Spin-averaged effective Hamiltonian of orders $m\alpha^6$ and $m\alpha^6(m/M)$ for hydrogen molecular ions

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The spin-averaged effective Hamiltonian of orders $m\alpha^6$ and $m\alpha^6(m/M)$ for a one-electron two-center Coulombic system is derived by using the theory of nonrelativistic quantum electrodynamics (NRQED), without assuming the Born-Oppenheimer approximation. The separated singularities from the first- and second-order perturbations are shown to be canceled out analytically for both order $m\alpha^6$ and $m\alpha^6(m/M)$ corrections by regularizing the effective Hamiltonian. Our results can be used to perform high-precision spectroscopic calculations of hydrogen molecular ions.

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I. INTRODUCTION

Atomic systems can be precisely described by bound-state quantum electrodynamic (QED) theories, such as the quasipotential method for light atomic systems [1] and the two-time Green's function method for medium and heavy atomic systems [2]. Among various forms of bound-state QED theories, the two-body relativistically covariant Bethe-Salpeter equation is considered to be exact, but its kernel has no closed expression even for a simple system such as positronium [3]. For a light system consisting of more than two charged particles, the leading-order relativistic corrections to an energy level can be calculated using the many-electron Dirac-Coulomb (DC) Hamiltonian, together with the electron-electron Breit operator [4]. The radiative corrections from high energy interactions can be treated using scattering theory. In 1986, a different approach, called nonrelativistic QED (NRQED), was suggested by Caswell and Lepage [5] to expand a bound-state energy level of a light atom in powers of the fine-structure constant α. In 2005, using NRQED theory a complete set of contributions up to order $m\alpha^6$ was derived by Pachucki [6,7] in the nonrecoil limit. The order $m\alpha^6$ recoil corrections were obtained and calculated only recently for atomic helium [8,9]. The validity of these calculations has been precisely tested through comparisons with high-precision experimental measurements [10–13].

For a molecular system, the transition frequency between two rovibrational states is much more sensitive to the nucleus to electron mass ratio than for an atomic system, due to the nature of rovibrational structure of its energy levels. It was recently demonstrated that a hydrogen molecular ion can be used not only for testing QED theory, but also holds the potential for deriving the proton (deuteron) to electron mass ratio [14], as well as for determining the proton (deuteron) charge radius [15], provided both theory and experiment can reach a sufficiently high precision. The current status of theory for hydrogen molecular ions is that the relative theoretical uncertainty of fundamental transitions was reduced to the level of 7×10^{-12} by taking into account the nonrecoil and recoil corrections of orders $m\alpha^6$ and $m\alpha^7$, and the contributions of order $m\alpha^8$ [16]. The whole procedure for achieving such a level of precision can be divided into two steps. The first step is three-body calculations of nonrelativistic energies [17] and the leading relativistic and QED corrections of orders $m\alpha^4$ and $m\alpha^5$ [18–23]. The three-body Schrödinger equation can be solved variationally [24] in Hylleraas-type coordinates, which allows nonrelativistic energies of the hydrogen molecular ions to reach a precision of 10^{-15} [25,26] for a wide range of rovibrational states and up to 10^{-30} or lower [17,27] for some particular low-lying rovibrational states. The order $m\alpha^4$ contribution is described by the Breit-Pauli Hamiltonian [28] and the leading nuclear recoil effects are well understood [29,30]. For the order $m\alpha^5$ contribution [21,31], it has been derived from the NRQED in a way similar to what has been done for the atomic helium [32,33]. All these contributions have been calculated numerically to sufficiently high precision nonadiabatically by treating three constituent charged particles on the same footing.

The second step of the procedure is to derive higher-order relativistic and QED corrections of orders $m\alpha^6$, $m\alpha^7$, and $m\alpha^8$. Korobov and coworkers have performed these calculations with the adiabatic approximation applied to the nonrelativistic wave functions [16,34,35], where the effective Hamiltonian is built for the interaction of an electron with the external field produced by the two nuclei [34] and the calculations are carried out in the framework of the Born-Oppenheimer (BO) approximation together with the adiabatic corrections [36]. This way of treating higher-order corrections is basically equivalent to a problem of an electron in an external field [3]. Moreover, the nuclear recoil effects are handled within the realm of two-body bound states. As an example, the relativistic recoil contribution of order $m(Z\alpha)^6(m/M)$ is taken from Ref. [37] and the radiative recoil contribution from Refs. [38,39]. It is, therefore, desirable to derive the effective Hamiltonian of order $m\alpha^6$, including the recoil terms, by treating all three constituent charged particles of a hydrogen

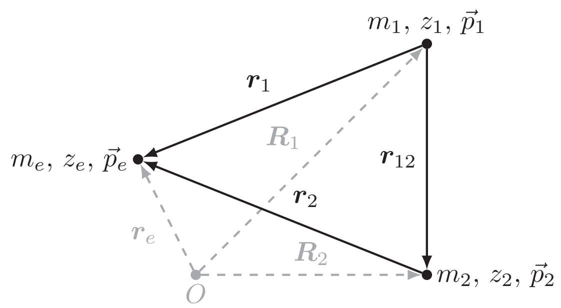

FIG. 1. The coordinates for a one-electron two-center system, where O is the origin of the laboratory frame, the electron is denoted as e, and the two nuclei are denoted as particle 1 and 2.

molecular ion on the same footing without explicitly resorting to the Born-Oppenheimer approximation.

The aim of this work is to derive the spin-averaged order $m\alpha^6$ effective Hamiltonian for one-electron molecular systems such as hydrogen molecular ions. We will give a detailed description about how to analytically cancel out the singularities in the first- and second-order corrections in order to obtain finite expressions. The remaining part of this paper is organized as follows. Section II introduces the NRQED used to calculate the energy levels. Section III presents the derivation of the spin-averaged effective Hamiltonian $H^{(6)}$ for the $m\alpha^6$-order corrections. The divergent terms of $m\alpha^6$-order corrections are separated and then canceled out in Sec. IV. Section V gives a conclusion and discussion.

II. NRQED APPROACH

In this section, natural units are used where $c = \hbar = 1$ and $\alpha = e^2/(4\pi)$. In NRQED theory, an energy level of a light system can be expanded in powers of α:

$$E(\alpha) = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + O(\alpha^8), \quad (1)$$

where $E^{(n)}$ is a contribution of order $m\alpha^n$ and may include nuclear recoil terms. Each term $E^{(n)}$ can be obtained from the expectation value of the corresponding effective Hamiltonian.

In Eq. (1), $E^{(2)} \equiv E_0$ is the eigenvalue of the nonrelativistic Hamiltonian $H^{(2)} \equiv H_0$ with the associated eigenstate ϕ satisfying $H_0\phi = E_0\phi$, where

$$H_0 = \frac{1}{2m_e}p_e^2 + \frac{1}{2m_1}p_1^2 + \frac{1}{2m_2}p_2^2 + \alpha\left(\frac{z_1 z_e}{r_1} + \frac{z_2 z_e}{r_2} + \frac{z_1 z_2}{r_{12}}\right). \quad (2)$$

The Hamiltonian H_0 is expressed in a way of explicitly embodying the kinetic energy operators for each particle in the center-of-mass frame with $\vec{p}_1 + \vec{p}_2 + \vec{p}_e = 0$, as shown in Fig. 1, where the adopted notations will be employed throughout this paper. The relative vector positions between particles are

$$\vec{r}_1 = \vec{r}_e - \vec{R}_1, \quad \vec{r}_2 = \vec{r}_e - \vec{R}_2, \quad \vec{r}_{12} = \vec{R}_2 - \vec{R}_1. \quad (3)$$

For the sake of convenience, we denote the individual components of Coulomb interactions as

$$V_{12} = \alpha\frac{z_1 z_2}{r_{12}}, \quad V_a = \alpha\frac{z_a z_e}{r_a}, \quad a = 1, 2, \quad (4)$$

and the total Coulomb potential is thus

$$V = V_1 + V_2 + V_{12}. \quad (5)$$

The term $E^{(4)}$ in Eq. (1) is the expectation value of the Breit-Pauli Hamiltonian $H^{(4)}$ [18,19,40], which represents all $m\alpha^4$-order interactions between the constituent particles. It is noted that the second-order perturbation of $H^{(4)}$ contributes to the spin-averaged $m\alpha^6$-order correction. Since we are interested in the nonrecoil and leading-order recoil corrections of $H^{(6)}$, we only consider the required operators here:

$$H^{(4)} = H_B + H_R + H_S, \quad (6)$$

where

$$H_B = -\frac{\vec{p}_e^{\,4}}{8m_e^3} - \frac{\pi\alpha}{2m_e^2}\sum_a z_a z_e \delta(\vec{r}_a), \quad (7)$$

$$H_R = \sum_a -\frac{z_a z_e \alpha}{m_e m_a} p_e^i \left[\frac{1}{2r_a}\left(\delta^{ij} + \frac{r_a^i r_a^j}{r_a^2}\right)\right] p_a^j, \quad (8)$$

$$H_S = \sum_a -z_a z_e \alpha\left[\frac{1 + 2a_e}{2m_e^2}\frac{1}{r_a^3}\vec{r}_a \times \vec{p}_e - \frac{1 + a_e}{m_e m_a}\frac{1}{r_a^3}\vec{r}_a \times \vec{p}_a\right] \cdot \vec{s}_e, \quad (9)$$

$a = 1, 2$ runs over the two nuclei, and a_e is anomalous magnetic moment of electron. H_B comes from the relativistic correction of the bound electron, H_R is so-called the orbit-orbit interaction between the electron and nuclei, and H_S stands for the interaction between the electron spin and the magnetic field generated by the motions of all three particles. The leading radiative correction $E^{(5)}$ [22,41] is not needed in the present investigation. The next term $E^{(6)}$ in Eq. (1) is the subject of this work, which can be expressed as a sum of two terms,

$$E^{(6)} = \langle\phi|H^{(4)}Q(E_0 - H_0)^{-1}QH^{(4)}|\phi\rangle + \langle\phi|H^{(6)}|\phi\rangle, \quad (10)$$

where $Q = 1 - |\phi\rangle\langle\phi|$ is the projection operator for the state of interest. The first term, denoted as $E^{(6)}_{\rm 2nd}$, is the second-order contribution from $H^{(4)}$, and $H^{(6)}$ in the second term is the spin-averaged effective Hamiltonian of order $m\alpha^6$. It has been pointed out that each term of $E^{(6)}$ has its own singular part and all the singular parts from these two terms should yield a finite result when added [6,36].

In the rest of this section, a brief introduction to the NRQED theory will be presented. First, the nonrelativistic expansion of the Dirac Hamiltonian will be obtained by using the Foldy-Wouthuysen (FW) transformation. Second, the many-body Lagrangian density will be built. The interactions corresponding to the exchanges of photons between particles will then be carried out using Feynman rules based on the Lagrangian obtained from the second step. Finally, combining all necessary interactions will result in the required effective Hamiltonian.

We start with the Dirac Hamiltonian in an external field,

$$H = \vec{\alpha}\cdot\vec{\pi} + \beta m_e + eA^0, \quad (11)$$

where $\vec{\pi} = \vec{p}_e - e\vec{A}$. The FW transformation is defined as [42]

$$H_{\rm FW} = e^{iS}(H - i\partial_t)e^{-iS}, \tag{12}$$

where the FW operator S is chosen to decouple the upper and lower components of the Dirac wave function up to a specified order in the $1/m$ expansion. According to Refs. [6,7], after performing the FW transformation, the nonrelativistic expansion of the Dirac Hamiltonian has the following form:

$$\begin{aligned} H_{\rm FW} = {} & eA^0 + \frac{1}{2m_e}(\pi^2 - e\vec{\sigma}_e\cdot\vec{B}) - \frac{1}{8m_e^3}(\pi^4 - \{e\vec{\sigma}_e\cdot\vec{B},\pi^2\}) \\ & - \frac{1}{8m_e^2}[e\vec{\nabla}_e\cdot\vec{E} + e\vec{\sigma}_e\cdot(\vec{E}\times\vec{\pi} - \vec{\pi}\times\vec{E})] \\ & - \frac{e}{16m_e^3}\{\vec{p}_e,\partial_t\vec{E}\} + \frac{3e}{32m_e^4}\{\vec{E}\times\vec{p}_e\cdot\vec{\sigma}_e, p_e^2\} \\ & + \frac{1}{128m_e^4}[p_e^2,[p_e^2,eA^0]] - \frac{3}{64m_e^4}\{p_e^2,\nabla_e^2(eA^0)\} \\ & + \frac{p_e^6}{16m_e^5}, \end{aligned} \tag{13}$$

where the first term eA^0 is just the potential V defined in Eq. (5), and

$$\vec{B} = \vec{\nabla}_e \times \vec{A}, \tag{14}$$

$$\vec{E} = -\vec{\nabla}_e A^0 - \partial_t\vec{A}. \tag{15}$$

It is noted that the expression $H_{\rm FW}$ depends on the choice of the FW operator S, which means that $H_{\rm FW}$ is not unique. The expression of $H_{\rm FW}$ in Eq. (13) differs from the one used in Refs. [8,9] since their transformation has some additional operators. However, all forms of $H_{\rm FW}$ should be equivalent when taking matrix elements with respect to an eigenstate of the Schrödinger equation.

Since we only consider the leading-order recoil terms, the nuclei can be treated nonrelativistically, and the corresponding Hamiltonian for nucleus a can thus be written in the form

$$H_a = \frac{1}{2m_a}(\vec{p}_a + z_a e\vec{A})^2. \tag{16}$$

With this, we can now construct the following effective nonrelativistic QED Lagrangian:

$$\mathcal{L} = \phi_e^\dagger(i\partial_t - H_{\rm FW})\phi_e + \sum_{a=1,2}\phi_a^\dagger(i\partial_t - H_a)\phi_a + \mathcal{L}_{\rm EM}, \tag{17}$$

where $\mathcal{L}_{\rm EM}$ is the Lagrangian for the electromagnetic field. Then the Feynman rules for this Lagrangian can be used to construct the effective Hamiltonian $H^{(6)}$; see Refs. [6,7] for details. The photon propagator in the Coulomb gauge is used:

$$G_{\mu\nu}(k) = \begin{cases} -\frac{1}{\vec{k}^2}, & \mu=\nu=0, \\ \frac{-1}{k_0^2-\vec{k}^2+i\varepsilon}\left(\delta_{ij} - \frac{k_ik_j}{\vec{k}^2}\right), & \mu=i,\ \nu=j. \end{cases} \tag{18}$$

Let us consider a typical interaction of exchanging one photon $G_{\mu\nu}(k)$ between two particles, for example the electron and nucleus a:

$$\begin{aligned} \langle\phi|\Sigma(E_0)|\phi\rangle = {} & z_a z_e e^2 \int \frac{d^4k}{(2\pi)^4 i} G_{\mu\nu}(k)\Bigg\{\langle\phi|j_e^\mu(k)e^{i\vec{k}\cdot\vec{r}_e} \\ & \times \frac{1}{E_0 - H_0 - k^0 + i\epsilon} j_a^\nu(-k)e^{-i\vec{k}\cdot\vec{R}_a}|\phi\rangle \\ & + (e\leftrightarrow a)\Bigg\}, \end{aligned} \tag{19}$$

where the operator $\Sigma(E_0)$ is the irreducible contribution due to the photon exchange, and j_e^μ and j_a^ν are, respectively, the electromagnetic current operators for the electron and nucleus a. Most calculations are carried out in the nonretardation approximation where $k^0 = 0$ is applied in the photon propagator and the current operators. Then the k^0 integral is performed after the symmetrization $k^0 \leftrightarrow -k^0$,

$$\frac{1}{2}\int\frac{dk^0}{2\pi i}\left[\frac{1}{-\Delta E - k^0 + i\epsilon} + \frac{1}{-\Delta E + k^0 + i\epsilon}\right] = -\frac{1}{2}, \tag{20}$$

which leads to

$$\begin{aligned} \langle\phi|\Sigma(E_0)|\phi\rangle = {} & -z_a z_e e^2 \int\frac{d^3k}{(2\pi)^3} G_{\mu\nu}(k_0=0,\vec{k})\langle\phi|j_e^\mu(\vec{k}) \\ & \times e^{i\vec{k}\cdot(\vec{r}_a-\vec{R}_a)} j_a^\nu(-\vec{k})|\phi\rangle. \end{aligned} \tag{21}$$

The retardation corrections are considered separately.

For the electron, its current operator can be extracted from $H_{\rm FW}$ and its scalar and vector parts j^0 and $\vec{j}$ are respectively (see Eqs. (33) and (34) of Ref. [6])

$$j_e^0(\vec{k}) = 1 + \frac{i}{4m_e^2}\vec{\sigma}_e\cdot\vec{k}\times\vec{p}_e - \frac{1}{8m_e^2}\vec{k}^2 + \cdots, \tag{22}$$

$$\vec{j}_e(\vec{k}) = \frac{\vec{p}_e}{m_e} + \frac{i}{2m_e}\vec{\sigma}_e\times\vec{k}. \tag{23}$$

On the other hand, the scalar and vector parts of the current operator for the nucleus a are respectively

$$j_a^0(\vec{k}) = 1 + O\left(\frac{1}{m_a^2}\right), \tag{24}$$

$$\vec{j}_a(\vec{k}) = \frac{\vec{p}_a}{m_a} + \frac{i}{2m_a}\vec{\sigma}_a\times\vec{k}. \tag{25}$$

The $\vec{k}$ integral in Eq. (21) is the Fourier transform of the Coulomb gauge photon propagator in the nonretardation approximation

$$\begin{aligned} G_{\mu\nu}(\vec{r}) &= \int\frac{d^3k}{(2\pi)^3}G_{\mu\nu}(\vec{k}) \\ &= \frac{1}{4\pi}\begin{cases} -\frac{1}{r}, & \mu=\nu=0, \\ \frac{1}{2r}\left(\delta_{ij} + \frac{r_ir_j}{r^2}\right), & \mu=i,\ \nu=j. \end{cases} \end{aligned} \tag{26}$$

III. $m\alpha^6$-ORDER SPIN-AVERAGED EFFECTIVE HAMILTONIAN

In this section the spin-averaged effective Hamiltonian $H^{(6)}$ will be derived, including the spin-independent operators and scalar contributions from the electron spin-spin interactions. To this end we will follow Refs. [6–8]. Since we investigate the interactions involving the nuclei, the effective Hamiltonian contains not only the nonrecoil terms but also the first-order recoil ones. For recoil terms higher than the first order, they are small enough to be ignored in the following derivation.

Before deriving the effective Hamiltonian, let us introduce some convenient notations. We employ the shorthand notation

$$\langle X\rangle = \langle\phi|X|\phi\rangle. \tag{27}$$

The individual vectors for static electric fields are denoted as

$$e\vec{\varepsilon}_{12} = \alpha z_1 z_2 \frac{\vec{r}_{12}}{r_{12}^3}, \quad e\vec{\varepsilon}_a = \alpha z_a z_e \frac{\vec{r}_a}{r_a^3}, \quad a = 1,2. \tag{28}$$

The static electric fields felt by the electron and two nuclei are respectively

$$e\vec{\mathcal{E}}_e = e(\vec{\varepsilon}_1 + \vec{\varepsilon}_2), \tag{29}$$

$$e\vec{\mathcal{E}}_a = -e[\vec{\varepsilon}_1 + (-1)^{a+1}\vec{\varepsilon}_{12}], \quad a = 1,2. \tag{30}$$

The vector potential at the position of electron produced by the two nuclei is

$$e\mathcal{A}_e^i = -\sum_a \frac{z_a\alpha}{2r_a}\left(\delta_{ij} + \frac{r_a^i r_a^j}{r_a^2}\right)\frac{p_a^j}{m_a}, \tag{31}$$

and the vector potential at the position of nucleus a produced by the electron and the other nucleus b is

$$e\mathcal{A}_a^i = \frac{z_e\alpha}{r_a}\left(\delta_{ij} + \frac{r_a^i r_a^j}{r_a^2}\right)\frac{p_e^j}{m_e} + \frac{z_e\alpha}{2m_e}\frac{(\vec{\sigma}_e\times\vec{r}_a)^i}{r_a^3} - \frac{z_b\alpha}{r_{ab}}\left(\delta_{ij} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right)\frac{p_b^j}{m_b}. \tag{32}$$

The spin-averaged $H^{(6)}$ can be expressed as a sum of various contributions:

$$H^{(6)} = \sum_{i=1}^{8}\delta H_i. \tag{33}$$

In the above, δH_1 is the kinetic energy correction of order $m\alpha^6$, which is the last term of H_{FW} in Eq. (13):

$$\delta H_1 = \frac{p_e^6}{16m_e^5}. \tag{34}$$

δH_2 is the total contribution from the remaining last three terms of Eq. (13). Since we consider the spin-averaged operators, the term involving $\vec{\sigma}_e$ can thus be ignored. Then the correction δH_2 includes the Coulomb interactions between the electron and nuclei:

$$\delta H_2 = \frac{1}{128m_e^4}[p_e^2,[p_e^2,V]] + \frac{3\alpha}{64m_e^4}\left\{p_e^2, 4\pi\sum_a z_a z_e\delta(\vec{r}_a)\right\}. \tag{35}$$

δH_3 is the correction from the fifth term in H_{FW} of Eq. (13):

$$-\frac{e}{16m_e^3}\{\vec{p}_e, \partial_t\vec{E}\}. \tag{36}$$

Assuming that the electron interacts via this term and the nucleus via the nonrelativistic coupling eA^0, we can write down this correction as an integral of one-photon exchange according to Eq. (19):

$$\delta E_3 = \sum_a -z_a z_e e^2\int\frac{d^4k}{(2\pi)^4 i}\frac{1}{\vec{k}^2}\frac{1}{16m_e^3}\Bigg\{\langle\phi|\{\vec{p}_e,\vec{k}e^{i\vec{k}\cdot r_e}\} \times \frac{k^0}{E_0 - H_0 - k^0 + i\epsilon}e^{-i\vec{k}\cdot\vec{R}_a}|\phi\rangle - \langle\phi|e^{-i\vec{k}\cdot\vec{R}_a}\frac{k^0}{E_0 - H_0 - k^0 + i\epsilon}\{\vec{p}_e,\vec{k}e^{i\vec{k}\cdot r_e}\}|\phi\rangle\Bigg\}. \tag{37}$$

Performing the k^0 integral yields

$$\delta E_3 = \sum_a -\frac{z_a z_e e^2}{2}\int\frac{d^3k}{(2\pi)^3}\frac{1}{\vec{k}^2}\frac{1}{16m_e^3}\{\langle\phi|\{\vec{p}_e,\vec{k}e^{i\vec{k}\cdot\vec{r}_e}\} \times (H_0 - E_0)e^{-i\vec{k}\cdot\vec{R}_a}|\phi\rangle + \langle\phi|e^{-i\vec{k}\cdot\vec{R}_a}(H_0 - E_0)\{\vec{p}_e,\vec{k}e^{i\vec{k}\cdot\vec{r}_e}\}|\phi\rangle\}. \tag{38}$$

By using the commutation relation of $(H_0 - E_0)e^{-i\vec{k}\cdot\vec{R}_a}\phi = [p_a^2/(2m_a), e^{-i\vec{k}\cdot\vec{R}_a}]\phi$, one can obtain the effective operator for this correction,

$$\delta H_3 = \sum_a -\frac{1}{32m_e^3 m_a}[p_a^2,[p_e^2,V_a]]. \tag{39}$$

δH_4 is the relativistic correction to the transverse photon exchange between the electron and one of the two nuclei. The nucleus is coupled to $\vec{A}$ by the nonrelativistic term

$$-\frac{z_a e}{m_a}\vec{p}_a\cdot\vec{A} - \frac{z_a e}{2m_a}\vec{\sigma}_a\cdot\vec{B} \tag{40}$$

and the electron by the relativistic correction from the third term of H_{FW},

$$-\frac{1}{8m_e^3}(\pi^4 - \{e\vec{\sigma}_e\cdot\vec{B}, p_e^2\}) \to -\frac{z_e e}{8m_e^3}\{p_e^2, 2\vec{p}_e\cdot\vec{A}_e + \vec{\sigma}_e\cdot\vec{B}\}. \tag{41}$$

In the non-retardation approximation, the $\vec{A}_e$ field of the electron can be replaced by the static field $\vec{\mathcal{A}}_e$ produced by the two nuclei. Thus after discarding the pure spin-dependent terms, one obtains

$$\delta H_4 = -\frac{z_e e}{8m_e^3}\{p_e^2, 2\vec{p}_e\cdot\vec{\mathcal{A}}_e\} = -\frac{1}{8m_e^2}\{p_e^2, 2H_R\}, \tag{42}$$

where $H_R = z_e\vec{p}_e\cdot e\vec{\mathcal{A}}_e$ is the transverse photon exchange correction of order $m\alpha^4$ that is part of the Breit-Pauli Hamiltonian $H^{(4)}$, as shown in Eq. (8).

δH_5 comes from the coupling of the second term in H_{FW},

$$\frac{e^2}{2m_e}\vec{A}^2. \tag{43}$$

Again, in the nonretardation approximation the $\vec{A}_a$ field of nucleus a is replaced by the static fields $\vec{\mathcal{A}}_a$ produced by other two particles. Therefore, δH_5 has the following form:

$$\delta H_5 = \frac{e^2}{2m_e}\vec{\mathcal{A}}_e^2 + \sum_{a=1,2}\frac{z_a^2 e^2}{2m_a}\vec{\mathcal{A}}_a^2. \tag{44}$$

Examining the expressions of $\vec{\mathcal{A}}_e$ and $\vec{\mathcal{A}}_a$ in Eqs. (31) and (32), δH_5 contains some operators which contribute to the second-order recoil correction and can thus be ignored in this work. The remaining δH_5 can thus be recast as

$$\delta H_5 = \sum_a \frac{z_a^2}{2m_a}\left\{\left[\frac{z_e\alpha}{2r_a}\left(\delta_{ij} + \frac{r_a^i r_a^j}{r_a^2}\right)\frac{p_e^j}{m_e}\right]\left[\frac{z_e\alpha}{2r_a}\left(\delta_{il} + \frac{r_a^i r_a^l}{r_a^2}\right)\frac{p_e^l}{m_e}\right] + \frac{z_e^2\alpha^2}{4m_e^2}\frac{\vec{\sigma}_e\times\vec{r}_a\cdot\vec{\sigma}_e\times\vec{r}_a}{r_a^6}\right\}. \tag{45}$$

δH_6 comes from the nonrelativistic one-transverse-photon exchange between the electron and the nuclei. One can write down the corresponding integral for this interaction from Eq. (19) and perform the k^0 integration to obtain

$$\delta E_6 = z_a z_e e^2 \int \frac{d^3k}{(2\pi)^3 2k}\left(\delta_{ij} - \frac{k^i k^j}{k^2}\right)\langle\phi|j_e^i(k)e^{i\vec{k}\cdot\vec{r}_e}\frac{1}{E_0 - H_0 - k}j_a^j(-k)e^{-i\vec{k}\cdot\vec{R}_a}|\phi\rangle + (e\leftrightarrow a), \tag{46}$$

where $k = |\vec{k}|$. It can be further expanded by using the following expansion:

$$\frac{1}{E_0 - H_0 - k} = -\frac{1}{k} + \frac{H_0 - E_0}{k^2} - \frac{(H_0 - E_0)^2}{k^3} + \cdots. \tag{47}$$

The first term gives rise to the Breit-Pauli Hamiltonian, the second term to $E^{(5)}$, and the third term to δE_6. It can further be split into three parts of non-spin, single-spin, and double-spin terms. In this work, we will only consider the non-spin term,

$$\delta E_6 = \sum_{a=1,2} -z_a z_e e^2 \int \frac{d^3k}{(2\pi)^3 2k^4}\left(\delta_{ij} - \frac{k^i k^j}{k^2}\right)\langle\phi|\frac{\vec{p}_e}{m_e}\{e^{i\vec{k}\cdot\vec{r}_e}(H_0 - E_0)^2 e^{-i\vec{k}\cdot\vec{r}_a} - (E_0 - H_0)^2\}\frac{\vec{p}_a}{m_a}|\phi\rangle. \tag{48}$$

Using the commutator identity

$$\begin{aligned} e^{i\vec{k}\cdot\vec{r}_e}(H_0 - E_0)^2 e^{-i\vec{k}\cdot\vec{R}_a} - (E_0 - H_0)^2 &= (H_0 - E_0)(e^{i\vec{k}\cdot\vec{r}_a} - 1)(E_0 - E_0) + (H_0 - E_0)\left[\frac{p_a^2}{2m_a}, e^{i\vec{k}\cdot\vec{r}_a} - 1\right] \\ &+ \left[e^{i\vec{k}\cdot\vec{r}_a} - 1, \frac{p_e^2}{2m_e}\right](H_0 - E_0) + \left[\frac{p_a^2}{2m_a}, \left[e^{i\vec{k}\cdot\vec{r}_a} - 1, \frac{p_e^2}{2m_e}\right]\right], \end{aligned} \tag{49}$$

the effective Hamiltonian δH_6 can be extracted from δE_6

$$\delta H_6 = \sum_a -\frac{\alpha}{m_e m_a}\left\{[p_e^i, V]\mathcal{X}^{ij}(r_a)[V, p_a^j] + p_e^i\left[\mathcal{X}^{ij}(r_a), \frac{p_e^2}{2m_e}\right][V, p_a^j]\right\}, \tag{50}$$

where all the second-order recoil terms are ignored, and

$$\mathcal{X}^{ij}(r) = \int d^3k \frac{4\pi}{k^4}\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right)(e^{i\vec{k}\cdot\vec{r}} - 1) = \frac{1}{8r}[r^i r^j - 3\delta^{ij}r^2]. \tag{51}$$

The next term, δH_7, is the $m\alpha^6$-order nonrecoil radiative correction that can be treated approximately as a bound electron in an external field instead of the whole Coulomb three-body framework. It can thus be obtained from the bound-state hydrogen theory using the external field approximation [3]. The nonrecoil radiative correction of order $m\alpha^6$ can be expressed in the form [34]

$$\delta H_7 = \alpha^3\frac{4\pi}{m_e^2}\sum_a\left\{\left(\frac{139}{128} - \frac{\ln 2}{2} + \frac{5}{192}\right)z_a^2\delta(\vec{r}_a) - \left(\frac{1}{4\pi^2}\right)\left[\frac{2179}{648} + \frac{10}{27}\pi^2 - \frac{3}{2}\pi^2\ln 2 + \frac{9}{5}\zeta(3)\right]z_a\delta(\vec{r}_a)\right\}. \tag{52}$$

δH_8 is the leading radiative recoil correction of order $m\alpha^6$ due to the interactions between the electron and the nuclei. Again, these interactions can be obtained from the bound-state hydrogen theory and δH_8 can thus be written as

$$\delta H_8 = \delta H_8^A + \delta H_8^B + \delta H_8^C, \tag{53}$$

where the first term comes from the pure recoil correction due to three-photon exchange [43],

$$\delta H_8^A = \sum_a (z_a\alpha)^3\frac{m_e}{m_a}\left(\ln 2 - \frac{7}{8}\right)4\pi\delta(\vec{r}_a), \tag{54}$$

the second term comes from the forward-scattering radiative recoil diagrams and has the form (see Fig. 1 and Eq. (8) of Ref. [38])

$$\delta H_8^B = \sum_a \alpha(z_a\alpha)^2\frac{m_e}{m_a}\left[\frac{3}{4} + \frac{6}{\pi^2}\zeta(3) - \frac{14}{\pi^2} - 2\ln 2\right]\pi\delta(\vec{r}_a), \tag{55}$$

and the last contribution comes from the vacuum polarization-recoil correction (see Fig. 2 and Eq. (72) of Ref. [44])

$$\delta H_8^C = \sum_a \alpha(z_a\alpha)^2\frac{m_e}{m_a}\left(\frac{2}{9}\pi^2 - \frac{70}{27}\right)\frac{1}{\pi}\delta(\vec{r}_a). \tag{56}$$

IV. CANCELLATION OF SINGULARITIES

As has been demonstrated before [6,36], both the first-order and second-order contributions of $m\alpha^6$-order correction are individually divergent; the divergence, however, cancels out analytically when summing up all the divergent terms.

A. The first-order correction

In this subsection, we investigate the correction from the first-order terms in Eq. (10). Using Eq. (33), the matrix elements of the effective Hamiltonian are denoted as $\delta E_i = \langle \delta H_i \rangle$ with $i = 1$–8, see Eqs. (57)–(65). Since the procedure of separating the singularity is very tedious, we move the derivation to Appendix A. Here we only present the final results (in atomic units $e = m_e = \hbar = 1$)

$$E^{(6)}_{\rm 1st} = \alpha^4 \sum_{i=1}^{8} \delta E_i, \tag{57}$$

where

$$\begin{aligned}\delta E_1 = \frac{1}{16}\bigg\{ & E_0\big[2\langle p_e^4\rangle - 4\langle (V_1+V_2)p_e^2\rangle + 16\langle V_{12}V\rangle\big] - 8E_0^2\langle V_{12}\rangle + 8\vec{\varepsilon}_1\vec{\varepsilon}_2 + 4\langle (2V_1V_2 + V_1V_{12} + V_2V_{12})p_e^2\rangle \\ & + \sum_{a\neq b} 4\left(1-\frac{2}{m_a}\right)\langle \varepsilon_a^2\rangle - 8\left(1-\frac{3}{m_a}\right)\big[\langle V_a^3\rangle + \langle V_a^2(V_b+V_{12})\rangle - E_0\langle V_a^2\rangle\big] \\ & + \frac{4}{m_a}\big[\langle \varepsilon_{12}^2\rangle + 3(-1)^a\langle \vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle + E_0\langle (2V+V_1+V_2)p_a^2\rangle + 2E_0\langle V_{12}^2p_a^2\rangle - E_0^2\langle p_a^2\rangle \\ & - 3\langle V_a^2(p_a^2-p_e^2)\rangle - \langle (4V_1V_2 + 5V_1V_{12} + 5V_2V_{12} + 3V_b^2 + 3V_{12}^2)p_a^2\rangle\big]\bigg\},\end{aligned} \tag{58}$$

$$\begin{aligned}\delta E_2 = {} & \frac{1}{128}\sum_{b\neq a}\left\{ -4\left(1-\frac{1}{m_a}\right)\langle \varepsilon_a^2\rangle - 4\langle \vec{\varepsilon}_a\vec{\varepsilon}_b\rangle - \frac{4}{m_a}(-1)^a\langle \vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle + \frac{6}{m_a}\langle V_a^2(p_a^2-p_e^2)\rangle + \frac{2}{m_a}\langle V_bVp_a^2\rangle\right\} \\ & + \frac{3\pi}{8}\sum_{b\neq a} z_az_e\left\{2\left(1-\frac{1}{m_a}\right)[E_0\langle \delta(\vec{r}_a)\rangle - \langle (V_b+V_{12})\delta(\vec{r}_a)\rangle - \langle V_a\delta(\vec{r}_a)\rangle] - \frac{1}{m_a}\langle \delta(\vec{r}_a)(p_a^2-p_e^2)\rangle - \frac{1}{m_b}\langle \delta(\vec{r}_a)p_b^2\rangle\right\},\end{aligned} \tag{59}$$

$$\delta E_3 = \frac{1}{8}\sum_{b\neq a}\frac{1}{m_a}\{\langle \varepsilon_a^2\rangle + (-1)^{a+1}\langle \vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle\}, \tag{60}$$

$$\delta E_4 = -E_0\langle H_R\rangle - \sum_a \frac{1}{2m_a}\left\{\langle \vec{p}_eV_aV\vec{p}_a\rangle + \left\langle (\vec{p}_e\cdot\vec{r}_a)\frac{V_aV}{r_a^2}(\vec{r}_a\cdot\vec{p}_a)\right\rangle + \langle \varepsilon_a^2\rangle\right\}, \tag{61}$$

$$\delta E_5 = \sum_a \frac{1}{8m_a}\left\{\langle \vec{p}_eV_a^2\vec{p}_e\rangle + 3\left\langle (\vec{p}_e\cdot\vec{r}_a)\frac{V_a^2}{r_a^2}(\vec{r}_a\cdot\vec{p}_e)\right\rangle + 2\langle \varepsilon_a^2\rangle\right\}, \tag{62}$$

$$\delta E_6 = \sum_a -\frac{1}{8m_a}\left\{7\left\langle (\vec{p}_e\cdot\vec{r}_a)\frac{V_a^2}{r_a^2}(\vec{r}_a\cdot\vec{p}_e)\right\rangle - 3\langle \vec{p}_eV_a^2\vec{p}_e\rangle\right\}, \tag{63}$$

$$\delta E_7 = 4\pi\sum_a\{0.7654055763\ldots z_a^2\langle \delta(\vec{r}_a)\rangle + 0.02735334841\ldots z_a\langle \delta(\vec{r}_a)\rangle\}, \tag{64}$$

$$\delta E_8 = -4\pi\sum_a\frac{1}{m_a}\{0.1818528194\ldots z_a^3\langle \delta(\vec{r}_a)\rangle + 0.4615527501\ldots z_a^2\langle \delta(\vec{r}_a)\rangle\}. \tag{65}$$

Here the convention $\vec{v}_1\vec{v}_2 \equiv \vec{v}_1\cdot\vec{v}_2$ is used for some terms and the common factor α^4 has been pulled out from each δE_i. In the above expressions, all the singularities are absorbed into the matrix elements $\langle \varepsilon_a^2\rangle$ and $\langle V_a^3\rangle$. Let us denote S_i be the singular part of δE_i, which can be written as

$$S_1 = \frac{1}{4}\left[\left(1-\frac{2}{m_a}\right)\langle \varepsilon_a^2\rangle_S - 2\left(1-\frac{3}{m_a}\right)\langle V_a^3\rangle_S\right], \tag{66}$$

$$S_2 = -\frac{1}{32}\left[7\left(1-\frac{1}{m_a}\right)\langle \varepsilon_a^2\rangle_S - 12\left(1-\frac{2}{m_a}\langle V_a^3\rangle_S\right)\right], \tag{67}$$

$$S_3 = \frac{1}{8m_a}\langle \varepsilon_a^2\rangle_S, \tag{68}$$

$$S_4 = -\frac{1}{2m_a}\langle \varepsilon_a^2\rangle_S, \tag{69}$$

$$S_5 = \frac{1}{4m_a}\langle \varepsilon_a^2\rangle_S, \tag{70}$$

$$S_6 = S_7 = S_8 = 0. \tag{71}$$

Here the subscript S stands for the singular part of the corresponding matrix element. Summing up all the singular parts, one finally isolates the total singularity of $\langle H^{(6)}\rangle$:

$$S_{1\text{st}} = \sum_a \frac{1}{32}\left[\left(1-\frac{13}{m_a}\right)\langle\varepsilon_a^2\rangle_S - 4\left(1-\frac{6}{m_a}\right)\langle V_a^3\rangle_S\right]. \tag{72}$$

B. The second-order correction of the Breit-Pauli Hamiltonian

The second-order correction $E_{2\text{nd}}^{(6)}$ of the Breit-Pauli Hamiltonian Eqs. (6) and (10) can be divided into three terms:

$$E_{2\text{nd}}^{(6)} = \alpha^4[E_B + E_R + E_S], \tag{73}$$

$$E_B = \langle H_B Q(E_0 - H_0)^{-1} Q H_B\rangle, \tag{74}$$

$$E_R = \langle H_B Q(E_0 - H_0)^{-1} Q H_R\rangle + \langle H_R Q(E_0 - H_0)^{-1} Q H_B\rangle, \tag{75}$$

$$E_S = \langle H_S Q(E_0 - H_0)^{-1} Q H_S\rangle, \tag{76}$$

where H_B, H_R, and H_S are defined in Eqs. (7)–(9) and expressed in a.u. while the common factor α^2 has been pulled out.

The singularities of the second-order terms are mainly caused by the Dirac delta functions appeared in the Breit-Pauli Hamiltonian H_B. Consider the Hamiltonian H_B acting on the eigenstate ϕ:

$$H_B\phi \sim \sum_a \pi\left(\frac{1}{2} - \frac{1}{m_a}\right) z_a z_e \delta(\vec{r}_a)\phi. \tag{77}$$

Usually, a transformation for H_B is used to separate singularities:

$$H_B' = H_B - (E_0 - H_0)U - U(E_0 - H_0), \tag{78}$$

where

$$U = \lambda_1 V_1 + \lambda_2 V_2. \tag{79}$$

The parameters λ_1 and λ_2 are chosen below in such a way that the Dirac delta functions can be eliminated from $H_B'\phi$:

$$\lambda_a = -\frac{1}{4}\left[1 - \frac{3}{m_a}\right] + O\left(\frac{1}{m_a^2}\right), \quad a = 1, 2. \tag{80}$$

From Eq. (78), the second-order correction E_B is thus transformed to

$$E_B = \langle H_B' Q(E_0 - H_0)^{-1} Q H_B'\rangle + \langle\{H_B, U\}\rangle - 2\langle U\rangle\langle H_B\rangle - \langle U(E_0 - H_0)U\rangle. \tag{81}$$

The divergent matrix element $\langle\{H_B, U\}\rangle$ above can be expressed as follows:

$$\langle\{H_B, U\}\rangle = \sum_{a\neq b} -\frac{\lambda_a}{8}\left[\left\langle\left\{p_e^4, V_a\right\}\right\rangle + 8\pi\,\langle V_a(z_a z_e\delta(\vec{r}_a) + z_b z_e \delta(\vec{r}_b))\rangle\right], \tag{82}$$

where the divergent matrix elements $4\pi z_a z_e\langle V_a\delta(\vec{r}_a)\rangle$ and $\langle\{p_e^4, V_a\}\rangle$ can be found in Eqs. (A10) and (A15) respectively.

Thus $\langle\{H_B, U\}\rangle$ becomes

$$\begin{aligned}\langle\{H_B, U\}\rangle = &-\frac{1}{8}\sum_{a\neq b}\lambda_a\Bigg\{4E_0\left[\langle V_a p_e^2\rangle - \frac{1}{m_a}\langle V_a p_a^2\rangle - \frac{1}{m_b}\langle V_a p_b^2\rangle\right] + \frac{4}{m_b}\langle V_a V p_b^2\rangle - 4\left[\langle\vec{\varepsilon}_a\vec{\varepsilon}_b\rangle\right.\\ &\left. + \left\langle V_a(V_b + V_{12})p_e^2\right\rangle\right] + \frac{4}{m_a}\left[(-1)^{a+1}\langle\vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle\right.\\ &\left. + \left\langle V_a^2\left(p_a^2 - p_e^2\right)\right\rangle + \left\langle V_a(V_b + V_{12})p_a^2\right\rangle\right]\\ &+ 8\pi[z_b z_e\langle V_a\delta(\vec{r}_b)\rangle + z_a z_e\langle V_a\delta(\vec{r}_a)\rangle]\\ &- 4\left(1 - \frac{1}{m_a}\right)\left\langle V_a p_e^2 V_a\right\rangle\Bigg\}.\end{aligned} \tag{83}$$

The other divergent matrix element $\langle U(E_0 - H_0)U\rangle$ in E_B can be simplified to

$$\langle U(E_0 - H_0)U\rangle = -\sum_{a\neq b}\left\{\frac{1}{2}\left(1 + \frac{1}{m_a}\right)\lambda_a^2\langle\varepsilon_a^2\rangle + \lambda_a\lambda_b\langle\vec{\varepsilon}_a\vec{\varepsilon}_b\rangle\right\}, \tag{84}$$

where Eqs. (A6)–(A9) have been applied. We can now identify the singular part of E_B as

$$S_B = -\sum_a \frac{1}{32}\left[\left(1 - \frac{5}{m_a}\right)\langle\varepsilon_a^2\rangle_S - 4\left(1 - \frac{6}{m_a}\right)\langle V_a^3\rangle_S\right]. \tag{85}$$

We now turn to E_R, which can be expanded using the transformation Eq. (78):

$$E_R = \langle H_B' Q(E_0 - H_0)^{-1} Q H_R\rangle + \langle H_R Q(E_0 - H_0)^{-1} Q H_B'\rangle + \langle\{H_R, U\}\rangle - 2\langle H_R\rangle\langle U\rangle. \tag{86}$$

The matrix element $\langle\{H_R, U\}\rangle$ can be reduced to

$$\begin{aligned}\langle\{H_R, U\}\rangle = &-\sum_a \frac{\lambda_a}{m_a}\left[\langle\varepsilon_a^2\rangle - 2(z_a z_e)^3\langle\pi\delta(\vec{r}_a)\rangle\right]\\ &- \sum_a \frac{1}{m_a}\Bigg[\langle\vec{p}_e V_a U\vec{p}_a\rangle\\ &+ \langle(\vec{p}_e\cdot\vec{r}_a)\frac{V_a U}{r_a^2}(\vec{r}_a\cdot\vec{p}_a)\rangle\Bigg],\end{aligned} \tag{87}$$

where its singular part is

$$S_R = \sum_a \frac{1}{4m_a}\langle\varepsilon_a^2\rangle_S. \tag{88}$$

As for E_S it is convergent. We thus finally obtain the total singular part of $E_{2\text{nd}}^{(6)}$ by summing up Eqs. (85) and (88)

$$S_{2\text{nd}} = -\sum_a \frac{1}{32}\left[\left(1 - \frac{13}{m_a}\right)\langle\varepsilon_a^2\rangle_S - 4\left(1 - \frac{6}{m_a}\right)\langle V_a^3\rangle_S\right]. \tag{89}$$

V. DISCUSSION AND CONCLUSION

The spin-averaged effective Hamiltonian $H^{(6)}$ of orders $m_e\alpha^6$ and $m\alpha^6(m/M)$ for a one-electron two-center system has been obtained nonadiabatically in Eqs. (34), (35), (39), (42), (45), (50), (52), and (53) by using NRQED theory, where we have considered not only the nonrecoil contributions but also the first-order recoil contributions. The first two terms, Eqs. (34) and (35), are due to the $m\alpha^6$-order relativistic correction for the electron, which can be taken directly from $H_{\rm FW}$. These two terms contain both nonrecoil and recoil contributions that belong to the $m\alpha^6$-order and $m\alpha^6(m/M)$-order corrections respectively. The other terms are pure recoil corrections due to the interactions between the electron and two nuclei. The nonrecoil effective Hamiltonian used for a one-electron system [36,45] can be expressed as

$$H^{(6)}_{\rm 1\text{-}e} = \frac{p_e^6}{16m_e^5} + \frac{5}{128}[p_e^2,[p_e^2,V]] + \frac{1}{8m_e^3}\mathcal{E}_e^2 + \frac{3}{64m_e^4}\left\{p_e^2, 4\pi\sum_a z_a z_e \delta(\vec{r}_a)\right\}, \tag{90}$$

which corresponds to our first three effective Hamiltonians

$$\delta H_1+\delta H_2+\delta H_3 = \frac{p_e^6}{16m_e^5} + \frac{1}{128}[p_e^2,[p_e^2,V]] - \sum_a \frac{1}{32m_a}[p_a^2,[p_e^2,V_a]] + \frac{3}{64m_e^4}\left\{p_e^2, 4\pi\sum_a z_a z_e \delta(\vec{r}_a)\right\}. \tag{91}$$

The equivalence between $H^{(6)}_{\rm 1\text{-}e}$ and $\delta H_1+\delta H_2+\delta H_3$ can be explained by the equation

$$\frac{1}{128}\langle[p_e^2,[p_e^2,V]]\rangle - \sum_a \frac{1}{32m_a}\langle[p_a^2,[p_e^2,V_a]]\rangle = \frac{5}{128}\langle[p_e^2,[p_e^2,V]]\rangle + \frac{1}{8}\langle\mathcal{E}_e^2\rangle, \tag{92}$$

which comes from the identity

$$\langle[p_e^2,[p_e^2,V]]\rangle = -4\langle\mathcal{E}_e^2\rangle - \sum_a \frac{1}{m_a}\langle[p_a^2,[p_e^2,V_a]]\rangle. \tag{93}$$

Although some similar operators can be read from Eq. (50) of Ref. [8], it is not meaningful to compare our one-electron results with the two-electron formulas derived in the dimensional regularization scheme [8,9]. The obtained effective Hamiltonian is also valid for a hydrogen-like system that contains one nucleus, and thus only one pair of electron-nucleus interaction needs to be considered.

In addition to the effective Hamiltonian $H^{(6)}$ of the first-order perturbation, the total spin-averaged contribution requires the second-order perturbation by the Breit-Pauli Hamiltonian Eq. (6). In Sec. IV, the singularities of the first- and second-order corrections have been separated as $S_{\rm 1st}$ of Eq. (72) and $S_{\rm 2nd}$ of Eq. (89) respectively, while the remaining effective Hamiltonian is suitable for numerical calculations. Both $S_{\rm 1st}$ and $S_{\rm 2nd}$ contain not only the $m\alpha^6$-order but also the $m\alpha^6(m/M)$-order singularities, and they cancel out with each other, namely $S_{\rm 1st}+S_{\rm 2nd}=0$. The complete cancellation of the singularities between the first- and second-order terms itself is a strong confirmation of the correctness of our procedure. In addition, as shown in Appendix B, our results can be reduced to the known results of atomic hydrogen obtained from the Dirac equation with the relativistic recoil terms included. Finally our results are valid not only for the hydrogen molecular ions but also for the antiprotonic helium. Our finite operators of orders $m_e\alpha^6$ and $m\alpha^6(m/M)$ can be evaluated numerically to study relativistic and QED effects in these two-center systems.

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APPENDIX A: DIVERGENT MATRIX ELEMENTS

In this Appendix, the singularities of the effective Hamiltonian $H^{(6)}$ and the second-order corrections are transformed into terms of various regular and divergent matrix elements, such as $\langle V_a p_e^2 V_a\rangle$, $\langle\{p_e^4, V_a\}\rangle$, and $\langle p_e^2 V_a p_e^2\rangle$. Relations between these matrix elements will be established to separate the singularities.

1. Matrix elements $\langle V_a p_e^2 V_a\rangle$, $\langle V_a p_a^2 V_a\rangle$, and $4\pi z_a z_e\langle V_a \delta(\vec{r}_a)\rangle$

Let us consider the matrix element $\langle(1/r)\nabla^2(1/r)\rangle$. This matrix element can be expressed in different forms:

$$\left\langle\frac{1}{r}\nabla^2\frac{1}{r}\right\rangle = \left\langle\frac{1}{r^2}\nabla^2\right\rangle - 2\left\langle\frac{\vec{r}}{r^4}\nabla\right\rangle - 4\pi\left\langle\frac{\delta(\vec{r})}{r}\right\rangle, \tag{A1}$$

$$\left\langle\frac{1}{r}\nabla^2\frac{1}{r}\right\rangle = \left\langle\nabla\frac{1}{r^2}\nabla\right\rangle + 2\left\langle\frac{\vec{r}}{r^4}\nabla\right\rangle - \left\langle\frac{1}{r^4}\right\rangle. \tag{A2}$$

On the other hand, the matrix element of $\langle\frac{1}{r^2}\nabla^2\rangle$ can be expressed as

$$\left\langle\frac{1}{r^2}\nabla^2\right\rangle = \left\langle\nabla^2\frac{1}{r^2}\right\rangle = \left\langle\nabla\frac{1}{r^2}\nabla\right\rangle - 4\pi\left\langle\frac{\delta(\vec{r})}{r}\right\rangle + \left\langle\frac{1}{r^4}\right\rangle. \tag{A3}$$

Thus one can deduce the following results from Eqs. (A1)–(A3):

$$\left\langle\frac{1}{r}\nabla^2\frac{1}{r}\right\rangle = \left\langle\frac{1}{r^2}\nabla^2\right\rangle - \left\langle\frac{1}{r^4}\right\rangle, \tag{A4}$$

$$4\pi\left\langle\frac{\delta(\vec{r})}{r}\right\rangle = \left\langle\frac{1}{r^4}\right\rangle - \left\langle\frac{1}{r^2}\nabla^2\right\rangle + \left\langle\nabla\frac{1}{r^2}\nabla\right\rangle. \tag{A5}$$

Similarly, one can derive the following formulas for a three-body system:

$$\langle V_a p_e^2 V_a\rangle = \langle\varepsilon_a^2\rangle + \langle V_a^2 p_e^2\rangle, \tag{A6}$$

$$\langle V_a p_e^2 V_b\rangle = \langle\vec{\varepsilon}_a\vec{\varepsilon}_b\rangle + \langle V_a V_b p_e^2\rangle, \tag{A7}$$

$$\langle V_a p_a^2 V_a\rangle = \langle\varepsilon_a^2\rangle + \langle V_a^2 p_a^2\rangle, \tag{A8}$$

$$\langle V_a p_a^2 V_{12}\rangle = (-1)^{a+1}\langle\vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle + \langle V_a V_{12} p_a^2\rangle, \tag{A9}$$

$$4\pi z_a z_e\langle V_a\delta(\vec{r}_a)\rangle = \langle\varepsilon_a^2\rangle + \langle V_a^2 p_e^2\rangle - \langle\vec{p}_e V_a^2\vec{p}_e\rangle, \tag{A10}$$

where $a, b = 1, 2$ and $b \neq a$.

We now introduce the transformed Schrödinger equation

$$p_e^2\phi = \left[2(E_0 - V) - \sum_a \frac{1}{m_a} p_a^2\right]\phi, \tag{A11}$$

which will be used extensively in the procedure of singularity separation. As an example, the matrix element $\langle V_a^2 p_e^2\rangle$ can be transformed into

$$\begin{aligned}\langle V_a^2 p_e^2\rangle = {} & 2\left(1 - \frac{1}{m_a}\right)\left[E_0\langle V_a^2\rangle - \langle V_a^2(V_b + V_{12})\rangle\right] \\ & - \frac{1}{m_a}\langle V_a^2(p_a^2 - p_e^2)\rangle - \frac{1}{m_b}\langle V_a^2 p_b^2\rangle \\ & - 2\left(1 - \frac{1}{m_a}\right)\langle V_a^3\rangle,\end{aligned} \tag{A12}$$

where the singularity is absorbed into the matrix element $\langle V_a^3\rangle$. Thus, the singular part of $\langle V_a p_e^2 V_a\rangle$ can be isolated as

$$\langle V_a p_e^2 V_a\rangle_S = \langle\varepsilon_a^2\rangle_S - 2\left(1 - \frac{1}{m_a}\right)\langle V_a^3\rangle_S. \tag{A13}$$

The matrix element $\langle V_a p_a^2 V_a\rangle$ in Eq. (A8) can be recast into

$$\langle V_a p_a^2 V_a\rangle = \langle\varepsilon_a^2\rangle + \langle V_a^2 p_e^2\rangle + \langle V_a^2(p_a^2 - p_e^2)\rangle = \langle V_a p_e^2 V_a\rangle + \langle V_a^2(p_a^2 - p_e^2)\rangle. \tag{A14}$$

Since the matrix element $\langle V_a^2(p_a^2 - p_e^2)\rangle$ is convergent, the matrix element $\langle V_a p_a^2 V_a\rangle$ has the same singularity as $\langle V_a p_e^2 V_a\rangle$.

2. Matrix element $\langle\{p_e^4, V_a\}\rangle$

By applying the transformed Schrödinger Eq. (A11) one can rewrite the matrix element $\langle\{p_e^4, V_1\}\rangle$ in the form

$$\begin{aligned}\langle\{p_e^4, V_a\}\rangle = {} & 4E_0\left[\langle V_a p_e^2\rangle - \frac{1}{m_a}\langle V_a p_a^2\rangle - \frac{1}{m_b}\langle V_a p_b^2\rangle\right] - 4\left[\langle\vec{\varepsilon}_a\vec{\varepsilon}_b\rangle + \langle V_a(V_b + V_{12})p_e^2\rangle\right] \\ & + \frac{4}{m_a}\left[(-1)^{a+1}\langle\vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle + \langle V_a^2(p_a^2 - p_e^2)\rangle + \langle V_a(V_b + V_{12})p_a^2\rangle\right] + \frac{4}{m_b}\langle V_a V p_b^2\rangle - 4\left(1 - \frac{1}{m_a}\right)\langle V_a p_e^2 V_a\rangle,\end{aligned} \tag{A15}$$

from which one can identify the singular part as

$$\langle\{p_e^4, V_a\}\rangle_S = -4\left(1 - \frac{1}{m_a}\right)\langle V_a p_e^2 V_a\rangle_S. \tag{A16}$$

3. Matrix element $\langle p_e^2 V_a p_e^2\rangle$

Using Eq. (A11) the matrix element $\langle p_e^2 V_a p_e^2\rangle$ can be recast into

$$\begin{aligned}\langle p_e^2 V_a p_e^2\rangle = {} & 2E_0\left[\langle V_a p_e^2\rangle - \frac{1}{m_a}\langle V_a p_a^2\rangle - \frac{1}{m_b}\langle V_a p_b^2\rangle\right] + \frac{1}{m_b}\langle V_a V p_b^2\rangle \\ & - 2\left[\langle V_a(V_b + V_{12})p_e^2\rangle - \frac{1}{m_a}\langle V_a(V_b + V_{12})p_a^2\rangle - \frac{1}{m_a}\langle V_a^2(p_a^2 - p_e^2)\rangle\right] - 2\left(1 - \frac{1}{m_a}\right)\langle V_a^2 p_e^2\rangle,\end{aligned} \tag{A17}$$

where $b \neq a$. Using the expression Eq. (A12) for $\langle V_a^2 p_e^2\rangle$, the singular part of this matrix element is identified as

$$\langle p_e^2 V_a p_e^2\rangle_S = 4\left(1 - \frac{2}{m_a}\right)\langle V_a^3\rangle_S. \tag{A18}$$

4. Matrix element $\langle\{p_e^2, 4\pi\delta(\vec{r}_a)\}\rangle$

The matrix element $\langle\{p_e^2, 4\pi\delta(\vec{r}_a)\}\rangle$ can be recast in the form

$$\langle\{p_e^2, 4\pi\delta(\vec{r}_a)\}\rangle = 4\pi\left\{4\left(1 - \frac{1}{m_a}\right)\left[E_0\langle\delta(\vec{r}_a)\rangle - \langle(V_b + V_{12})\delta(\vec{r}_a)\rangle - \langle V_a\delta(\vec{r}_a)\rangle\right] - \frac{1}{m_a}\langle\{p_a^2 - p_e^2, \delta(\vec{r}_a)\}\rangle - \frac{1}{m_b}\langle\{p_b^2, \delta(\vec{r}_a)\}\rangle\right\}, \tag{A19}$$

where the expansion of $4\pi\langle V_a\delta(\vec{r}_a)\rangle$ can be taken from Eq. (A10).

5. Matrix element $\langle p_e^6\rangle$

The matrix element $\langle p_e^6\rangle$ can be written in a symmetric form,

$$\langle p_e^6\rangle = 2E_0\langle p_e^4\rangle - \langle\{p_e^4, V_{12}\}\rangle - \sum_a \left[\langle\{p_e^4, V_a\} + \frac{1}{2m_a}\langle\{p_e^4, p_a^2\}\rangle\right], \tag{A20}$$

where the matrix element $\langle\{p_e^4, V_a\}\rangle$ is expressed in Eq. (A15). Concerning $\langle\{p_e^4, V_{12}\}\rangle$, it is convergent and can be rewritten as

$$\langle\{p_e^4, V_{12}\}\rangle = 8\left[E_0^2\langle V_{12}\rangle - 2E_0\langle V_{12}V\rangle + \langle V_{12}V^2\rangle\right] - \sum_a \frac{8}{m_a}\left[E_0\langle V_{12}p_a^2\rangle - \langle V_{12}Vp_a^2\rangle\right]. \tag{A21}$$

The matrix element $(1/m_a)\langle\{p_e^4, p_a^2\}\rangle$ is expressible according to

$$\frac{1}{m_a}\langle\{p_e^4, p_a^2\}\rangle = \frac{8}{m_a}\left[E_0^2\langle p_a^2\rangle - 2E_0\langle Vp_a^2\rangle + \langle Vp_a^2V\rangle\right], \tag{A22}$$

where the divergent matrix element $\langle Vp_a^2V\rangle$ is

$$\langle Vp_a^2V\rangle = \langle[\vec{\varepsilon}_a + (-1)^{a+1}\vec{\varepsilon}_{12}]^2\rangle + \langle V^2p_a^2\rangle. \tag{A23}$$

We can thus transform $\langle p_e^6\rangle$ into

$$\begin{aligned}\langle p_e^6\rangle =& 2E_0\langle p_e^4\rangle - 8\left[E_0^2\langle V_{12}\rangle - 2E_0\langle V_{12}V\rangle + \langle V_{12}V^2\rangle\right] - \sum_a\langle\{p_e^4, V_a\}\rangle \\ &- \sum_a \frac{4}{m_a}\left[E_0^2\langle p_a^2\rangle - 2E_0\langle (V+V_{12})p_a^2\rangle + 2\langle V_a(V_b+V_{12})p_a^2\rangle + \langle (V_b+V_{12})^2p_a^2\rangle\right. \\ &\left. + \langle V_a^2(p_a^2-p_e^2)\rangle + 2\langle V_{12}Vp_a^2\rangle + 2(-1)^{a+1}\langle\vec{\varepsilon}_a\vec{\varepsilon}_{12}\rangle + \langle\varepsilon_{12}^2\rangle + \langle V_ap_e^2V_a\rangle\right],\end{aligned} \tag{A24}$$

and its singular part can be deduced as

$$\langle p_e^6\rangle_S = \sum_a 4\left(1 - \frac{2}{m_a}\right)\langle V_ap_e^2V_a\rangle_S. \tag{A25}$$

6. Matrix element $(1/m_a)\langle[p_a^2, [p_e^2, V_a]]\rangle$

The matrix element $(1/m_a)\langle[p_a^2, [p_e^2, V_a]]\rangle$ can be written as

$$\frac{1}{m_a}\langle[p_a^2, [p_e^2, V_a]]\rangle = \frac{1}{m_a}\left[\langle p_a^2p_e^2V_a\rangle + \langle V_ap_a^2p_e^2\rangle - \langle p_a^2V_ap_e^2\rangle - \langle p_e^2V_ap_a^2\rangle\right]. \tag{A26}$$

Using the transformed Schrödinger equation Eq. (A11), it can be simplified as

$$\frac{1}{m_a}\langle[p_a^2, [p_e^2, V_a]]\rangle = -\frac{4}{m_a}\langle\vec{\varepsilon}_a(\vec{\varepsilon}_a + (-1)^{a+1}\vec{\varepsilon}_{12})\rangle, \tag{A27}$$

and thus its singular part is

$$\frac{1}{m_a}\langle[p_a^2, [p_e^2, V_a]]\rangle_S = -\frac{4}{m_a}\langle\varepsilon_a^2\rangle. \tag{A28}$$

7. Matrix element $\langle\mathcal{W}^{ij}(r_a)p_e^ip_a^jV\rangle + \langle V\mathcal{W}^{ij}(r_a)p_e^ip_a^j\rangle$

Let us denote $\mathcal{W}^{ij}(r)$ as

$$\mathcal{W}^{ij}(r) = \frac{1}{2r}\left[\delta^{ij} + \frac{r^ir^j}{r^2}\right]. \tag{A29}$$

Then the sum of the divergent matrix elements $\langle\mathcal{W}^{ij}(r_a)p_e^ip_a^jV\rangle$ and $\langle V\mathcal{W}^{ij}(r_a)p_e^ip_a^j\rangle$ can be expressed as

$$\langle\mathcal{W}^{ij}(r_a)p_e^ip_a^jV\rangle + \langle V\mathcal{W}^{ij}(r_a)p_e^ip_a^j\rangle = \langle\mathcal{W}^{ij}(r_a)[p_e^i, [p_a^j, V_a]]\rangle + \langle\mathcal{W}^{ij}(r_a)p_e^iVp_a^j\rangle + \langle\mathcal{W}^{ij}(r_a)p_a^jVp_e^i\rangle, \tag{A30}$$

where the first term involves singularity that can be further simplified as

$$z_az_e\langle\mathcal{W}^{ij}(r_a)[p_e^i, [p_a^j, V_a]]\rangle = \langle\varepsilon_a^2\rangle, \tag{A31}$$

and the last two terms are regular:

$$z_a z_e\big[\langle \mathcal{W}^{ij}(r_a)p_e^i V p_a^j\rangle + \langle \mathcal{W}^{ij}(r_a)p_a^j V p_e^i\rangle\big] = \langle \vec{p}_e V_a V \vec{p}_a\rangle + \left\langle (\vec{p}_e\cdot\vec{r}_a)\frac{V_a V}{r_a^2}(\vec{r}_a\cdot\vec{p}_a)\right\rangle. \tag{A32}$$

8. Matrix elements $\langle[p_e^i, V]\mathcal{X}^{ij}(r_a)[V, p_a^j]\rangle$ and $\langle p_e^i[\mathcal{X}^{ij}(r_a), \frac{p_e^2}{2}](-i)\mathcal{E}_a^j\rangle$

Consider the following divergent matrix elements from δH_6:

$$Q_1 = \langle[p_e^i, V]\mathcal{X}^{ij}(r_a)[V, p_a^j]\rangle = \langle\mathcal{E}_e^i\mathcal{X}^{ij}(r_a)\mathcal{E}_a^j\rangle \tag{A33}$$

and

$$\begin{aligned} Q_2 &= \left\langle p_e^i\left[\mathcal{X}^{ij}(r_a), \frac{p_e^2}{2}\right](-i)\mathcal{E}_a^j\right\rangle = \left\langle p_e^i\mathcal{X}^{ij}(r_a)\frac{p_e^2}{2}(-i)\mathcal{E}_a^j\right\rangle - v\left\langle\frac{p_e^2}{2}p_e^i\mathcal{X}^{ij}(r_a)(-i)\mathcal{E}_a^j\right\rangle \\ &= \left\langle p_e^i\mathcal{X}^{ij}(r_a)\left[\frac{p_e^2}{2}, (-i)\mathcal{E}_a^j\right]\right\rangle - \left\langle\left[\frac{p_e^2}{2}, p_e^i\mathcal{X}^{ij}(r_a)(-i)\mathcal{E}_a^j\right]\right\rangle, \end{aligned} \tag{A34}$$

where the last term in Q_2 can be identified as Q_1. The sum of Q_1 and Q_2 will thus eliminate the singularities according to

$$Q_1 + Q_2 = \left\langle p_e^i\mathcal{X}^{ij}(r_a)\left[\frac{p_e^2}{2}, (-i)\mathcal{E}_a^j\right]\right\rangle = \frac{1}{8}\big[7\langle(\vec{p}_e\cdot\vec{r}_a)(V_a/r_a)^2(\vec{r}_a\cdot\vec{p}_e)\rangle - 3\langle\vec{p}_e V_a^2\vec{p}_e\rangle\big], \tag{A35}$$

where all the matrix elements are finite.

APPENDIX B: HYDROGEN LIMIT

In this Appendix, the effective Hamiltonian $H^{(6)}$ is studied for the case of atomic hydrogen in S states. Within the Breit approximation, we will show that our results of the $m\alpha^6$-order correction reproduce the known formulas for hydrogen derived from the Dirac equation, including the recoil corrections.

Consider the hydrogen atom where the proton has a finite mass M. The nonrelativistic Hamiltonian is (in atomic units)

$$H = \frac{1}{2\mu}p_e^2 + V, \tag{B1}$$

where the Coulomb potential $V = Zz/r$, with Z and z being the charges of the nucleus and the electron respectively, the momentum operator of the proton $\vec{P} = -\vec{p}_e$, and the reduced mass μ has the expansion $\mu^n \approx 1 - n/M$. For the sake of convenience, a common factor α^4 has been removed from both the first- and second-order contributions in the following context.

We obtain the hydrogenic limit by assuming that the index a runs only over one nucleus in Eqs. (34), (35), (39), (42), (45), and (50). The effective Hamiltonian $H^{(6)}$ can thus be reduced to

$$\begin{aligned} H^{(6)} = {}& \frac{p_e^6}{16} + \frac{1}{128}\left(1 - \frac{4}{M}\right)\big[p_e^2, [p_e^2, V]\big] + \frac{3}{64}\big\{p_e^2, 4\pi Zz\delta(\vec{r})\big\} - \frac{1}{8}\big\{p_e^2, 2H_R\big\} + \frac{1}{2M}(Zz)^2\big[p_e^i\mathcal{W}^{ij}(r)\mathcal{W}^{jk}(r)p_e^k\big] + \frac{1}{4M}\varepsilon^2 \\ &- \frac{1}{M}\left(\big[p_e^i, V\big]\mathcal{X}^{ij}(x)\big[p_e^j, V\big] + p_e^i\left[\mathcal{X}^{ij}(r), \frac{p_e^2}{2}\right]\big[p_e^j, V\big]\right), \end{aligned} \tag{B2}$$

where $\vec{\varepsilon} = (Zz)\vec{r}/r^3$, $\varepsilon^2 = (Zz)^2/r^4$, and $H_R = (1/M)(Zz)p_e^i\mathcal{W}^{ij}(r)p_e^j$. The various operators in $H^{(6)}$ can be rewritten according to

$$\langle p_e^6\rangle = 4\mu^2\big[E_n^2 - 4\mu E_n^2\langle V\rangle + 6\mu E_n\langle V^2\rangle) + \langle\varepsilon^2\rangle - 2\mu\langle V^3\rangle\rangle\big], \tag{B3}$$

$$\langle\big[p_e^2, [p_e^2, V]\big]\rangle = -4\mu\langle\varepsilon^2\rangle, \tag{B4}$$

$$\langle\big\{p_e^2, 4\pi Zz\delta(\vec{r})\big\}\rangle = 4\mu[4\pi E_n Zz\langle\delta(\vec{r})\rangle - \langle\varepsilon^2\rangle + 2\mu\langle V^3\rangle - 2\mu E_n\langle V^2\rangle + \langle\vec{p}_e V^2\vec{p}_e\rangle], \tag{B5}$$

$$\langle\big\{p_e^2, H_R\big\}\rangle = 8E_n\langle H_R\rangle + \frac{4}{M}[\langle\varepsilon^2\rangle - \langle\vec{p}_e V^2\vec{p}_e\rangle - \langle(\vec{p}_e\cdot\vec{r})(V^2/r^2)(\vec{r}\cdot\vec{p}_e)\rangle], \tag{B6}$$

$$(Zz)^2\langle p_e^i\mathcal{W}^{ij}(r)\mathcal{W}^{ik}(r)p_e^k\rangle = \frac{1}{4}[\langle\vec{p}_e V^2\vec{p}_e\rangle + 3\langle(\vec{p}_e\cdot\vec{r})(V^2/r^2)(\vec{r}\cdot\vec{p}_e)\rangle], \tag{B7}$$

$$\left\langle\big[p_e^i, V\big]\mathcal{X}^{ij}(r)\big[p_e^j, V\big] + p_e^i\left[\mathcal{X}^{ij}(r), \frac{p_e^2}{2}\right]\big[p_e^j, V\big]\right\rangle = \frac{1}{8}[7\langle(\vec{p}_e\cdot\vec{r})(V^2/r^2)(\vec{r}\cdot\vec{p}_e)\rangle - 3\langle\vec{p}_e V^2\vec{p}_e\rangle], \tag{B8}$$

where we have used the identities

$$p_e^2\phi = 2\mu(E_n - V)\phi, \tag{B9}$$

$$\langle V p_e^2 V\rangle = \langle \varepsilon^2\rangle - 2\mu\langle V^3\rangle + 2\mu E_n\langle V^2\rangle. \tag{B10}$$

The expectation values of the relevant operators with respect to an S-state hydrogenic wave function are

$$E_n = -\frac{\mu Z^2}{2n^2}, \tag{B11}$$

$$\langle V\rangle = 2E_n, \tag{B12}$$

$$\langle V^2\rangle = 2\mu^2\frac{Z^4}{n^3}, \tag{B13}$$

$$\langle Zz\delta(\vec{r})\rangle = -\frac{Z}{\pi}\left(\frac{\mu Z}{n}\right)^3, \tag{B14}$$

$$\langle H_R\rangle = \frac{\mu^3 Z^4}{M}\left(\frac{1}{n^4} - \frac{2}{n^3}\right), \tag{B15}$$

$$\langle \vec{p}_e V^2 \vec{p}_e\rangle = \mu^4 Z^6\left(-\frac{2}{3n^5} + \frac{8}{3n^3}\right), \tag{B16}$$

$$\langle(\vec{p}_e\cdot\vec{r})(V^2/r^2)(\vec{r}\cdot\vec{p}_e)\rangle = \mu^4 Z^6\left(-\frac{2}{3n^5} + \frac{8}{3n^3}\right). \tag{B17}$$

Substituting these values into $\langle H^{(6)}\rangle$ yields the first-order correction

$$\begin{aligned}\langle H^{(6)}\rangle &= \frac{1}{32}\left(1 - \frac{13}{M}\right)\langle\varepsilon^2\rangle - \frac{1}{8}\left(1 - \frac{6}{M}\right)\langle V^3\rangle \\ &+ Z^6\left(\frac{5}{16n^6} - \frac{7}{8n^5} + \frac{1}{2n^3}\right) \\ &+ \frac{Z^6}{M}\left(-\frac{11}{8n^6} + \frac{101}{24n^5} + \frac{1}{6n^3}\right).\end{aligned} \tag{B18}$$

For a hydrogen in an S state, the second-order correction is $E_{\rm sec} = E_B + E_R$ with

$$\begin{aligned}E_B &= \langle H_B' Q(E_n - H)^{-1} Q H_B'\rangle + \langle\{H_B, U\}\rangle \\ &- 2\langle H_B\rangle\langle U\rangle - \langle U(E_n - H)U\rangle,\end{aligned} \tag{B19}$$

$$E_R = 2\langle H_B' Q(E_n - H)^{-1} Q H_R\rangle + \langle\{H_R, U\}\rangle - 2\langle H_R\rangle\langle U\rangle, \tag{B20}$$

where

$$H_B' = H_B - \{U, E_n - H\}, \tag{B21}$$

$$U = \lambda V, \quad \lambda = -\frac{1}{4}\left(1 - \frac{3}{M}\right), \tag{B22}$$

$$H_B = -\frac{1}{8}\left[p_e^4 + 4\pi Zz\delta(\vec{r})\right]. \tag{B23}$$

The operators appearing in E_B and E_R can be reduced as

$$\langle\{H_B, U\}\rangle = -\frac{\lambda}{2}\mu\left[2\mu E_n^2\langle V\rangle - 4\mu E_n^2\langle V^2\rangle - \langle\varepsilon^2\rangle + 2\mu\langle V^3\rangle\right], \tag{B24}$$

$$\langle U(E_n - H)U\rangle = \frac{\lambda^2}{2\mu}\langle\varepsilon^2\rangle, \tag{B25}$$

$$\begin{aligned}\langle\{H_R, U\}\rangle &= -\frac{\lambda}{M}\langle\varepsilon^2\rangle + \frac{\lambda}{M}[\langle\vec{p}_e V^2\vec{p}_e\rangle \\ &+ \langle(\vec{p}_e\cdot\vec{r})(V^2/r^2)(\vec{r}\cdot\vec{p}_e)\rangle].\end{aligned} \tag{B26}$$

When H_B' acts on an S state wave function, it can be simplified as

$$H_B' = -\frac{\mu^2}{2}(E_n - V)^2 + \frac{1}{4}i\vec{\varepsilon}\cdot\vec{p}_e. \tag{B27}$$

Therefore, the second-order correction of H_B' can be expressed according to

$$E_Q = \langle H_B' Q(E_n - H)^{-1} Q H_B'\rangle = E_Q^1 + E_Q^2 + E_Q^3, \tag{B28}$$

where

$$E_Q^1 = \frac{\mu^4}{4}\langle(E_n - V)^2 Q(E_n - H)^{-1} Q(E_n - V)^2\rangle, \tag{B29}$$

$$E_Q^2 = \frac{1}{16}\langle(i\vec{\varepsilon}\cdot\vec{p}_e)Q(E_n - H)^{-1}Q(i\vec{\varepsilon}\cdot\vec{p}_e)\rangle, \tag{B30}$$

$$E_Q^3 = -\frac{\mu^2}{4}\langle(i\vec{\varepsilon}\cdot\vec{p}_e)Q(E_n - H)^{-1}Q(E_n - V)^2\rangle. \tag{B31}$$

By using the analytical form of the reduced Coulomb Green's function developed by Swainson and Drake [46], one can evaluate the second-order corrections analytically and obtain the following results:

$$E_Q^1 = \mu^7 Z^6\left(-\frac{1}{8n^6} + \frac{1}{n^5} - \frac{3}{2n^4} - \frac{1}{n^3}\right), \tag{B32}$$

$$E_Q^2 = \mu^5 Z^6\left(-\frac{7}{24n^5} - \frac{3}{7n^4} + \frac{1}{24n^3}\right), \tag{B33}$$

$$E_Q^3 = \mu^6 Z^6\left(-\frac{1}{4n^6} + \frac{1}{4n^5} + \frac{3}{2n^4} + \frac{1}{2n^3}\right). \tag{B34}$$

The second-order term $E_{\rm QR}$ due to H_R and H_B' has the following analytical expression:

$$\begin{aligned}E_{\rm QR} &= 2\langle H_B' Q(E_n - H)^{-1} Q H_R\rangle \\ &= -\frac{1}{M}Z^6\left(\frac{2}{n^6} - \frac{37}{6n^5} + \frac{3}{n^4} + \frac{11}{3n^3}\right).\end{aligned} \tag{B35}$$

Inserting all these values into $E_{\rm sec}$ yields

$$\begin{aligned}E_{\rm sec} &= -\frac{1}{32}\left(1 - \frac{13}{M}\right)\langle\varepsilon^2\rangle + \frac{1}{8}\left(1 - \frac{6}{M}\right)\langle V^3\rangle \\ &+ Z^6\left(-\frac{5}{8n^6} + \frac{13}{8n^5} - \frac{3}{8n^4} - \frac{5}{8n^3}\right) \\ &+ \frac{Z^6}{M}\left(\frac{15}{8n^6} - \frac{125}{24n^5} + \frac{3}{8n^4} - \frac{1}{24n^3}\right).\end{aligned} \tag{B36}$$

Summing up $E_{\rm sec}$ and $\langle H^{(6)}\rangle$, we obtain the final result

$$\begin{aligned}E^{(6)} &= Z^6\left(-\frac{5}{16n^6} + \frac{3}{4n^5} - \frac{3}{8n^4} - \frac{1}{8n^3}\right) \\ &+ \frac{Z^6}{M}\left(\frac{1}{2n^6} - \frac{1}{n^5} + \frac{3}{8n^4} + \frac{1}{8n^3}\right).\end{aligned} \tag{B37}$$

One can see that the singularities in $E_{\rm sec}$ and $\langle H^{(6)}\rangle$ totally cancel out with each other. Moreover, the nonrecoil part of $E^{(6)}$ is in agreement with the exact solution of the Dirac equation by expanding

$$E_{\rm D}=\frac{f(n)}{\alpha^2},\quad f(n)=\left\{1+\frac{(Z\alpha)^2}{[n-1+\sqrt{1-(Z\alpha)^2}]^2}\right\}^{-\frac{1}{2}}, \tag{B38}$$

at the order of α^4 a.u. Meanwhile, the recoil part of $E^{(6)}$ agrees with the derived result from the Breit equation [47,48],

$$E_{\rm M}=\frac{1-E_{\rm D}^2}{2M}. \tag{B39}$$

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