sigma}_+ + \vec{\sigma}_-$ and $\sigma_\pm^i$ act on $w_\pm$, respectively. Similarly,

$$M_C^{(2)} = \frac{e^2}{16m^4}(w_-'^\dagger w_+'^\dagger)\left[\frac{1}{2}(3 + \vec{\sigma}_+\cdot\vec{\sigma}_-)\vec{p}_-^2 - \sigma^i\sigma^j p_{-i}p_{-j}\right]\times(w_- w_+). \tag{C23}$$

Finally, the amplitude (C11) reads

$$M^{(2)} = \frac{e^2}{16m^4}(w_-'^\dagger w_+'^\dagger)\left[\frac{4}{3}(3 + \vec{\sigma}_+\cdot\vec{\sigma}_-)(\vec{p}_-^2 + \vec{p}_+'^2) - \left(\sigma^i\sigma^j - \frac{1}{3}\delta_{ij}\vec{\sigma}^2\right)(p_{-i}p_{-j} + p'_{+i}p'_{+j})\right](w_- w_+). \tag{C24}$$

Now we can write an effective operator that reproduces the amplitude (C24),

$$V_{\rm eff} = \frac{e^2}{4m^4}\left[-\frac{2}{3}\vec{S}^2(\vec{p}_-^2 + \vec{p}_+'^2) + \left(S^iS^j - \frac{1}{3}\delta_{ij}\vec{S}^2\right)\times(p_{-i}p_{-j} + p'_{+i}p'_{+j})\right]. \tag{C25}$$

In the position representation,

$$\tilde{V}_{\rm eff}(\vec{r}) = \frac{\pi\alpha}{m^4}\left[-\frac{2}{3}\vec{S}^2[\delta^{(3)}(\vec{r})\vec{p}^2 + \vec{p}^2\delta^{(3)}(\vec{r})] + \left(S^iS^j - \frac{1}{3}\delta_{ij}\vec{S}^2\right)\times[\delta^{(3)}(\vec{r})p_ip_j + p_ip_j\delta^{(3)}(\vec{r})]\right], \tag{C26}$$

where the operators $\vec{r}$, $\vec{p}$, and $\vec{S}$ are defined by Eqs. (17)–(19). Owing to the fact that the traceless symmetric tensor part of operator (C25) vanishes for S states, we find a agreement between our result and the one from Ref. [20]. Clearly, the expectation value of $V_{\rm eff}$ vanishes for $l>0$ states.

[1] A result of A. P. Mills, Jr., and G. H. Bearman, Phys. Rev. Lett. **34**, 246 (1975) was corrected by A. P. Mills, Jr., Phys. Rev. A **27** 262 (1983).

[2] M. W. Ritter, P. O. Egan, V. W. Hughes, and K. A. Woodle, Phys. Rev. A **30**, 1331 (1984).

[3] K. Danzmann, M. S. Fee, and S. Chu, Phys. Rev. A **39**, 6072 (1989).

[4] M. S. Fee, A. P. Mills, Jr., S. Chu, E. D. Shaw, K. Danzmann, R. J. Chichester, and D. M. Zuckerman, Phys. Rev. Lett. **70**, 1397 (1993); M. S. Fee, S. Chu, A. P. Mills, Jr., R. J. Chichester, D. M. Zuckerman, E. D. Shaw, and K. Danzmann, Phys. Rev. A **48**, 192 (1993).

[5] A. P. Mills, Jr., S. Berko, and K. F. Canter, Phys. Rev. Lett. **34**, 1541 (1975).

[6] S. Hatamian, R. S. Conti, and A. Rich, Phys. Rev. Lett. **58**, 1833 (1987).

[7] D. Hagena, R. Ley, D. Weil, G. Werth, W. Arnold, and H. Schneider, Phys. Rev. Lett. **71**, 2887 (1993).

[8] R. S. Conti, S. Hatamian, L. Lapidus, A. Rich, and M. Skalsey, Phys. Lett. A **177**, 43 (1993).

[9] R. Ley, D. Hagena, D. Weil, G. Werth, W. Arnold, and H. Schneider, Hyperfine Interact. **89**, 327 (1994).

[10] S. G. Karshenboim, Int. J. Mod. Phys. A **19**, 3879 (2004).

[11] J. R. Sapirstein and D. R. Yennie, in *Quantum Electrodynamics*, edited by T. Kinoshita (World Scientific, Singapore, 1990).

[12] A. Pineda and J. Soto, Phys. Rev. D **59**, 016005 (1998).

[13] K. Pachucki and S. G. Karshenboim, Phys. Rev. Lett. **80**, 2101 (1998).

[14] A. Czarnecki, K. Melnikov, and A. Yelkhovsky, Phys. Rev. A **59**, 4316 (1999).

[15] I. B. Khriplovich, A. I. Milstein, and A. S. Yelkhovsky, Zh. Eksp. Teor. Fiz. **105**, 299 (1994).

[16] D. Gotta, K. Rashid, B. Fricke, P. Indelicato, and L. M. Simons, Eur. Phys. J. D **47**, 11–26 (2008).

[17] K. Pachucki, Phys. Rev. A **71**, 012503 (2005).

[18] K. Pachucki, Phys. Rev. A **74**, 062510 (2006).

[19] V. M. Shabaev, Phys. Rep. **356**, 119 (2002).

[20] A. H. Hoang, P. Labelle, and S. M. Zebarjad, Phys. Rev. Lett. **79**, 3387 (1997).

[21] W. E. Caswell and G. P. Lepage, Phys. Rev. A **20**, 36 (1979).

[22] C. Itzykson and J. B. Zuber, *Quantum Field Theory* (McGraw-Hill, New York, 1990).

[23] G. Łach and K. Pachucki, Phys. Rev. A **64**, 042510 (2001).

[24] S. Wolfram, *The Mathematica Book* (Cambridge University Press, Cambridge, U.K., 1999).

[25] V. B. Berestetsky, E. M. Lifshitz, and L. P. Pitaevsky, *Quantum Electrodynamics* (Pergamon Press, Oxford, 1982).

[26] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, NJ, 1974).

[27] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Butterworth-Heinemann, London, 1981).

[28] P. J. Mohr, B. N. Taylor, and D. B. Newell, Rev. Mod. Phys. **80**, 633 (2008).

[29] G. W. F. Drake and R. A. Swainson, Phys. Rev. A **41**, 1243 (1990).

[30] U. D. Jentschura, A. Czarnecki and K. Pachucki, Phys. Rev. A **72**, 062102 (2005).

[31] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977), p. 17.