Higher-order recoil corrections for triplet states of the helium atom

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Nuclear recoil corrections of order $\alpha^6 m^2/M$ are calculated for the lowest-lying triplet states of the helium atom. It improves the theoretical prediction for the isotope shift of the $2\,^3S$ -$2\,^3P$ transition energy and influences the determination of the ^{3}He -^{4}He nuclear charge radii difference. This calculation is a step forward on the way towards the direct determination of the charge radius of the helium nucleus from spectroscopic measurements.

I. INTRODUCTION

The direct determination of the nuclear charge radius from the measured transition energies has been so far carried out only for the hydrogenlike atoms [1]. In more complex systems, the possibilities of such determination are limited by our insufficient knowledge of the QED effects. The main advantage of hydrogenlike atoms is that the relativistic electron wave function can be determined analytically in the limit of infinite nuclear mass. It is then possible to express all QED and nuclear recoil corrections within the Furry picture of QED and calculate them either analytically in terms of the $Z\alpha$ expansion or numerically to all orders in $Z\alpha$ (where Z is the nuclear charge number and α is the fine-structure constant).

Calculations of QED effects in few-electron systems are much more difficult than in hydrogen. Presently the best theoretical accuracy is achieved for the helium atom, whose (low-lying) energy levels are calculated rigorously within QED up to orders $\alpha^6 m$ and $\alpha^5 m^2/M$ [2,3] (where m is the electron mass and M is the nuclear mass). The theoretical accuracy achieved in these calculations was not sufficient for determination of the charge radius of the helium nucleus (i.e., α particle). Significant progress, however, can be achieved by calculating the next-order QED and nuclear recoil effects, namely $\alpha^6 m^2/M$ and $\alpha^7 m$ corrections. These calculations will bring the theoretical accuracy of the helium $n=2$ transition energies on a 10-kHz level, which will allow us to determine the α-particle charge radius with an accuracy of a few parts of 10^{-3}. Such a project is challenging but looks feasible, at least for the triplet states. Indeed, the most suitable transition is $2\,^3S$ -$2\,^3P$, which has already been measured with sufficient accuracy [4,5],

$$E(2\,^3S\text{ -}2\,^3P\,,{}^4\text{He})_{\text{centroid}} = 276\,736\,495\,649.5(2.1)\,\text{kHz}\,h. \quad (1)$$

The finite nuclear size contribution to this transition energy is $E_{\text{fs}} = 3427\,\text{kHz}\,h$. Taking into account that E_{fs} is proportional to the nuclear charge radius squared, R^2, the expected 10-kHz theoretical accuracy will determine the nuclear charge radius with 0.15% accuracy,

$$\frac{\Delta R}{R} = \frac{1}{2}\frac{\delta E_{\text{fs}}}{E_{\text{fs}}} \approx \frac{1}{2}\frac{10}{3427} \approx 1.5 \times 10^{-3}. \quad (2)$$

After the project is accomplished, we shall be able to compare the charge radius of the α particle with the result from muonic helium, which is expected soon from the CREMA collaboration [6]. Such a comparison would be of particular interest in view of the discrepancy for the proton charge radius observed in the muonic hydrogen experiment [7,8]. Additional motivations for this project are the yet unexplained 4σ discrepancy for the difference in ^{3}He and ^{4}He nuclear charge radii [9] and plans to measure the charge radii difference from isotope shifts in heliumlike ions [10]. In this work we make the first step towards the absolute nuclear charge radius determination and calculate the nuclear recoil correction to order $\alpha^6 m^2/M$ for the $2\,^3S$ and $2\,^3P$ states of the helium atom.

This paper is organized as follows. Section II introduces notations that will be used throughout the paper. Section III describes our approach to the calculation of the energy levels by an expansion in the fine-structure constant α. Section IV reports the Foldy-Wouthuysen transformed nonrelativistic QED (NRQED) Lagrangian, which is the starting point for our derivation. The derivation of the $\alpha^6 m^2/M$ correction is presented in Sec. V. Section VI is devoted to the rearrangements of terms in such a way that all matrix elements become finite. Section VII presents the final formulas. Section VIII describes the numerical evaluation of all matrix elements. Results and discussion are presented in Sec. IX. The principles of the dimensional regularization, details about the elimination of singularities, the simplification of the formulas, and the reduction to the hydrogenic limit are presented in Appendixes.

II. NOTATIONS

We will use the following notations throughout the paper. The operators, energies, and wave functions for a nucleus with a finite mass M will be marked with indices "M": X_M, E_M, ϕ_M. The operators, energies, and wave functions in the infinite nuclear mass limit are without indices: X, E, ϕ. The recoil corrections to the operators and energies are denoted by $\delta_M X$ and $\delta_M E$,

$$X_M \equiv X + \frac{m}{M}\delta_M X + O\left(\frac{m}{M}\right)^2, \quad (3)$$

$$E_M = E + \frac{m}{M}\delta_M E + O\left(\frac{m}{M}\right)^2. \quad (4)$$

We also introduce the shorthand notations

$$\langle X \rangle_M \equiv \langle \phi_M | X | \phi_M \rangle \quad (5)$$

and

$$\delta_M \langle X \rangle \equiv \langle \phi | \frac{\vec{P}_I^2}{2} \frac{1}{(E-H)'} X | \phi \rangle + \langle \phi | X \frac{1}{(E-H)'} \frac{\vec{P}_I^2}{2} | \phi \rangle, \tag{6}$$

where $\vec{P}_I$ is the momentum of the nucleus in the center-of-mass frame, and H, E, and ϕ are the nonrelativistic Hamiltonian, energy, and the wave function in the infinite nuclear mass limit.

III. NRQED APPROACH

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

$$E_M(\alpha) = E_M^{(2)} + E_M^{(4)} + E_M^{(5)} + E_M^{(6)} + E_M^{(7)} + O(\alpha^8), \tag{7}$$

where $E_M(\alpha) \equiv E(\alpha, \frac{m}{M})$ and $E_M^{(n)}$ is a contribution of order $m\alpha^n$ and may include powers of $\ln \alpha$. $E_M^{(n)}$ is, in turn, expanded in powers of the electron-to-nucleus mass ratio m/M,

$$E_M^{(n)} = E^{(n)} + \frac{m}{M} \delta_M E^{(n)} + O\left(\frac{m}{M}\right)^2. \tag{8}$$

Each term of the expansion $E_M^{(n)}$ can be expressed as an expectation value of some effective operator. Namely, $E_M^{(2)} \equiv E_M$ is the eigenenergy of the nonrelativistic Hamiltonian $H_M^{(2)} \equiv H_M$ with the eigenstate ϕ_M:

$$H_M = \sum_a \left(\frac{\vec{p}_a^2}{2m} - \frac{Z\alpha}{r_{aI}} \right) + \sum_{a>b} \sum_b \frac{\alpha}{r_{ab}} + \frac{\vec{P}_I^2}{2M}. \tag{9}$$

Here $\vec{P}_I$ is the momentum of the nucleus; in the center-of-mass system it is just $\vec{P}_I = -\sum_a \vec{p}_a$. $E_M^{(4)}$ is the expectation value of the Breit-Pauli Hamiltonian $H_M^{(4)}$ [11],

$$E_M^{(4)} = \langle H_M^{(4)} \rangle_M, \tag{10}$$

$$H_M^{(4)} = \sum_a \left[-\frac{\vec{p}_a^4}{8m^3} + \frac{\pi Z\alpha}{2m^2} \delta^3(r_{aI}) + \frac{Z\alpha}{4m^2} \vec{\sigma}_a \cdot \frac{\vec{r}_{aI}}{r_{aI}^3} \times \vec{p}_a \right]$$

$$+ \sum_{a<b} \left\{ -\frac{\pi\alpha}{m^2} \delta^3(r_{ab}) - \frac{\alpha}{2m^2} p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right) p_b^j \right.$$

$$- \frac{2\pi\alpha}{3m^2} \vec{\sigma}_a \cdot \vec{\sigma}_b \delta^3(r_{ab}) + \frac{\alpha}{4m^2} \frac{\sigma_a^i \sigma_b^j}{r_{ab}^3} \left(\delta^{ij} - 3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2} \right)$$

$$+ \frac{\alpha}{4m^2 r_{ab}^3} [2(\vec{\sigma}_a \cdot \vec{r}_{ab} \times \vec{p}_b - \vec{\sigma}_b \cdot \vec{r}_{ab} \times \vec{p}_a)$$

$$+ (\vec{\sigma}_b \cdot \vec{r}_{ab} \times \vec{p}_b - \vec{\sigma}_a \cdot \vec{r}_{ab} \times \vec{p}_a)] \Big\}$$

$$- \frac{Z\alpha}{2mM} \sum_a \left[\frac{\vec{r}_{aI}}{r_{aI}^3} \times \vec{P}_I \cdot \vec{\sigma}_a - p_a^i \left(\frac{\delta^{ij}}{r_{aI}} + \frac{r_{aI}^i r_{aI}^j}{r_{aI}^3} \right) P_I^j \right], \tag{11}$$

and $E_M^{(5)}$ is the leading QED correction (see, e.g., [12–14]), which will not be needed in the present investigation. The next

expansion term $E_M^{(6)}$ is the sum of two parts:

$$E_M^{(6)} = \left\langle H_M^{(4)} \frac{1}{(E_M - H_M)'} H_M^{(4)} \right\rangle_M + \langle H_M^{(6)} \rangle_M. \tag{12}$$

In this paper we derive the recoil part of this expression, $\delta_M E^{(6)}$, for triplet states in helium and heliumlike ions. The approach is similar to that in Refs. [2,15], with some modifications that simplify the derivation of the recoil correction.

IV. FOLDY-WOUTHUYSEN TRANSFORMATION

In order to derive the effective Hamiltonians $H_M^{(n)}$, and in particular $H_M^{(6)}$, we transform the QED Lagrangian to the NRQED form by using the Foldy-Wouthuysen (FW) transformation [16]. This transformation is the nonrelativistic expansion of the Dirac Hamiltonian in an external electromagnetic field,

$$H = \vec{\alpha} \cdot \vec{\pi} + \beta m + eA^0, \tag{13}$$

where $\vec{\pi} = \vec{p} - e\vec{A}$. The FW transformation S

$$H_{FW} = e^{iS}(H - i\partial_t)e^{-iS} = H + \delta H, \tag{14}$$

leads to a new Hamiltonian, which decouples the upper and lower components of the Dirac wave function up to a specified order in the $1/m$ expansion. In order to simplify the derivation of $m^2/M\alpha^6$ corrections, we start from FW Hamiltonian from Ref. [2],

$$H_{FW} = eA^0 + \frac{\pi^2}{2m} - \frac{e}{4m} \sigma^{ij} B^{ij} - \frac{\pi^4}{8m^3} + \frac{e}{16m^3} \{\sigma^{ij} B^{ij}, p^2\}$$

$$- \frac{e}{8m^2} (\vec{\nabla} \cdot \vec{E} + \sigma^{ij} \{E^i, \pi^j\}) - \frac{e}{16m^3} \{\vec{p}, \partial_t \vec{E}\}$$

$$+ \frac{3e}{32m^4} \{\sigma^{ij} E^i p^j, p^2\} + \frac{1}{128m^4} [p^2, [p^2, eA^0]]$$

$$- \frac{3}{64m^4} [p^2 \nabla^2(eA^0) + \nabla^2(eA^0)p^2] + \frac{1}{16m^5} p^6, \tag{15}$$

where $\{x,y\}$ and $[x,y]$ stand for the anticommutator and commutator, correspondingly,

$$\sigma^{ij} = \frac{1}{2i}[\sigma^i, \sigma^j], \tag{16}$$

$$B^{ij} = \partial^i A^j - \partial^j A^i, \tag{17}$$

$$E^i = -\nabla^i A^0 - \partial_t A^i, \tag{18}$$

and apply further transformations. The first one,

$$S_1 = -\frac{e}{16m^3} \{\vec{\pi}, \vec{E}\}, \tag{19}$$

eliminates $\partial_t \vec{E}$ from H_{FW}:

$$\delta_1 H \approx \frac{e}{16m^3} \{\vec{p}, \partial_t \vec{E}\} + \frac{e}{8m^3} \vec{E}^2 + \frac{1}{32m^4} [p^2, [p^2, eA^0]]. \tag{20}$$

The second one,

$$S_2 = \frac{e}{8m^2} \sigma^{ij} \{A^i, \pi^j\}, \tag{21}$$

eliminates the transverse part $\vec{E}_\perp = -\partial_t \vec{A}$,

$$\delta_2 H \approx \frac{e}{8m^2}\sigma^{ij}\{E_\perp^i, \pi^j\} - \frac{e}{4m^2}\sigma^{ij}A^i E^j$$
$$+ \frac{ie}{16m^3}[\sigma^{ij}\{A^i, p^j\}, p^2]. \tag{22}$$

The resulting new FW Hamiltonian is

$$H_{FW} = eA^0 + \frac{\pi^2}{2m} - \frac{e}{4m}\sigma^{ij}B^{ij} - \frac{\pi^4}{8m^3} + \frac{e}{16m^3}\{\sigma^{ij}B^{ij}, p^2\}$$
$$- \frac{e}{8m^2}(\vec{\nabla}\cdot\vec{E}_\parallel + \sigma^{ij}\{E_\parallel^i, p^j\}) + \frac{e^2}{2m^2}\sigma^{ij}E_\parallel^i A^j$$
$$+ \frac{ie}{16m^3}[\sigma^{ij}\{A^i, p^j\}, p^2] + \frac{e^2}{8m^3}\vec{E}_\parallel^2$$
$$+ \frac{3e}{32m^4}\{p^2, \sigma^{ij}E_\parallel^i p^j\} + \frac{5}{128m^4}[p^2, [p^2, eA^0]]$$
$$- \frac{3}{64m^4}\{p^2, \nabla^2(eA^0)\} + \frac{1}{16m^5}p^6, \tag{23}$$

where $\vec{E}_\parallel = -\vec{\nabla}A^0$. Since we are interested here in the leading $O(m/M)$ term, the nucleus can be treated nonrelativistically, so

$$\delta_M H_{FW} = \frac{1}{2M}(\vec{P}_I + Ze\vec{A})^2. \tag{24}$$

V. THE HIGHER-ORDER BREIT-PAULI HAMILTONIAN

In this section we derive the effective operator $H_M^{(6)}$. The derivation is similar to that in Ref. [2], including the use of the dimensional regularization. For the simplicity of the presentation, all the derivations here will be performed in $d = 3$, but in such a way that allows for a straightforward (and unique) generalization to the $d = 3 - 2\epsilon$ form. This generalization will be needed only for a few divergent terms, and details of the dimensional regularization are presented in Appendix A.

Using the nomenclature described in Appendix A, we denote by V the nonrelativistic interaction potential,

$$V \equiv \sum_a -\frac{Z\alpha}{r_{aI}} + \sum_{a>b}\sum_b \frac{\alpha}{r_{ab}}, \tag{25}$$

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

$$e\vec{\mathcal{E}}_a \equiv -\nabla_a V = -Z\alpha\frac{\vec{r}_{aI}}{r_{aI}^3} + \sum_{b\neq a}\alpha\frac{\vec{r}_{ab}}{r_{ab}^3}, \tag{26}$$

by $\vec{\mathcal{A}}_a$ the vector potential at the position of particle a, which is produced by all other particles,

$$e\mathcal{A}_a^i \equiv \sum_{b\neq a}\left[\frac{\alpha}{2r_{ab}}\left(\delta^{ij} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right)\frac{p_b^j}{m} + \frac{\alpha}{2m}\sigma_b^{ki}\frac{r_{ab}^k}{r_{ab}^3}\right]$$
$$- \frac{Z\alpha}{2r_{aI}}\left(\delta^{ij} + \frac{r_{aI}^i r_{aI}^j}{r_{aI}^2}\right)\frac{P_I^j}{M}, \tag{27}$$

and by $\vec{\mathcal{A}}_I$ the vector potential at the position of nucleus, which is produced by electrons,

$$e\mathcal{A}_I^i \equiv \sum_a \frac{\alpha}{2r_{aI}}\left(\delta^{ij} + \frac{r_{aI}^i r_{aI}^j}{r_{aI}^2}\right)\frac{p_a^j}{m}. \tag{28}$$

Following Ref. [15], $H_M^{(6)}$ is expressed as a sum of various contributions:

$$H_M^{(6)} = \sum_{i=1,11} H_i^M. \tag{29}$$

H_1^M is the kinetic-energy correction:

$$H_1^M = \sum_a \frac{p_a^6}{16m^5}. \tag{30}$$

H_2^M is a correction due to the static electric interaction, namely,

$$H_2^M = \sum_a\left(\frac{e^2}{8m^3}\vec{\mathcal{E}}_a^2 + \frac{3}{32m^4}\{p_a^2, e\sigma_a^{ij}\mathcal{E}_a^i p_a^j\}\right.$$
$$\left. + \frac{5}{128m^4}[p_a^2, [p_a^2, V]] - \frac{3}{64m^4}\{p_a^2, \nabla_a^2 V\}\right). \tag{31}$$

H_3^M is a correction to the Coulomb interaction between electrons, which comes from the sixth term in H_{FW}, namely,

$$-\frac{e}{8m^2}(\vec{\nabla}\cdot\vec{E}_\parallel + \sigma^{ij}\{E_\parallel^i, p^j\}). \tag{32}$$

If the interaction of both electrons is modified by this term, it can be obtained in the nonretardation approximation, so

$$H_3^M = \sum_{a>b}\sum_b \int d^3k \frac{4\pi}{k^2}\frac{1}{64m^4}\left(k^2 + 2i\sigma_a^{ij}k^i p_a^j\right)$$
$$\times e^{i\vec{k}\cdot\vec{r}_{ab}}\left(k^2 + 2i\sigma_b^{kl}k^k p_b^l\right)$$
$$= \sum_{a>b}\sum_b \frac{1}{64m^4}\left\{-4\pi\nabla^2\delta^3(r_{ab}) - 8\pi i\sigma_a^{ij}p_a^i\delta^3(r_{ab})p_a^j\right.$$
$$- 8\pi i\sigma_b^{ij}p_b^i\delta^3(r_{ab})p_b^j + 4\sigma_a^{ki}p_a^k$$
$$\left.\times\left[\frac{\delta^{ij}}{3}4\pi\delta^3(r_{ab}) + \frac{1}{r_{ab}^3}\left(\delta^{ij} - 3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right)\right]\sigma_b^{lj}p_b^l\right\}. \tag{33}$$

H_4^M is the relativistic correction due to transverse photon exchange:

$$H_4^M = \sum_a -\frac{e}{8m^3}\left(\pi_a^4 - \frac{e}{2}\{\sigma_a^{ij}B_a^{ij}, p_a^2\}\right)$$
$$= \sum_a \frac{e}{8m^3}\left(2\{p_a^2, \vec{p}_a\cdot\vec{\mathcal{A}}_a\} + \{p_a^2, \sigma_a^{ij}\nabla_a^i\mathcal{A}_a^j\}\right). \tag{34}$$

H_5^M comes from the remaining transverse photon exchange:

$$H_5^M = \sum_a\left(\frac{e^2}{2m^2}\sigma_a^{ij}\mathcal{E}_a^i\mathcal{A}_a^j + \frac{ie}{16m^3}[\sigma^{ij}\{\mathcal{A}_a^i, p_a^j\}, p_a^2]\right). \tag{35}$$

H_6^M comes from the double transverse photon exchange:

$$H_6^M = \sum_a \frac{e^2}{2m^2} \mathcal{A}_a^2 + \frac{Z^2 e^2}{2M} \mathcal{A}_I^2. \tag{36}$$

H_7^M is a retardation correction in the nonrelativistic single transverse photon exchange:

$$E_7^M = -e^2 \int \frac{d^3k}{(2\pi)^3 2k^4} \left(\delta^{ij} - \frac{k^i k^j}{k^2} \right) \left[\sum_{a \neq b} \sum_b \langle \phi_M | \left(\frac{p_a^i}{m} + \frac{1}{2m} \sigma_a^{ki} \nabla_a^k \right) e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 \left(\frac{p_b^j}{m} + \frac{1}{2m} \sigma_b^{lj} \nabla_b^l \right) e^{-i\vec{k}\cdot\vec{r}_b} | \phi_M \rangle \right.$$

$$\left. - Z \sum_b \langle \phi | \frac{P_I^i}{M} e^{i\vec{k}\cdot\vec{r}_I} (H-E)^2 \left(\frac{p_b^j}{m} + \frac{1}{2m} \sigma_b^{lj} \nabla_b^l \right) e^{-i\vec{k}\cdot\vec{r}_b} | \phi \rangle - Z \sum_a \langle \phi | \left(\frac{p_a^i}{m} + \frac{1}{2m} \sigma_a^{ki} \nabla_a^k \right) e^{i\vec{k}\cdot\vec{r}_a} (H-E)^2 \frac{P_I^j}{M} e^{-i\vec{k}\cdot\vec{r}_I} | \phi \rangle \right]. \tag{37}$$

This is the most complicated term in the evaluation, and we have to split it into four parts with no-spin, single-spin, and double-spin terms, and the nuclear part,

$$E_7^M = E_{7a}^M + E_{7b}^M + E_{7c}^M + E_{7d}^M. \tag{38}$$

The part with double-spin operators is

$$E_{7c}^M = \sum_a \sum_{a \neq b} -e^2 \int \frac{d^3k}{(2\pi)^3 2k^4} \frac{(\sigma_a^{ki} k^k)(\sigma_b^{li} k^l)}{4m^2} \langle \phi_M | e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 e^{-i\vec{k}\cdot\vec{r}_b} | \phi_M \rangle. \tag{39}$$

One uses the commutation identity

$$\langle e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 e^{-i\vec{k}\cdot\vec{r}_b} \rangle_M + (a \leftrightarrow b) = \langle [e^{i\vec{k}\cdot\vec{r}_a}, [(H_M - E_M)^2, e^{-i\vec{k}\cdot\vec{r}_b}]] \rangle_M = -\frac{1}{2m^2} \langle [p_a^2, [p_b^2, e^{i\vec{k}\cdot\vec{r}_{ab}}]] \rangle_M \tag{40}$$

to express this correction in terms of the effective operator H_{7c}^M:

$$H_{7c}^M = \sum_{a>b} \sum_b \frac{\alpha}{16m^4} \left[p_a^2, \left[p_b^2, \sigma_a^{ij} \sigma_b^{ij} \frac{1}{3r_{ab}} + \sigma_a^i \sigma_b^j \frac{1}{2r_{ab}} \left(\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2} - \frac{\delta^{ij}}{3} \right) \right] \right]. \tag{41}$$

The part with no spin operator is

$$E_{7a}^M = \sum_{a \neq b} \sum_b -e^2 \int \frac{d^3k}{(2\pi)^3 2k^4} \left(\delta^{ij} - \frac{k^i k^j}{k^2} \right) \langle \phi_M | \frac{p_a^i}{m} \{ e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 e^{-i\vec{k}\cdot\vec{r}_b} - (H_M - E_M)^2 \} \frac{p_b^j}{m} | \phi_M \rangle. \tag{42}$$

We subtracted here the term with $k = 0$. We ought to perform this in Eq. (37), but for simplicity of writing we have not done it until now. We use another commutator identity,

$$e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 e^{-i\vec{k}\cdot\vec{r}_b} - (H_M - E_M)^2 = (H_M - E_M)(e^{i\vec{k}\cdot\vec{r}_{ab}} - 1)(H_M - E_M) + (H_M - E_M) \left[\frac{p_b^2}{2m}, e^{i\vec{k}\cdot\vec{r}_{ab}} - 1 \right]$$

$$+ \left[e^{i\vec{k}\cdot\vec{r}_{ab}} - 1, \frac{p_a^2}{2m} \right] (H_M - E_M) + \left[\frac{p_b^2}{2m}, \left[e^{i\vec{k}\cdot\vec{r}_{ab}} - 1, \frac{p_a^2}{2m} \right] \right], \tag{43}$$

and the integration formula

$$\int d^3k \frac{4\pi}{k^4} \left(\delta^{ij} - \frac{k^i k^j}{k^2} \right) (e^{i\vec{k}\cdot\vec{r}} - 1) = \frac{1}{8r} (r^i r^j - 3\delta^{ij} r^2) \tag{44}$$

to obtain the effective operator H_{7a}^M:

$$H_{7a}^M = \sum_{a>b} \sum_b -\frac{\alpha}{8m^2} \left\{ [p_a^i, V] \frac{r_{ab}^i r_{ab}^j - 3\delta^{ij} r_{ab}^2}{r_{ab}} [V, p_b^j] + [p_a^i, V] \left[\frac{p_b^2}{2m}, \frac{r_{ab}^i r_{ab}^j - 3\delta^{ij} r_{ab}^2}{r_{ab}} \right] p_b^j \right.$$

$$\left. + p_a^i \left[\frac{r_{ab}^i r_{ab}^j - 3\delta^{ij} r_{ab}^2}{r_{ab}}, \frac{p_a^2}{2m} \right] [V, p_b^j] + p_a^i \left[\frac{p_b^2}{2m}, \left[\frac{r_{ab}^i r_{ab}^j - 3\delta^{ij} r_{ab}^2}{r_{ab}}, \frac{p_a^2}{2m} \right] \right] p_b^j \right\}. \tag{45}$$

The part with the single-spin operator is

$$E_{7b}^M = \sum_{a \neq b} \sum_b -\frac{ie^2}{4m^2} \int \frac{d^3k}{(2\pi)^3 k^4} \langle \phi_M | \{ e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 e^{-i\vec{k}\cdot\vec{r}_b} \sigma_a^{ki} k^k p_b^i - \sigma_b^{lj} p_a^j k^l e^{i\vec{k}\cdot\vec{r}_a} (H_M - E_M)^2 e^{-i\vec{k}\cdot\vec{r}_b} \} | \phi_M \rangle. \tag{46}$$

With the help of the commutator in Eq. (43) and the integral

$$\int d^3k \frac{4\pi \vec{k}}{k^4} e^{i\vec{k}\cdot\vec{r}} = \frac{i}{2}\frac{\vec{r}}{r}, \tag{47}$$

one obtains

$$H_{7b}^M = \sum_{a>b}\sum_b \frac{\alpha}{4m^2}\left\{\left[\sigma_a^{ij}\frac{r_{ab}^i}{r_{ab}},\frac{p_a^2}{2m}\right][V,p_b^j] + \left[\frac{p_b^2}{2m},\left[\sigma_a^{ij}\frac{r_{ab}^i}{r_{ab}},\frac{p_a^2}{2m}\right]\right]p_b^j - [p_a^j,V]\left[\frac{p_b^2}{2m},\sigma_b^{ij}\frac{r_{ab}^i}{r_{ab}}\right] - p_a^j\left[\frac{p_a^2}{2m},\left[\sigma_a^{ij}\frac{r_{ab}^i}{r_{ab}},\frac{p_b^2}{2m}\right]\right]\right\}. \tag{48}$$

Finally, the nuclear part is

$$
\begin{aligned}
E_{7d}^M &= -e^2\int\frac{d^3k}{(2\pi)^3 2k^4}\left(\delta^{ij}-\frac{k^i k^j}{k^2}\right)\frac{Z}{M}\sum_{a,b}\langle\phi|p_a^i(H-E)^2\left(\frac{p_b^j}{m}+\frac{1}{2m}\sigma_b^{lj}\nabla_b^l\right)e^{-i\vec{k}\cdot\vec{r}_{bI}}|\phi\rangle + \text{H.c.}\\
&= -\frac{Z\alpha}{M}\sum_{a,b}\langle\phi|[p_a^i,V]\left[H-E,\frac{(r_{bI}^i r_{bI}^j - 3\delta^{ij}r_{bI}^2)}{8r_{bI}}\frac{p_b^j}{m}-\frac{1}{4m}\sigma_b^{lj}\frac{r_{bI}^l}{r_{bI}}\right]|\phi\rangle\\
&\equiv \langle\phi|H_{7d}^M|\phi\rangle. \tag{49}
\end{aligned}
$$

We have checked that the nonrecoil part agrees with that derived in Ref. [15] and that the spin-dependent recoil part agrees with that in Ref. [17]. Here, we are interested in the spin-independent part, which in the center-of-mass system $\vec{P}_I = -\sum_a \vec{p}_a$ is (from now on we use atomic units $m = 1$)

$$H_1^M = \sum_a \frac{p_a^6}{16},$$

$$H_2^M = \sum_a\left[\frac{(\nabla_a V)^2}{8}+\frac{5}{128}[p_a^2,[p_a^2,V]]-\frac{3}{64}\{p_a^2,\nabla_a^2 V\}\right],$$

$$H_3^M = \sum_{a>b}\sum_b\frac{1}{64}\left\{-4\pi\nabla^2\delta^3(r_{ab})+\frac{2}{3}\sigma_a^{ij}\sigma_b^{ij}\left[\frac{2}{3}\vec{p}_a 4\pi\delta^3(r_{ab})\vec{p}_b - p_a^i\frac{1}{r_{ab}^3}\left(\delta^{ij}-3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right)p_b^j\right]\right\},$$

$$H_4^M = \frac{1}{8}\sum_a\left[\sum_{b\neq a}\left\{p_a^2,p_a^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right)p_b^j\right\}-\frac{\sigma_a^{ij}\sigma_b^{ij}}{6}\{p_a^2,4\pi\delta^3(r_{ab})\}+\frac{Z}{M}\sum_b\left\{p_a^2,p_a^i\left(\frac{\delta^{ij}}{r_{aI}}+\frac{r_{aI}^i r_{aI}^j}{r_{aI}^3}\right)p_b^j\right\}\right],$$

$$H_5^M = \sum_{a\neq b,b}\frac{\sigma_a^{ij}\sigma_b^{ij}}{6}\left(-\frac{1}{2}\frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\nabla_a V + \frac{1}{16}\left[\left[\frac{1}{r_{ab}},p_a^2\right],p_a^2\right]\right),$$

$$H_6^M = \sum_a\sum_{b\neq a}\sum_{c\neq a}\left[\frac{1}{8}p_b^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right)\left(\frac{\delta^{jk}}{r_{ac}}+\frac{r_{ac}^j r_{ac}^k}{r_{ac}^3}\right)p_c^k + \frac{\sigma_b^{ij}\sigma_c^{ij}}{24}\frac{\vec{r}_{ab}}{r_{ab}^3}\frac{\vec{r}_{ac}}{r_{ac}^3}+\frac{Z}{4}\frac{m}{M}p_b^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right)\left(\frac{\delta^{jk}}{r_{aI}}+\frac{r_{aI}^j r_{aI}^k}{r_{aI}^3}\right)p_c^k\right]$$

$$+\sum_a\sum_b\frac{Z^2}{8}\frac{m}{M}\left[p_a^i\left(\frac{\delta^{ij}}{r_{aI}}+\frac{r_{aI}^i r_{aI}^j}{r_{aI}^3}\right)\left(\frac{\delta^{jk}}{r_{bI}}+\frac{r_{bI}^j r_{bI}^k}{r_{bI}^3}\right)p_b^k + \frac{\sigma_a^{ij}\sigma_b^{ij}}{3}\frac{\vec{r}_{aI}}{r_{aI}^3}\frac{\vec{r}_{bI}}{r_{bI}^3}\right],$$

$$
\begin{aligned}
H_{7a}^M &= \sum_{a>b}\sum_b -\frac{1}{8}\left\{[p_a^i,V]\frac{r_{ab}^i r_{ab}^j - 3\delta^{ij}r_{ab}^2}{r_{ab}}[V,p_b^j]+[p_a^i,V]\left[\frac{p_b^2}{2},\frac{r_{ab}^i r_{ab}^j - 3\delta^{ij}r_{ab}^2}{r_{ab}}\right]p_b^j\right.\\
&\quad\left.+p_a^i\left[\frac{r_{ab}^i r_{ab}^j - 3\delta^{ij}r_{ab}^2}{r_{ab}},\frac{p_a^2}{2}\right][V,p_b^j]+p_a^i\left[\frac{p_b^2}{2},\left[\frac{r_{ab}^i r_{ab}^j - 3\delta^{ij}r_{ab}^2}{r_{ab}},\frac{p_a^2}{2}\right]\right]p_b^j\right\},
\end{aligned}
$$

$$H_{7c}^M = \sum_{a>b}\sum_b\frac{\sigma_a^{ij}\sigma_b^{ij}}{48}\left[p_a^2,\left[p_b^2,\frac{1}{r_{ab}}\right]\right],$$

$$H_{7d}^M = \frac{iZ}{8}\frac{m}{M}\sum_{a,b}\nabla_a^i V\left[H-E,\frac{(r_{bI}^i r_{bI}^j - 3\delta^{ij}r_{bI}^2)}{r_{bI}}p_b^j\right]. \tag{50}$$

Further Hamiltonians $H_8^M, \ldots, H_{11}^M$ come from the high-energy contributions, so they are proportional to Dirac δ's, and we will account for them in the next paragraph. These H_i^M form a general $m\alpha^6$ effective Hamiltonian for an arbitrary atom and an arbitrary state, neglecting the spin-dependent operators.

From now on we consider the specific case of the triplet states of the He atom, where the expectation value of $\delta^3(r_{ab})$ vanishes and almost all matrix elements become finite.

The Breit-Pauli Hamiltonian of Eq. (11) is split into four parts (with $r_{12} \equiv r$, $r_{aI} \equiv r_a$, and $\vec{P} \equiv \vec{p}_1 + \vec{p}_2$),

$$H_M^{(4)} = H_A^M + H_B^M + H_C^M + H_D^M, \tag{51}$$

where

$$H_A^M = -\frac{1}{8}\left(p_1^4 + p_2^4\right) + \frac{Z\pi}{2}[\delta^3(r_1) + \delta^3(r_2)] - \frac{1}{2}p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j - \frac{Z}{2}\frac{m}{M}\left[p_1^i\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right) + p_2^i\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)\right]P^j, \tag{52}$$

$$H_B^M = \left[\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3} \times \vec{p}_1 + \frac{\vec{r}_2}{r_2^3} \times \vec{p}_2\right) - \frac{3}{4}\frac{\vec{r}}{r^3} \times (\vec{p}_1 - \vec{p}_2) + \frac{Z}{2}\frac{m}{M}\left(\frac{\vec{r}_1}{r_1^3} + \frac{\vec{r}_2}{r_2^3}\right) \times \vec{P}\right]\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}, \tag{53}$$

$$H_C^M = \left[\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3} \times \vec{p}_1 - \frac{\vec{r}_2}{r_2^3} \times \vec{p}_2\right) + \frac{1}{4}\frac{\vec{r}}{r^3} \times (\vec{p}_1 + \vec{p}_2) + \frac{Z}{2}\frac{m}{M}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right) \times \vec{P}\right]\frac{\vec{\sigma}_1 - \vec{\sigma}_2}{2}, \tag{54}$$

$$H_D^M = \frac{1}{4}\left(\frac{\vec{\sigma}_1\vec{\sigma}_2}{r^3} - 3\frac{\vec{\sigma}_1 \cdot \vec{r}\vec{\sigma}_2 \cdot \vec{r}}{r^5}\right). \tag{55}$$

The corresponding second-order correction is

$$A_M = \sum_{I=A,B,C,D}\left\langle H_I^M \frac{1}{(E_M - H_M)'}H_I^M\right\rangle_M, \tag{56}$$

whereas the first-order contribution is given by

$$B_M = \left\langle H_M^{(6)}\right\rangle_M. \tag{57}$$

$H_M^{(6)}$ consists of 11 parts, according to Eq. (29), with $H_1^M, \ldots, H_7^M$ already defined and

$$H_8^M = Z^3\frac{m}{M}\left(4\ln 2 - \frac{7}{2}\right)[\delta^3(r_1) + \delta^3(r_2)], \tag{58}$$

$$H_9^M = Z^2\frac{m}{M}\left[\frac{35}{36} - \frac{448}{27\pi^2} - 2\ln(2) + \frac{6\zeta(3)}{\pi^2}\right][\delta^3(r_1) + \delta^3(r_2)], \tag{59}$$

$$H_{10}^M = \pi Z^2\left[\frac{139}{32} - 2\ln(2) + \frac{5}{48}\right][\delta^3(r_1) + \delta^3(r_2)], \tag{60}$$

$$H_{11}^M = \frac{Z}{\pi}\left[-\frac{4358}{1296} - \frac{10}{27}\pi^2 + \frac{3}{2}\pi^2\ln(2) - \frac{9}{4}\zeta(3)\right][\delta^3(r_1) + \delta^3(r_2)]. \tag{61}$$

Here H_8^M is the high-energy pure recoil correction taken from hydrogenic results, H_9^M stands for the radiative recoil correction, and H_{10}^M and H_{11}^M stand for the one-loop and two-loop radiative corrections, correspondingly [18].

reference state E, and the nonrelativistic Hamiltonian H by the nuclear kinetic energy $\vec{P}^2/(2M)$; and (ii) corrections due to the extra recoil operators in $H_M^{(4)}$ and $H_M^{(6)}$. We will use this fact in the following derivations.

VI. ELIMINATION OF SINGULARITIES

The principal problem of the used approach is that both the first-order and the second-order contributions are divergent; the divergence cancels out only in the sum of these contributions. To achieve the cancellation of the divergences, we (i) regularize the divergent contributions by switching to $d = 3 - 2\epsilon$ dimensions, (ii) move singularities from the second-order contributions to the first-order ones, and (iii) cancel algebraically the $1/\epsilon$ terms. Moreover, we notice that the recoil corrections are of two types: (i) corrections due to the perturbation of the wave function ϕ, the energy of the

A. Recoil correction from the second-order contribution

In this section we consider the recoil correction coming from the second-order matrix elements, i.e., the first term in Eq. (12), which is denoted by A_M. The recoil correction from the second term in Eq. (12), denoted by B_M, will be examined in the next section.

The second-order contribution with H_A^M is divergent and has to be regularized. Regularization is performed by rewriting H_A^M in such a way that the singularities are moved from the second-order matrix element into the first-order ones, where

they cancel each other. To do this, we write H_A^M as

$$H_A^M = H_R^M - \frac{1}{4}\left\{ H_M - E_M, \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r} - 3\frac{m}{M}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\right\} = H_R^M + \{H_M - E_M, Q_M\}. \tag{62}$$

The operator Q_M is the same as in Ref. [2] with the exception that it also includes a recoil part $\delta_M Q$. The regular part of operator H_A^M can be evaluated to yield

$$H_R^M = H_R + \frac{m}{M}\delta_M H_R, \tag{63}$$

$$H_R|\phi\rangle = \left\{ -\frac{1}{2}(E - V)^2 - \frac{Z}{4}\frac{\vec{r}_1 \cdot \vec{\nabla}_1}{r_1^3} - \frac{Z}{4}\frac{\vec{r}_2 \cdot \vec{\nabla}_2}{r_2^3} + \frac{1}{4}\nabla_1^2\nabla_2^2 - p_1^i V^{ij}(r)p_2^j \right\}|\phi\rangle, \tag{64}$$

$$\delta_M H_R|\phi\rangle = \left\{ (E - V)\left(\frac{\vec{P}^2}{2} - \left\langle\frac{\vec{P}^2}{2}\right\rangle\right) + \frac{3Z}{4}\frac{\vec{r}_1 \cdot \vec{\nabla}_2}{r_1^3} + \frac{3Z}{4}\frac{\vec{r}_2 \cdot \vec{\nabla}_1}{r_2^3} - Zp_1^i V^{ij}(r_1)P^j - Zp_2^i V^{ij}(r_2)P^j \right\}|\phi\rangle, \tag{65}$$

where

$$V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r}, \tag{66}$$

$$V^{ij}(x) = \frac{1}{2x}\left(\delta^{ij} + \frac{x^i x^j}{x^2}\right). \tag{67}$$

Moreover, the kinetic energy of the nucleus is $\langle \vec{P}^2/2\rangle = \delta_M E$. After regularization, the first term in Eq. (12) takes the form

$$A_M = \sum_{a=R,B,C,D}\left\langle H_a^M \frac{1}{(E_M - H_M)'}H_a^M\right\rangle_M + \langle Q_M(H_M - E_M)Q_M\rangle_M + 2E_M^{(4)}\langle Q_M\rangle_M - 2\langle H_M^{(4)}Q_M\rangle_M$$

$$= A_1^M + A_2^M, \tag{68}$$

where A_1^M stands for the first term (i.e., the second-order contribution) and A_2^M incorporates the remaining first-order matrix elements. Recoil corrections are obtained by perturbing the second-order matrix element by the kinetic energy of the nucleus and keeping the first-order terms in the nuclear mass. So, $\delta_M A_1$ is

$$\delta_M A_1 = \sum_{a=R,B,C,D}\left\langle H_a \frac{1}{(E - H)'}\left[\frac{\vec{P}^2}{2} - \delta_M E\right]\frac{1}{(E - H)'}H_a\right\rangle$$

$$+ 2\left\langle H_a \frac{1}{(E - H)'}[H_a - \langle H_a\rangle]\frac{1}{(E - H)'}\frac{\vec{P}^2}{2}\right\rangle + 2\left\langle \delta_M H_a \frac{1}{(E - H)'}H_a\right\rangle, \tag{69}$$

while the first-order terms are

$$A_2^M = \langle Q(H_M - E_M)Q\rangle_M + 2E_M^{(4)}\langle Q\rangle_M - 2\langle H_M^{(4)}Q\rangle_M + \frac{m}{M}\{2\langle Q(H - E)\delta_M Q\rangle + 2E^{(4)}\langle \delta_M Q\rangle - 2\langle H_A\delta_M Q\rangle\}. \tag{70}$$

Reduction of these terms will be left to the Appendix, and we present here the final result for the recoil part:

$$\delta_M A_2 = \delta_M\left\langle -\frac{3}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - \frac{1}{4r^4} + \frac{1}{4}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + 2E^{(4)}Q + \frac{Z(Z-2)}{4}\pi\left[\frac{\delta^3(r_1)}{r_2} + \frac{\delta^3(r_2)}{r_1}\right]\right.$$

$$- \frac{1}{4}p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j + \frac{1}{2}\left[p_1^i, \left[p_2^j, \frac{1}{r}\right]\right]\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right) + (E - V)^2 Q + \frac{1}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2$$

$$- \frac{1}{4}p_1^2\frac{1}{r}p_2^2 - \frac{1}{8}\left[p_1^2, [p_2^2, V]\right]\right\rangle + \delta_M E^{(4)}\left(E + \left\langle\frac{1}{2r}\right\rangle\right) + \left\langle\frac{11}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - \frac{3}{16}\frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3} + \frac{3}{2}\frac{E^{(4)}}{r} - 3EE^{(4)}\right.$$

$$+ \frac{3}{4}(E - V)^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) - \frac{3}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2 + \frac{3}{4}p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j + 2\delta_M E(E - V)Q$$

$$+ \frac{\pi Z}{4}\delta^3(r_1)\left(\frac{Z-6}{r_2} + 2E + 2Z^2\right) + \frac{\pi Z}{4}\delta^3(r_2)\left(\frac{Z-6}{r_1} + 2E + 2Z^2\right) + \vec{P}\left[\frac{E}{4}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) - \frac{E}{2r}\right.$$

$$\left.+ \frac{1}{4}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)^2 - \frac{3}{4r}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{1}{2r^2}\right]\vec{P} - \sum_a \frac{Z}{4}P^i\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)p_a^j\right\rangle. \tag{71}$$

B. Recoil correction from the first-order terms

In this section we examine the recoil correction coming from the first-order matrix elements, i.e., the second term in Eq. (12), which is denoted as B_M. Using Eq. (29), B_M can be written as

$$B_M = \langle H_M^{(6)} \rangle_M = \sum_{i=1,...,11} \langle H_i^M \rangle_M. \tag{72}$$

For each of the operators $H_i^M = H_i + \frac{m}{M} \delta_M H_i$, the recoil correction is the sum of two parts: (i) perturbation of the nonrelativistic wave function, E and H by the nuclear kinetic energy in the nonrecoil part; and (ii) the expectation value of the recoil part $\delta_M H_i$ (if present). The derivation is straightforward but tedious, so we have moved the description of this calculation to the Appendix and present only the final result for the recoil correction $\delta_M B$,

$$
\begin{aligned}
\delta_M B = \delta_M \Bigg\langle & \frac{7}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - \frac{25}{48}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + \frac{1}{4}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^2} - \frac{1}{4r^3} + \frac{41}{48r^4} + \frac{11}{96}\left[p_2^2,\left[p_1^2,\frac{1}{r}\right]\right] \\
& + \frac{1}{2}(E-V)^3 - \frac{3}{8}p_1^2(E-V)p_2^2 - \frac{3}{8}\pi Z\left[2\left(E+\frac{Z-1}{r_2}\right)\delta^3(r_1) + 2\left(E+\frac{Z-1}{r_1}\right)\delta^3(r_2) - p_1^2\delta^3(r_2) - p_2^2\delta^3(r_1)\right] \\
& - \frac{\pi}{12}\nabla^2\delta^3(r) + \frac{1}{2}p_1^i(E-V)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j - \frac{1}{8}\frac{Z^2 r_1^i r_2^j}{r_1^3 r_2^3}\left(\frac{r^i r^j}{r} - 3\delta^{ij}r\right) - \frac{Z}{8}\left[\frac{r_1^i}{r_1^3}p_2^k\left(\delta^{jk}\frac{r^i}{r} - \delta^{ik}\frac{r^j}{r}\right.\right. \\
& \left.\left. - \delta^{ij}\frac{r^k}{r} - \frac{r^i r^j r^k}{r^3}\right)p_2^j + (1 \leftrightarrow 2)\right] + \frac{1}{8}p_1^k p_2^l\left[-\frac{\delta^{il}\delta^{jk}}{r} + \frac{\delta^{ik}\delta^{jl}}{r} - \frac{\delta^{ij}\delta^{kl}}{r} - \frac{\delta^{jl}r^i r^k}{r^3} - \frac{\delta^{ik}r^j r^l}{r^3} + 3\frac{r^i r^j r^k r^l}{r^5}\right]p_1^i p_2^j \\
& + \frac{1}{4}\left(\vec{p}_1\frac{1}{r^2}\vec{p}_1 + \vec{p}_2\frac{1}{r^2}\vec{p}_2\right) + H_{10} + H_{11}\Bigg\rangle + \Bigg\langle\frac{3}{2}\delta_M E(E-V)^2 - \frac{3}{4}\vec{P}(E-V)^2\vec{P} - \frac{3}{8}\delta_M E p_1^2 p_2^2 + \frac{3}{16}P^2 p_1^2 p_2^2 \\
& - \frac{3}{4}\left[\delta_M E + 3E + \frac{3(Z-1)}{r_2} - \vec{p}_1\cdot\vec{p}_2\right]\pi Z\delta^3(r_1) + (1 \leftrightarrow 2) + \frac{1}{2}\delta_M E p_1^i\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j \\
& - \frac{1}{4}\vec{P}^2 p_1^i\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j + \frac{13}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{13}{16}\frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\Bigg\rangle + \langle\delta_M H^{(6)}\rangle, \tag{73}
\end{aligned}
$$

where

$$
\begin{aligned}
\langle\delta_M H^{(6)}\rangle = \Bigg\langle & \frac{Z}{2}\left[p_1^i(E-V)\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right) + p_2^i(E-V)\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)\right]P^j - \frac{Z}{4}\left[p_1^i p_2^k\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)p_2^k P^j\right. \\
& + p_2^i p_1^k\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)p_1^k P^j\Bigg] + \frac{Z^2}{6}\frac{\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3} + \frac{Z}{4}\left[p_2^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_1} + \frac{r_1^j r_1^k}{r_1^3}\right)\right. \\
& + p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_2} + \frac{r_2^j r_2^k}{r_2^3}\right)\Bigg]P^k + \frac{Z^2}{4}\left[\vec{p}_1\frac{1}{r_1^2}\vec{p}_1 + \vec{p}_2\frac{1}{r_2^2}\vec{p}_2 + p_1^i\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)\left(\frac{\delta^{jk}}{r_2} + \frac{r_2^j r_2^k}{r_2^3}\right)p_2^k\right] \\
& + \frac{Z^3\vec{r}_1\cdot\vec{r}_2}{4r_1^3 r_2^2} + \frac{Z^3\vec{r}_1\cdot\vec{r}_2}{4r_1^2 r_2^3} + \frac{Z^2}{8}\left(\frac{r_1^i}{r_1^3} + \frac{r_2^i}{r_2^3}\right)\left(\frac{r_1^i r_1^j - 3\delta^{ij}r_1^2}{r_1} - \frac{r_2^i r_2^j - 3\delta^{ij}r_2^2}{r_2}\right)\frac{r^j}{r^3} \\
& + \frac{Z^2}{8}\left[p_2^k\frac{r_1^i}{r_1^3}\left(-\delta^{ik}\frac{r_2^j}{r_2} + \delta^{jk}\frac{r_2^i}{r_2} - \delta^{ij}\frac{r_2^k}{r_2} - \frac{r_2^i r_2^j r_2^k}{r_2^3}\right)p_2^j + (1 \leftrightarrow 2)\right] \\
& + \frac{Z^3}{4r_1^3} + \frac{Z^3}{4r_2^3} - \frac{Z^2}{8r_1^4} - \frac{Z^2}{8r_2^4} - \frac{3Z^3}{2}[\pi\delta^3(r_1) + \pi\delta^3(r_2)] + \delta_M H_8 + \delta_M H_9\Bigg\rangle. \tag{74}
\end{aligned}
$$

At this point we have obtained all the terms contributing to the recoil correction.

C. Cancellation of singularities

The first-order terms $\delta_M A_2$ and $\delta_M B$ could be further transformed using various identities, namely,

$$\left[p_2^2,\left[p_1^2,\frac{1}{r}\right]\right] = \left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{2}{r^4} + P^i P^j\frac{3r^i r^j - \delta^{ij}r^2}{r^5}, \tag{75}$$

$$\frac{1}{r^4} = \frac{1}{r^3} + \frac{1}{2}\left(\vec{p}_1\frac{1}{r^2}\vec{p}_1 + \vec{p}_2\frac{1}{r^2}\vec{p}_2\right) - \left(E + \frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r^2} - \frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\frac{1}{r^2}, \tag{76}$$

$$\frac{Z^2}{r_1^4} = \vec{p}_1 \frac{Z^2}{r_1^2} \vec{p}_1 - 2\left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r}\right)\frac{Z^2}{r_1^2} + p_2^2 \frac{Z^2}{r_1^2} - 2\frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\frac{Z^2}{r_1^2}, \tag{77}$$

$$p_1^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j = -2H_M^{(4)} - (E - V)^2 + \frac{1}{2}p_1^2 p_2^2 + Z\pi[\delta^3(r_1) + \delta^3(r_2)] - 2\frac{m}{M}\left[(E-V)\left(\delta_M E - \frac{\vec{P}^2}{2}\right) - \delta_M H^{(4)}\right], \tag{78}$$

$$\nabla^2 \delta^3(r) = 2\vec{p}\,\delta^3(r)\vec{p}. \tag{79}$$

Using these identities, we remove all the remaining singularities and transform the results into a form suitable for numerical calculation. The final result for recoil correction is presented in the next section.

VII. FINAL FORMULA

The final results are split into seven parts: (i) the second-order and third-order matrix elements containing H_R; (ii) the second-order and third-order matrix elements containing H_B; (iii) the second-order and third-order matrix elements containing H_C; (iv) the third-order matrix elements containing H_D; (v) the first-order matrix elements with the reference state and the perturbed wave function; and (vi) the remaining first-order terms with the exception of (vii) pure recoil, the radiative recoil, and the recoil corrections to one-loop and two-loop radiative corrections.

The final formula is then

$$E_{\text{recoil}} = E_\text{i} + E_\text{ii} + E_\text{iii} + E_\text{iv} + E_\text{v} + E_\text{vi} + E_\text{vii}, \tag{80}$$

$$E_\text{i} = \left\langle H_R \frac{1}{(E-H)'}\left(\frac{\vec{P}^2}{2} - \delta_M E\right)\frac{1}{(E-H)'} H_R\right\rangle + 2\left\langle H_R \frac{1}{(E-H)'}[H_R - \langle H_R \rangle]\frac{1}{(E-H)'}\frac{\vec{P}^2}{2}\right\rangle + 2\left\langle \delta_M H_R \frac{1}{(E-H)'} H_R\right\rangle, \tag{81}$$

$$E_\text{ii} = \left\langle H_B \frac{1}{(E-H)}\left(\frac{\vec{P}^2}{2} - \delta_M E\right)\frac{1}{(E-H)} H_B\right\rangle + 2\left\langle H_B \frac{1}{(E-H)} H_B \frac{1}{(E-H)}\frac{\vec{P}^2}{2}\right\rangle + 2\left\langle H_B \frac{1}{(E-H)}\delta_M H_B\right\rangle, \tag{82}$$

$$E_\text{iii} = \left\langle H_C \frac{1}{(E-H)}\left(\frac{\vec{P}^2}{2} - \delta_M E\right)\frac{1}{(E-H)} H_C\right\rangle + 2\left\langle H_C \frac{1}{(E-H)} H_C \frac{1}{(E-H)}\frac{\vec{P}^2}{2}\right\rangle + 2\left\langle H_C \frac{1}{(E-H)}\delta_M H_C\right\rangle, \tag{83}$$

$$E_\text{iv} = \left\langle H_D \frac{1}{(E-H)}\left(\frac{\vec{P}^2}{2} - \delta_M E\right)\frac{1}{(E-H)} H_D\right\rangle + 2\left\langle H_D \frac{1}{(E-H)} H_D \frac{1}{(E-H)}\frac{\vec{P}^2}{2}\right\rangle. \tag{84}$$

Here

$$\delta_M E = \left\langle \frac{\vec{P}^2}{2}\right\rangle = -E + \langle \vec{p}_1 \cdot \vec{p}_2 \rangle. \tag{85}$$

For E_v and E_vi the results can be brought into a more suitable form by introducing set of operators Q_i (see Tables I and II),

$$E_\text{v} = -\frac{E}{8} Z\delta_M \langle Q_1 \rangle + \frac{1}{8} Z(1 - 2Z)\delta_M \langle Q_3 \rangle + \frac{3}{16} Z\delta_M \langle Q_4 \rangle - \frac{1}{24}\delta_M \langle Q_6 \rangle + \frac{E^2 + 2E^{(4)}}{4}\delta_M \langle Q_7 \rangle - \frac{9}{8} E\delta_M \langle Q_8 \rangle$$

$$+ \frac{7}{8}\delta_M \langle Q_9 \rangle + \frac{E}{2} Z^2 \delta_M \langle Q_{11} \rangle + E Z^2 \delta_M \langle Q_{12} \rangle - E Z \delta_M \langle Q_{13} \rangle - Z^2 \delta_M \langle Q_{14} \rangle + Z^3 \delta_M \langle Q_{15} \rangle - \frac{Z^2}{2}\delta_M \langle Q_{16} \rangle$$

$$- \frac{7}{4} Z\delta_M \langle Q_{17} \rangle - \frac{9}{16} Z\delta_M \langle Q_{18} \rangle + \frac{Z}{2}\delta_M \langle Q_{19} \rangle - \frac{Z^2}{8}\delta_M \langle Q_{20} \rangle + \frac{Z^2}{4}\delta_M \langle Q_{21} \rangle + \frac{Z^2}{4}\delta_M \langle Q_{22} \rangle + \frac{13}{8}\delta_M \langle Q_{23} \rangle$$

$$+ \frac{Z}{2}\delta_M \langle Q_{24} \rangle - \frac{1}{96}\delta_M \langle Q_{25} \rangle - \frac{Z}{4}\delta_M \langle Q_{26} \rangle - \frac{E}{8}\delta_M \langle Q_{27} \rangle - \frac{Z}{2}\delta_M \langle Q_{28} \rangle + \frac{1}{4}\delta_M \langle Q_{29} \rangle + \frac{1}{8}\delta_M \langle Q_{30} \rangle \tag{86}$$

and

$$E_\text{vi} = \left\langle -\frac{3}{2} E^3 - 3E E^{(4)} - 2E^2 \delta_M E - \frac{3E + \delta_M E + 4Z^2}{8} Z Q_1 - \frac{Z(8Z - 3)}{8} Q_3 + \frac{3E^2 + 2E\delta_M E + 6E^{(4)} + 2\delta_M E^{(4)}}{4} Q_7 \right.$$

$$- \frac{9}{8}\delta_M E Q_8 + \frac{2E + \delta_M E}{2} Z^2 Q_{11} + (3E + \delta_M E)(Z^2 Q_{12} - Z Q_{13}) - 3Z^2 Q_{14} + \frac{5}{2} Z^3 Q_{15} - Z^2 Q_{16} + \frac{3}{2} Z Q_{17}$$

$$+ Z^2 Q_{21} + \frac{3}{2} Z^2 Q_{22} + \frac{3}{2} Z Q_{24} - \frac{1}{8}\delta_M E Q_{27} - \frac{3}{4} Z Q_{28} + \frac{3}{8} Z Q_{31} + \frac{19}{24} Z^2 Q_{32} - \frac{3}{2} E Z Q_{34}$$

$$+ \frac{1}{2} E Q_{35} - \frac{3}{4} Z^2 Q_{36} - Z^2 Q_{37} + \frac{3}{2} Z Q_{38} + \frac{5}{16} Q_{39} + \frac{3}{16} Q_{40} - \frac{1}{4} Q_{41} + \frac{Z^2}{2} Q_{42} + \frac{Z^2}{2} Q_{43} - \frac{Z}{2} Q_{44}$$

$$\left. + \frac{Z}{2} Q_{45} + \frac{Z^2}{4} Q_{46} + \frac{Z^3}{2} Q_{47} + \frac{Z^2}{4} Q_{48} - \frac{Z^2}{4} Q_{49} + \frac{Z^2}{4} Q_{50}\right\rangle. \tag{87}$$

TABLE I. Expectation values of operators Q_i and the corresponding recoil corrections for $i = 1, \ldots, 30$.

	$2\,^3S$		$2\,^3P$	
	$\langle Q_i \rangle$	$\delta_M \langle Q_i \rangle$	$\langle Q_i \rangle$	$\delta_M \langle Q_i \rangle$
$Q_1 = 4\pi \delta^3(r_1)$	16.592 071	$-49.748\,907$	15.819 309	$-48.358\,598$
$Q_2 = 4\pi \delta^3(r)$	0	0	0	0
$Q_3 = 4\pi \delta^3(r_1)/r_2$	4.648 724	$-18.821\,266$	4.349 766	$-14.576\,147$
$Q_4 = 4\pi \delta^3(r_1)\, p_2^2$	2.095 714	$-10.638\,077$	4.792 830	$-17.366\,064$
$Q_5 = 4\pi \delta^3(r)/r_1$	0	0	0	0
$Q_6 = 4\pi \, \vec{p}\, \delta^3(r)\, \vec{p}$	0.028 099	$-0.163\,026$	0.077 524	$-0.100\,949$
$Q_7 = 1/r$	0.268 198	$-0.272\,645$	0.266 641	$-0.082\,865$
$Q_8 = 1/r^2$	0.088 906	$-0.182\,363$	0.094 057	$-0.052\,275$
$Q_9 = 1/r^3$	0.038 861	$-0.121\,355$	0.047 927	$-0.036\,603$
$Q_{10} = 1/r^4$	0.026 567	$-0.113\,712$	0.043 348	$-0.042\,669$
$Q_{11} = 1/r_1^2$	4.170 446	$-8.338\,455$	4.014 865	$-8.127\,584$
$Q_{12} = 1/(r_1 r_2)$	0.560 730	$-1.147\,101$	0.550 342	$-0.709\,019$
$Q_{13} = 1/(r_1 r)$	0.322 696	$-0.657\,458$	0.317 639	$-0.381\,158$
$Q_{14} = 1/(r_1 r_2 r)$	0.186 586	$-0.576\,097$	0.198 346	$-0.295\,115$
$Q_{15} = 1/(r_1^2 r_2)$	1.242 704	$-3.791\,743$	1.196 631	$-2.687\,288$
$Q_{16} = 1/(r_1^2 r)$	1.164 599	$-3.545\,640$	1.109 463	$-2.554\,378$
$Q_{17} = 1/(r_1 r^2)$	0.112 360	$-0.346\,820$	0.121 112	$-0.166\,459$
$Q_{18} = (\vec{r}_1 \cdot \vec{r})/(r_1^3 r^3)$	0.011 331	$-0.055\,997$	0.030 284	$-0.030\,290$
$Q_{19} = (\vec{r}_1 \cdot \vec{r})/(r_1^3 r^2)$	0.054 635	$-0.211\,280$	0.075 373	$-0.104\,553$
$Q_{20} = r_1^i r_2^j (r^i r^j - 3\delta^{ij} r^2)/(r_1^3 r_2^3 r)$	0.027 082	$-0.256\,024$	0.090 381	$-0.166\,239$
$Q_{21} = p_2^2/r_1^2$	0.751 913	$-3.075\,881$	1.410 228	$-3.635\,740$
$Q_{22} = \vec{p}_1/r_1^2\, \vec{p}_1$	16.720 479	$-66.901\,955$	15.925 672	$-64.131\,339$
$Q_{23} = \vec{p}_1/r^2\, \vec{p}_1$	0.243 754	$-1.008\,306$	0.279 229	$-0.572\,398$
$Q_{24} = p_1^i (r^i r^j + \delta^{ij} r^2)/(r_1 r^3)\, p_2^j$	0.002 750	$-0.068\,255$	$-0.097\,364$	$-0.056\,872$
$Q_{25} = P^i (3 r^i r^j - \delta^{ij} r^2)/r^5\, P^j$	0.062 031	$-0.336\,586$	$-0.060\,473$	0.119 687
$Q_{26} = p_2^k r_1^i/r_1^3 (\delta^{jk} r^i/r - \delta^{ik} r^j/r - \delta^{ij} r^k/r - r^i r^j r^k/r^3)\, p_2^j$	$-0.009\,102$	0.035 209	0.071 600	$-0.134\,238$
$Q_{27} = p_1^2\, p_2^2$	0.488 198	$-1.988\,286$	1.198 492	$-3.171\,122$
$Q_{28} = p_1^2/r_1\, p_2^2$	1.597 727	$-8.106\,766$	3.883 405	$-13.814\,978$
$Q_{29} = \vec{p}_1 \times \vec{p}_2/r\, \vec{p}_1 \times \vec{p}_2$	0.070 535	$-0.358\,089$	0.399 306	$-1.076\,373$
$Q_{30} = p_1^k p_2^l (-\delta^{jl} r^i r^k/r^3 - \delta^{ik} r^j r^l/r^3 + 3 r^i r^j r^k r^l/r^5)\, p_1^i p_2^j$	$-0.034\,780$	0.177 968	$-0.187\,305$	0.490 555

Finally,

$$E_{\text{vii}} = \langle \delta_M H_8 + \delta_M H_9 \rangle + \delta_M \langle H_{10} + H_{11} \rangle. \tag{88}$$

VIII. NUMERICAL CALCULATIONS OF MATRIX ELEMENTS

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

$$\phi(^3S) = \sum_{i=1}^{\mathcal{N}} v_i [e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r} - (r_1 \leftrightarrow r_2)], \tag{89}$$

$$\phi(^3P) = \sum_{i=1}^{\mathcal{N}} v_i [\vec{r}_1 e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r} - (r_1 \leftrightarrow r_2)], \tag{90}$$

where α_i, β_i, and γ_i are generated quasirandomly with conditions:

$$
\begin{aligned}
A_1 < \alpha_i < A_2, & \quad \beta_i + \gamma_i > \varepsilon, \\
B_1 < \beta_i < B_2, & \quad \alpha_i + \gamma_i > \varepsilon, \\
C_1 < \gamma_i < C_2, & \quad \alpha_i + \beta_i > \varepsilon.
\end{aligned} \tag{91}
$$

In order to obtain a highly accurate representation of the wave function, following Korobov [19], we use a double set of the nonlinear parameters of the form (89). The parameters A_i, B_i, C_i, and ε are determined by the energy minimization, with the condition that $\varepsilon > 0$, which follows from the normalizability of the wave function. The linear coefficients v_i in Eq. (89) form a vector v, which is a solution of the generalized eigenvalue problem

$$H v = E N v, \tag{92}$$

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

$$E(2\,^3S) = -2.175\,229\,378\,236\,791\,306, \tag{93}$$

$$E(2\,^3P) = -2.133\,164\,190\,779\,283\,199. \tag{94}$$

TABLE II. Expectation values of operators Q_i for $i = 31, \ldots, 50$, the expectation value of the Breit Hamiltonian $E^{(4)}$ and the first-order recoil corrections $\delta_M E$ and $\delta_M E^{(4)}$.

	$2\,^3S$	$2\,^3P$
$Q_{31} = 4\pi\delta^3(r_1)\,\vec{p}_1 \cdot \vec{p}_2$	$0.040\,294$	$-0.457\,224$
$Q_{32} = (\vec{r}_1 \cdot \vec{r}_2)/(r_1^3 r_2^3)$	$-0.005\,797$	$-0.032\,383$
$Q_{33} = \vec{p}_1 \cdot \vec{p}_2$	$0.007\,442$	$-0.064\,572$
$Q_{34} = \vec{P}/r_1\,\vec{P}$	$4.974\,707$	$4.730\,359$
$Q_{35} = \vec{P}/r\,\vec{P}$	$1.232\,372$	$1.127\,146$
$Q_{36} = \vec{P}/r_1^2\,\vec{P}$	$17.504\,835$	$16.972\,775$
$Q_{37} = \vec{P}/(r_1 r_2)\,\vec{P}$	$2.489\,592$	$2.291\,176$
$Q_{38} = \vec{P}/(r_1 r)\,\vec{P}$	$1.454\,007$	$1.350\,214$
$Q_{39} = \vec{P}/r^2\,\vec{P}$	$0.438\,804$	$0.413\,144$
$Q_{40} = p_1^2\,p_2^2\,P^2$	$10.324\,509$	$24.527\,699$
$Q_{41} = P^2\,p_1^i\,(r^i r^j + \delta^{ij} r^2)/r^3\,p_2^j$	$0.151\,748$	$0.067\,201$
$Q_{42} = p_1^i\,(r_1^i r_1^j + \delta^{ij} r_1^2)/r_1^4\,P^j$	$33.461\,709$	$31.489\,835$
$Q_{43} = p_1^i\,(r_1^i r_1^j + \delta^{ij} r_1^2)/(r_1^3 r_2)\,P^j$	$2.486\,269$	$2.217\,310$
$Q_{44} = p_1^i\,p_2^k\,(r_1^i r_1^j + \delta^{ij} r_1^2)/r_1^3\,p_2^k\,P^j$	$1.100\,915$	$2.527\,505$
$Q_{45} = p_2^i(r^i r^j + \delta^{ij} r^2)(r_1^j r_1^k + \delta^{jk} r_1^2)/(r_1^3 r^3)\,P^k$	$0.540\,877$	$0.467\,623$
$Q_{46} = p_1^i(r_1^i r_1^j + \delta^{ij} r_1^2)(r_2^j r_2^k + \delta^{jk} r_2^2)/(r_1^3 r_2^3)\,p_2^k$	$0.006\,782$	$-0.201\,826$
$Q_{47} = (\vec{r}_1 \cdot \vec{r}_2)/(r_1^3 r_2^2)$	$-0.008\,117$	$-0.028\,621$
$Q_{48} = r_1^i r^j (r_1^i r_1^j - 3\delta^{ij} r_1^2)/(r_1^4 r^3)$	$-0.036\,861$	$-0.057\,404$
$Q_{49} = r_1^i r^j (r_2^i r_2^j - 3\delta^{ij} r_2^2)/(r_1^3 r_2 r^3)$	$-0.089\,086$	$-0.126\,780$
$Q_{50} = p_2^k r_1^i/r_1^3\,(\delta^{jk} r_2^i/r_2 - \delta^{ik} r_2^j/r_2 - \delta^{ij} r_2^k/r_2 - r_2^i r_2^j r_2^k/r_2^3)\,p_2^j$	$0.005\,856$	$-0.092\,036$
$E^{(4)}$	$-2.164\,477\,972$	$-1.967\,358\,377$
$\delta_M E$	$2.182\,671\,509$	$2.068\,591\,766$
$\delta_M E^{(4)}$	$0.089\,185\,018$	$0.230\,100\,830$

The calculation of matrix elements of the nonrelativistic Hamiltonian is based on the single master integral

$$\frac{1}{16\pi^2}\int d^3 r_1 \int d^3 r_2 \frac{e^{-\alpha r_1 - \beta r_2 - \gamma r}}{r_1 r_2 r} = \frac{1}{(\alpha + \beta)(\beta + \gamma)(\gamma + \alpha)}. \tag{95}$$

The integrals with any additional powers of r_i in the numerator can be obtained by differentiation with respect to the corresponding parameter α, β, or γ. The matrix elements of relativistic corrections involve inverse powers of r_1, r_2, r. These can be obtained by integration with respect to a corresponding parameter, which leads to the following formulas:

$$\frac{1}{16\pi^2}\int d^3 r_1 \int d^3 r_2 \frac{e^{-\alpha r_1 - \beta r_2 - \gamma r}}{r_1 r_2 r^2}$$
$$= \frac{1}{(\beta + \alpha)(\alpha + \beta)}\ln\left(\frac{\beta + \gamma}{\alpha + \gamma}\right), \tag{96}$$

$$\frac{1}{16\pi^2}\int d^3 r_1 \int d^3 r_2 \frac{e^{-\alpha r_1 - \beta r_2 - \gamma r}}{r_1^2 r_2 r^2}$$
$$= \frac{1}{2\beta}\left[\frac{\pi^2}{6} + \frac{1}{2}\ln^2\left(\frac{\alpha + \beta}{\beta + \gamma}\right)\right.$$
$$\left. + \mathrm{Li}_2\left(1 - \frac{\alpha + \gamma}{\alpha + \beta}\right) + \mathrm{Li}_2\left(1 - \frac{\alpha + \gamma}{\beta + \gamma}\right)\right]. \tag{97}$$

All matrix elements involved in the $\alpha^6 m^2/M$ correction (see Tables I and II) can be expressed in terms of rational, logarithmic, and dilogarithmic functions, as above. The high

quality of the wave function allowed us to obtain accurate values of the matrix elements of Q_i and $\delta_M Q_i$ operators. The corresponding numerical results are presented in Tables I and II.

For the second-order matrix elements, the inversion of the operator $E - H$ is performed in the basis of even or odd parity with $l = 0, 1, 2,$ and 3. In the case when the operator acting on the reference state does not change its symmetry (H_A; for $2\,^3P$, also H_B and H_D), it is necessary to subtract the reference state from the implicit sum over states. This is obtained by the orthogonalization with respect to the eigenstate with the closest-to-zero eigenvalue of $H - E$. This eigenvalue is not exactly equal to 0 because we use a basis set with

TABLE III. Individual $\alpha^6\,m^2/M$ recoil corrections to the ionization energies of the $2\,^3S$ and $2\,^3P$ states.

Term	$2\,^3S$	$2\,^3P$
E_{i}	$1.190\,05$	$0.853\,52(10)$
E_{ii}	$0.044\,46$	$0.032\,33(5)$
E_{iii}	$0.025\,11$	$1.197\,09(10)$
E_{iv}	$0.018\,48$	$0.013\,00(6)$
E_{v}	$-58.048\,06$	$-52.977\,21$
E_{vi}	$56.945\,69$	$52.339\,33$
Subtotal	$0.175\,72$	$1.458\,05(16)$
E_{vii}	$-11.867\,15$	$-1.891\,19$
Sum	$-11.691\,45$	$-0.433\,13(16)$
$\delta_M E^{(6)}$ (kHz)	-29.91	-1.11

TABLE IV. Breakdown of theoretical contributions to the $2\,^3S$-$2\,^3P$ centroid transition frequency for ^{4}He, in MHz. The uncertainty due to approximate α^7 contribution is assumed to be 1 MHz, i.e., four times less than in our previous work [3]. FNS is a finite nuclear size and NPOL the nuclear polarizability corrections.

	$(m/M)^0$	$(m/M)^1$	$(m/M)^2$	Sum
α^2	$-276\,775\,637.536$	$102\,903.459$	-4.781	$-276\,672\,738.857$
α^4	$-69\,066.189$	-6.769	-0.003	$-69\,072.961$
α^5	$5\,234.163$	-0.186	$-$	$5\,233.978$
α^6	87.067	-0.029	$-$	87.039
α^7	$-8.0\,(1.0)$	$-$	$-$	$-8.0\,(1.0)$
FNS	3.427	$-$	$-$	3.427
NPOL	-0.002	$-$	$-$	-0.002
Present theory				$-276\,736\,495.41\,(1.00)$
Previous theory [3]				$-276\,736\,495.37\,(4.00)$
Exp. [4] + theory $^3P_0$-$^3P_2$ [5]				$-276\,736\,495.649\,(2)$

different parameters, which are obtained by minimization of that particular term.

IX. RESULTS AND DISCUSSION

In this paper, we derived the complete recoil contribution of order $\alpha^6 m^2/M$ to the energy levels of the triplet states of helium. The final result is given by Eqs. (81)–(88). It is a combination of various contributions of two types: (i) perturbations of the nonrelativistic wave function, energy, and Hamiltonian in the nonrecoil matrix elements by the nuclear kinetic energy operator; and (ii) expectation values of extra recoil operators. In Tables I and II the matrix elements of individual operators entering Eqs. (86)–(88) are presented.

Results of our numerical calculation of $E_i, \ldots, E_{vii}$ for the $2\,^3S_1$ and $2\,^3P_1$ states of the helium atom are presented in Table III. For the $2\,^3S_1$ state, the total $\alpha^6 m^2/M$ recoil correction is dominated by the Dirac δ-like term coming from the one-loop radiative correction [see Eq. (60)], the result for the ionization energy being -29.91 kHz. Contrary to that, for the $2\,^3P_1$ state, the contributions from $E_i, \ldots, E_{vii}$ are of similar size but opposite sign. So, the total correction to the ionization energy is only -1.11 kHz in this case. Contributions of individual recoil terms to the $2\,^3S$-$2\,^3P$ transition energy of helium are presented in Table IV.

The obtained results can be used to improve the theoretical prediction of the ^{3}He-^{4}He isotope shift of the $2\,^3S$-$2\,^3P$

TABLE V. Breakdown of theoretical contributions to the ^{3}He-^{4}He isotope shift of the $2\,^3S$-$2\,^3P$ centroid transition energy, for the point nucleus, in kHz. EMIX is an additional correction in ^{3}He due to the second-order hyperfine singlet-triplet mixing [9].

	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum
α^2	$33\,673\,018.7$	$-3\,640.6$	0.4	$33\,669\,378.5$
α^4	$-2\,214.9$	-2.4	$-$	$-2\,217.3$
α^5	-60.7	$-$	$-$	-60.7
α^6	-9.4	$-$	$-$	-9.4
α^7	$0.0\,(0.9)$	$-$	$-$	$0.0\,(0.9)$
NPOL	-1.1	$-$	$-$	-1.1
EMIX	$-$	54.6	$-$	54.6
Present theory				$33\,667\,149.3\,(0.9)$

transition. In this case the total $m^2/M\alpha^6$ recoil correction calculated in this work is -9.4 kHz. Individual contributions for the point nucleus are summarized in Table V. In order to estimate the uncertainty due to omitted higher-order $m^2/M\alpha^{7+}$ terms, we considered two typical contributions. One of them is the hydrogenic recoil $m^2/M\alpha^{7+}$ contribution (as evaluated in Ref. [20]) scaled by the expectation value of $\delta(r_1)$ operator, whereas the second is the hydrogenic $m\alpha^{7+}$ contribution with the $\delta(r_1)$ operator perturbed by $\vec{p}_1 \cdot \vec{p}_2$. Since both contributions happen to be small and of opposite sign, we took the largest one and multiplied it by a conservative coefficient of 2.

The updated theoretical result for the ^{3}He-^{4}He isotope shift allows us to improve the accuracy of determination of the nuclear charge radii difference $\delta R^2 = R^2(^3$He$) - R^2(^4$He$)$, derived from the $2\,^3S - 2\,^3P$ transition [9], namely $\delta R^2 = 1.069(3)$ fm^2 [21] and $\delta R^2 = 1.061(3)$ fm^2 [22]. This reduces slightly the discrepancy with the result from the $2\,^1S - 2\,^3S$ transition [9], $\delta R^2 = 1.028(11)$ fm^2 [23], but does not remove it entirely. In order to clarify this further, one needs to calculate the complete $\alpha^6 m^2/M$ recoil correction also for singlet states of helium.

ACKNOWLEDGMENTS

APPENDIX A: DIMENSIONAL REGULARIZATION

Since the triplet state wave function vanishes at $r_{12} = 0$, the electron-electron operators do not lead to any singularities, and thus can be calculated directly in $d = 3$. There are, however, several terms arising from the electron-nucleus recoil operators, which need to be treated within the dimensional regularization in order to isolate the singular part of the operator. We essentially repeat the approach from [2], so only a brief introduction to dimensional regularization is presented here. The dimension of space is assumed to be $d = 3 - 2\epsilon$.

The surface area of the d-dimensional unit sphere is

$$\Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}, \tag{A1}$$

and the d-dimensional Laplacian is

$$\nabla^2 = r^{1-d}\partial_r r^{d-1}\partial_r. \tag{A2}$$

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

$$\mathcal{V}(r) = \int \frac{d^dk}{(2\pi)^d}\frac{4\pi}{k^2}e^{i\vec{k}\cdot\vec{r}}$$
$$= \pi^{\epsilon-1/2}\Gamma(1/2-\epsilon)r^{2\epsilon-1} \equiv \frac{C_1}{r^{1-2\epsilon}}. \tag{A3}$$

The elimination of singularities will be performed in atomic units. In accordance with [2] this is achieved by transformation

$$\vec{r} \rightarrow (m\alpha)^{-1/(1+2\epsilon)}\vec{r} \tag{A4}$$

and pulling factors $m^{(1-2\epsilon)/(1+2\epsilon)}\alpha^{2/(1+2\epsilon)}$ and $m^{(1-10\epsilon)/(1+2\epsilon)}\alpha^{6/(1+2\epsilon)}$ from H and $H^{(6)}$. The nonrelativistic Hamiltonian of hydrogenlike systems is

$$H = \frac{\vec{p}^2}{2} - Z\frac{C_1}{r^{1-2\epsilon}}, \tag{A5}$$

and that of heliumlike systems is

$$H = \frac{\vec{p}_1^2}{2} + \frac{\vec{p}_2^2}{2} - Z\frac{C_1}{r_1^{1-2\epsilon}} - Z\frac{C_1}{r_2^{1-2\epsilon}} + \frac{C_1}{r_{12}^{1-2\epsilon}}. \tag{A6}$$

The solution of the stationary Schrödinger equation $H\phi = E\phi$ is denoted by ϕ; we will never need its explicit (and unknown) form in d dimensions. Instead, we will use only the generalized cusp condition to eliminate various singularities from matrix elements with relativistic operators. Namely, we expect that for small $r \equiv r_1$,

$$\phi(r) \approx \phi(0)(1 - Cr^\gamma), \tag{A7}$$

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

$$\left[-\frac{\nabla^2}{2} - Z\mathcal{V}(r)\right]\phi(0)(1 - Cr^\gamma) \approx E\phi(0)(1 - Cr^\gamma). \tag{A8}$$

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

$$\gamma = 1 + 2\epsilon, \tag{A9}$$

$$C = -\tfrac{1}{2}Z\pi^{\epsilon-1/2}\Gamma(-1/2-\epsilon). \tag{A10}$$

Therefore, the two-electron wave function around $r_1 = 0$ behaves as

$$\phi(\vec{r_1},\vec{r_2}) \approx \phi(r_1 = 0)\left(1 - Cr_1^{1+2\epsilon}\right). \tag{A11}$$

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

$$\mathcal{V}_2(r) = \int \frac{d^dk}{(2\pi)^d}\frac{4\pi}{k^4}e^{i\vec{k}\cdot\vec{r}}, \tag{A12}$$

$$\mathcal{V}_3(r) = \int \frac{d^dk}{(2\pi)^d}\frac{4\pi}{k^6}e^{i\vec{k}\cdot\vec{r}}. \tag{A13}$$

They can be obtained from the differential equations

$$-\nabla^2\mathcal{V}_2(r) = \mathcal{V}(r), \tag{A14}$$

$$-\nabla^2\mathcal{V}_3(r) = \mathcal{V}_2(r), \tag{A15}$$

with the result

$$\mathcal{V}_2(r) = C_2 r^{1+2\epsilon}, \tag{A16}$$

$$\mathcal{V}_3(r) = C_3 r^{3+2\epsilon}, \tag{A17}$$

where

$$C_2 = \tfrac{1}{4}\pi^{\epsilon-1/2}\Gamma(-1/2-\epsilon), \tag{A18}$$

$$C_3 = \tfrac{1}{32}\pi^{\epsilon-1/2}\Gamma(-3/2-\epsilon). \tag{A19}$$

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

$$\int \frac{d^dk}{(2\pi)^d}\frac{4\pi}{k^4}\left(\delta^{ij} - \frac{k^ik^j}{k^2}\right)e^{i\vec{k}\cdot\vec{r}} = \delta^{ij}\mathcal{V}_2 + \partial^i\partial^j\mathcal{V}_3 = \pi^{\epsilon-1/2}r^{-1+2\epsilon}\left[\frac{3}{16}\delta^{ij}\Gamma(-1/2-\epsilon)r^2 + \frac{1}{8}\Gamma(1/2-\epsilon)r^ir^j\right]$$
$$\equiv \left[\frac{1}{8r}(r^ir^j - 3\delta^{ij}r^2)\right]_\epsilon = W_\epsilon^{ij}, \tag{A20}$$

and

$$\int \frac{d^dk}{(2\pi)^d}\frac{4\pi}{k^2}\left(\delta^{ij} - \frac{k^ik^j}{k^2}\right)e^{i\vec{k}\cdot\vec{r}} = \delta^{ij}\mathcal{V} + \partial^i\partial^j\mathcal{V}_2 = \pi^{\epsilon-1/2}r^{-3+2\epsilon}\left[\frac{1}{2}\delta^{ij}\Gamma(1/2-\epsilon)r^2 + \Gamma(3/2-\epsilon)r^ir^j\right]$$
$$\equiv \left[\frac{1}{2r^3}(\delta^{ij}r^2 + r^ir^j)\right]_\epsilon. \tag{A21}$$

Now we are ready to remove the singularities from matrix elements of various operators. By convention we pull out a common factor $[(4\pi)^\epsilon \Gamma(1+\epsilon)]^2$ from all matrix elements. Then, for example, the matrix element $\langle [Z^3/r^3]_\epsilon \rangle$, with $r = r_1$, is

$$\left\langle \left[\frac{Z}{r}\right]^3_\epsilon \right\rangle = Z^3 C_1^3 \int d^d r \phi^2(r) r^{-3+6\epsilon} = Z^3 C_1^3 \phi^2(0) \int_0^a d^d r r^{-3+6\epsilon} + Z^3 \int_a d^3 r \phi^2(r) r^{-3} = \left\langle \frac{Z^3}{r^3} \right\rangle + Z^3 \langle \pi \delta^d(r) \rangle \left(\frac{1}{\epsilon} + 2\right), \tag{A22}$$

where

$$\left\langle \frac{1}{r^3} \right\rangle = \lim_{a \to 0} \int d^3 r \phi^2(r) \left[\frac{1}{r^3}\Theta(r-a) + 4\pi\delta^3(r)(\gamma + \ln a)\right] \tag{A23}$$

is the regularized form of $1/r^3$. The matrix element $\langle [Z^2/r^4]_\epsilon \rangle$ is

$$\left\langle \left[\frac{Z^2}{r^4}\right]_\epsilon \right\rangle = Z^2 C_1^2 \int d^d r \phi^2(r) [\nabla(r^{-1+2\epsilon})]^2 = Z^2 C_1^2 (-1 + 2\epsilon)^2 \phi^2(0) \int_0^a d^d r r^{-4+4\epsilon} (1 - C r^{1+2\epsilon})^2 + Z^2 \int_a d^3 r \phi^2(r) r^{-4}$$

$$= \left\langle \frac{Z^2}{r^4} \right\rangle + Z^3 \langle \pi \delta^d(r) \rangle \left(-\frac{2}{\epsilon} + 8\right). \tag{A24}$$

$\langle 1/r^4 \rangle$ in the above is again a regularized form of $1/r^4$, where $1/a$ and $\ln a + \gamma$ are dropped, analogous to the $\langle 1/r^3 \rangle$ term. However, we do not need its explicit form because we can always rewrite it in terms of $\langle Z^3/r^3 \rangle$ using expectation value identities. Similarly,

$$Z^2 \left\langle \left[\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\right]_\epsilon \nabla^i \nabla^j \left[\frac{1}{r}\right]_\epsilon \right\rangle = \left\langle \left[\frac{Z^2}{r^4}\right]_\epsilon \right\rangle + 2Z^3 \langle \pi \delta^d(r) \rangle, \tag{A25}$$

$$-Z^3 \left\langle W_\epsilon^{ij} \nabla^i \left[\frac{1}{r}\right]_\epsilon \nabla^j \left[\frac{1}{r}\right]_\epsilon \right\rangle = \frac{1}{4}\left\langle \left[\frac{Z^3}{r^3}\right]_\epsilon \right\rangle - \frac{7Z^3}{4}\langle \pi \delta^d(r) \rangle, \tag{A26}$$

and

$$-iZ^2 \left\langle \nabla^i \left[\frac{1}{r}\right]_\epsilon \left[\frac{p^2}{2}, W_\epsilon^{ij}\right] p^j \right\rangle = \frac{1}{8}\left\langle p^i \frac{Z^2}{r^4}(\delta^{ij} r^2 - 3r^i r^j) p^j \right\rangle + \frac{1}{8}\left\langle \left[\frac{Z^2}{r^4}\right]_\epsilon \right\rangle + \frac{3Z^3}{4}\langle \pi \delta^d(r) \rangle. \tag{A27}$$

The last singular term appearing in these calculations is

$$\left\langle \frac{\sigma^{ij}\sigma^{ij}}{8d}\left[\frac{Z^2}{r^4}\right]_\epsilon \right\rangle = \left\langle \frac{d-1}{8}\left[\frac{Z^2}{r^4}\right]_\epsilon \right\rangle = \frac{1}{4}\left\langle \left[\frac{Z^2}{r^4}\right]_\epsilon \right\rangle + \frac{Z^3}{2}\langle \pi \delta^3(r) \rangle, \tag{A28}$$

where we used the identity

$$\sigma^{ij}\sigma^{ij} = d(d-1). \tag{A29}$$

All the singular terms can now be expressed in terms $\langle [Z^3/r^3]_\epsilon \rangle$ and $\langle [Z^2/r^4]_\epsilon \rangle$ and using the expectation value identity

$$\left[\frac{Z^2}{r_1^4}\right]_\epsilon = \vec{p}_1 \frac{Z^2}{r_1^2} \vec{p} - 2\left(E + \frac{Z}{r_2} - \frac{1}{r} - \frac{p_2^2}{2}\right)\frac{Z^2}{r_1^2} - 2\left[\frac{Z^3}{r_1^3}\right]_\epsilon, \tag{A30}$$

they eventually cancel out.

APPENDIX B: DERIVATION OF $\delta_M A_2$

Let us present here again the terms contributing to A_2^M:

$$A_2^M = \langle Q(H_M - E_M)Q \rangle_M + 2E_M^{(4)}\langle Q \rangle_M - 2\langle H_M^{(4)}Q \rangle_M + \frac{m}{M}\{2\langle Q(H-E)\delta_M Q \rangle + 2E^{(4)}\langle \delta_M Q \rangle - 2\langle H_A \delta_M Q \rangle\}$$

$$= A_{2a}^M + A_{2b}^M + A_{2c}^M + A_{2d}^M + A_{2e}^M + A_{2f}^M. \tag{B1}$$

The first three terms contain both recoil and nonrecoil parts, while the latter three are recoil only terms. Individual terms can be reduced by using expectation value identities,

$$A_{2a}^M = \langle Q(H_M - E_M)Q \rangle_M = \frac{1}{2}\langle [Q, [H_M - E_M, Q]] \rangle_M = \frac{1}{2}\langle (\nabla_1 Q)^2 + (\nabla_2 Q)^2 \rangle_M + \frac{1}{4}\frac{m}{M}\langle [Q, [\vec{P}^2, Q]] \rangle$$

$$= \left\langle \frac{1}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{1}{4r^4} - \frac{1}{8}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right) \cdot \frac{\vec{r}}{r^3} \right\rangle_M + \frac{m}{M}\left\langle \frac{1}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{1}{16}\frac{Z^2 \vec{r}_1 \cdot \vec{r}_2}{r_1^3 r_2^3} \right\rangle, \tag{B2}$$

$$A_{2b}^M = 2E^{(4)}\langle Q\rangle_M + 2\delta_M E^{(4)}\left(\frac{E}{2} + \left\langle\frac{1}{4r}\right\rangle\right), \tag{B3}$$

$$A_{2c}^M = -2\langle H_M^{(4)}Q\rangle_M = X_1 + X_2 + X_3 + X_4, \tag{B4}$$

where

$$X_4 = -2\langle\delta_M H^{(4)}Q\rangle = \sum_a\left\langle -\frac{Z}{4}P^i\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)p_a^j - \frac{Z^2}{8}\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left[p_a^i,\left[p_a^j,\frac{1}{r_a}\right]\right]\right\rangle$$

$$= \sum_a\left\langle -\frac{Z}{4}P^i\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)p_a^j + \frac{1}{4}\frac{Z^2}{r_a^4} + \frac{Z^3}{2}\pi\delta^3(r_a)\right\rangle. \tag{B5}$$

Here we used the identity (A25) from Appendix A to rewrite the singular term in the second equality in Eq. (B5) as

$$\left\langle\frac{Z^2}{8r_a}\left(\delta^{ij} + \frac{r_a^i r_a^j}{r_a^2}\right)\nabla_a^i\nabla_a^j\frac{1}{r_a}\right\rangle = \left\langle\frac{1}{4}\frac{Z^2}{r_a^4} + \frac{Z^3}{2}\pi\delta^3(r_a)\right\rangle. \tag{B6}$$

Further (using $\langle\delta^3(x)/x\rangle = 0$, which is valid in dimensional regularization),

$$X_3 = -\left\langle[Z\pi\delta^3(r_1) + Z\pi\delta^3(r_2)]Q\right\rangle_M = \left\langle\frac{Z(Z-2)\pi}{4}\left[\frac{\delta^3(r_1)}{r_2} + \frac{\delta^3(r_2)}{r_1}\right]\right\rangle_M, \tag{B7}$$

$$X_2 = \left\langle p_1^i\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j Q\right\rangle_M = \left\langle -\frac{1}{4}p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j + \frac{1}{2}\left[p_1^i,\left[p_2^j,\frac{1}{r}\right]\right]\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\right\rangle_M, \tag{B8}$$

$$X_1 = \frac{1}{4}\langle[(p_1^2 + p_2^2) - 2p_1^2 p_2^2]Q\rangle_M = \frac{1}{4}\langle(p_1^2 + p_2^2)Q(p_1^2 + p_2^2) + \frac{1}{2}[p_1^2 + p_2^2,[Q,p_1^2 + p_2^2]] - 2p_1^2 Q p_2^2 - [p_1^2,[p_2^2,Q]]\rangle_M$$

$$= X_{1A} + X_{1B} + X_{1C} + X_{1D}, \tag{B9}$$

where

$$X_{1A} = \langle(E-V)^2 Q\rangle_M + 2\frac{m}{M}\left\langle(E-V)Q\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\right\rangle$$

$$= \langle(E-V)^2 Q\rangle_M + \frac{m}{M}\left\langle 2\delta_M E(E-V)Q - \vec{P}(E-V)Q\vec{P} - \frac{1}{2}[\vec{P},[\vec{P},(E-V)Q]]\right\rangle, \tag{B10}$$

$$X_{1B} = -\frac{1}{4}\left\langle\left[V + \frac{m}{M}\frac{\vec{P}^2}{2},\left[p_1^2 + p_2^2,Q\right]\right]\right\rangle_M = \left\langle -\frac{1}{8}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{1}{2r^4}\right\rangle_M$$

$$+ \frac{m}{M}\left\langle\frac{1}{8}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{1}{4}\frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right\rangle, \tag{B11}$$

$$X_{1C} = \left\langle\frac{1}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2 - \frac{1}{4}p_1^2\frac{1}{r}p_2^2\right\rangle_M, \tag{B12}$$

$$X_{1D} = \left\langle -\frac{1}{8}\left[p_1^2,\left[p_2^2,\frac{1}{r}\right]\right]\right\rangle_M. \tag{B13}$$

The remaining terms are

$$A_{2d}^M = \frac{m}{M}\langle[Q,[H-E,\delta_M Q]]\rangle = \frac{m}{M}\langle(\nabla_1 Q)(\nabla_1\delta_M Q) + (\nabla_2 Q)(\nabla_2\delta_M Q)\rangle$$

$$= \frac{m}{M}\left\langle -\frac{3}{16}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle, \tag{B14}$$

$$A_{2e}^M = \frac{m}{M}\left(\frac{3}{2}E^{(4)}\left\langle\frac{1}{r}\right\rangle - 3EE^{(4)}\right), \tag{B15}$$

$$A_{2f}^M = -2\frac{m}{M}\langle H_A\delta_M Q\rangle = F_1 + F_2 + F_3, \tag{B16}$$

where

$$F_3 = -\frac{m}{M}\left\langle \frac{3Z^2\pi}{4}\left(\frac{\delta^3(r_1)}{r_2} + \frac{\delta^3(r_2)}{r_1}\right)\right\rangle, \tag{B17}$$

$$F_2 = \frac{m}{M}\left\langle \frac{3}{4}p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j\right\rangle, \tag{B18}$$

$$F_1 = \frac{1}{4}\frac{m}{M}\left\langle\left[(p_1^2 + p_2^2)^2 - 2p_1^2 p_2^2\right]\delta Q\right\rangle = \frac{1}{4}\frac{m}{M}\left\langle (p_1^2 + p_2^2)\delta Q(p_1^2 + p_2^2) + \frac{1}{2}\left[p_1^2 + p_2^2, \left[p_1^2 + p_2^2, \delta Q\right]\right] - 2p_1^2\delta Q p_2^2\right\rangle$$
$$= F_{1A} + F_{1B} + F_{1C}, \tag{B19}$$

and where

$$F_{1A} = \frac{m}{M}\left\langle \frac{3}{4}(E-V)^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\right\rangle, \tag{B20}$$

$$F_{1B} = \frac{m}{M}\left\langle \frac{3}{8}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle, \tag{B21}$$

$$F_{1C} = -\frac{m}{M}\left\langle \frac{3}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2\right\rangle. \tag{B22}$$

Taking now only the recoil part of terms $A_{2a}^M, \dots, A_{2f}^M$ we obtain the results

$$\delta_M A_{2a} = \delta_M\left\langle \frac{1}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{1}{4r^4} - \frac{1}{8}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle + \left\langle \frac{1}{32}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{1}{16}\frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right\rangle, \tag{B23}$$

$$\delta_M A_{2b} = 2E^{(4)}\delta_M\langle Q\rangle + 2\delta_M E^{(4)}\left(\frac{E}{2} + \left\langle\frac{1}{4r}\right\rangle\right), \tag{B24}$$

$$\delta_M A_{2c} = \delta_M\left\langle \frac{Z(Z-2)\pi}{4}\left[\frac{\delta^3(r_1)}{r_2} + \frac{\delta^3(r_2)}{r_1}\right] - \frac{1}{4}p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j\right.$$
$$+ \frac{1}{2}\left[p_1^i, \left[p_2^j, \frac{1}{r}\right]\right]\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right) + (E-V)^2 Q - \frac{1}{8}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right)$$
$$+ \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{1}{2r^4} + \frac{1}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2 - \frac{1}{4}p_1^2\frac{1}{r}p_2^2 - \frac{1}{8}\left[p_1^2, \left[p_2^2, \frac{1}{r}\right]\right]\right\rangle$$
$$+ \left\langle -\frac{Z}{4}\sum_a P^i\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)p_a^j + \frac{3}{8}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right)\right.$$
$$+ \frac{Z^3}{2}[\pi\delta^3(r_1) + \pi\delta^3(r_2)] + 2\delta_M E(E-V)Q - \vec{P}(E-V)Q\vec{P}$$
$$\left. - \frac{1}{2}[\vec{P}, [\vec{P}, (E-V)Q]] + \frac{1}{4}\frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right\rangle, \tag{B25}$$

$$\delta_M A_{2d} = \left\langle -\frac{3}{16}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle, \tag{B25}$$

$$\delta_M A_{2e} = \frac{3}{2}E^{(4)}\left\langle\frac{1}{r}\right\rangle - 3EE^{(4)}, \tag{B26}$$

$$\delta_M A_{2f} = \left\langle -\frac{3Z^2\pi}{4}\left[\frac{\delta^3(r_1)}{r_2} + \frac{\delta^3(r_2)}{r_1}\right] + \frac{3}{4}p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j\right.$$
$$\left. + \frac{3}{4}(E-V)^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{3}{8}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{3}{8}p_1^2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)p_2^2\right\rangle. \tag{B27}$$

Summing all of the recoil parts $\delta_M A_{2a}, \dots, \delta_M A_{2f}$ and using the identity

$$[\vec{P}, [\vec{P}, (E-V)Q]] = \frac{1}{2}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3} - \left(E + \frac{2Z-3}{r_2}\right)\pi Z\delta^3(r_1) - \left(E + \frac{2Z-3}{r_1}\right)\pi Z\delta^3(r_2), \tag{B28}$$

we get the final result (71).

APPENDIX C: DERIVATION OF $\delta_M B$

In the following we perform only derivation of terms $B_1^M, \ldots, B_7^M$ defined as

$$B_i^M = \langle H_i^M \rangle_M, \tag{C1}$$

and the evaluation of the remaining terms is trivial since they contain only Dirac δ-like contributions. The expectation value of the kinetic term

$$H_1^M = \tfrac{1}{16}\left(p_1^6 + p_2^6\right) \tag{C2}$$

is

$$\begin{aligned}
B_1^M &= \frac{1}{16}\langle(p_1^2 + p_2^2)^3 - 3p_1^2 p_2^2 (p_1^2 + p_2^2)\rangle_M = \Bigg\langle \frac{1}{8}\left[V + \frac{m}{M}\frac{\vec{P}^2}{2}, \left[p_1^2 + p_2^2, V\right]\right] + \frac{1}{2}\left[E - V + \frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\right]^3 \\
&\quad - \frac{3}{8}p_1^2 p_2^2 \left[E - V + \frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\right]\Bigg\rangle_M = \Bigg\langle \frac{1}{4}[(\nabla_1 V)^2 + (\nabla_2 V)^2] + \frac{1}{2}(E - V)^3 - \frac{3}{8}p_1^2(E - V)p_2^2 \\
&\quad + \frac{3}{16}\left[p_1^2, [p_2^2, V]\right]\Bigg\rangle_M + \frac{m}{M}\Bigg\langle \frac{3}{2}(E - V)^2\left(\delta_M E - \frac{\vec{P}^2}{2}\right) - \frac{3}{8}p_1^2 p_2^2\left(\delta_M E - \frac{\vec{P}^2}{2}\right) \\
&\quad - \frac{1}{2}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - \frac{Z^2 \vec{r}_1 \cdot \vec{r}_2}{r_1^3 r_2^3}\Bigg\rangle.
\end{aligned} \tag{C3}$$

The recoil correction $\delta_M B_1$ is then

$$\begin{aligned}
\delta_M B_1 &= \delta_M \Bigg\langle \frac{Z^2}{4r_1^4} + \frac{Z^2}{4r_2^4} - \frac{1}{2}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + \frac{1}{2r^4} + \frac{1}{2}(E - V)^3 + \frac{3}{16}\left[p_1^2, \left[p_2^2, \frac{1}{r}\right]\right] - \frac{3}{8}p_1^2(E - V)p_2^2 \Bigg\rangle \\
&\quad + \Bigg\langle \frac{3}{2}\delta_M E(E - V)^2 - \frac{3}{4}\vec{P}(E - V)^2\vec{P} + \frac{1}{4}\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) + \frac{1}{2}\frac{Z^2 \vec{r}_1 \cdot \vec{r}_2}{r_1^3 r_2^3} \\
&\quad - 3\left(E + \frac{Z - 1}{r_2}\right)\pi Z\delta^3(r_1) + (1 \leftrightarrow 2) - \frac{3}{8}p_1^2 p_2^2\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\Bigg\rangle.
\end{aligned} \tag{C4}$$

Here we used

$$[\vec{P}, [\vec{P}, (E - V)^2]] = -2\left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right) - 4\frac{Z^2 \vec{r}_1 \cdot \vec{r}_2}{r_1^3 r_2^3} + 2(E - V)[4\pi Z\delta^3(r_1) + 4\pi Z\delta^3(r_2)]. \tag{C5}$$

The operator H_2^M is

$$H_2^M = \sum_a \frac{(\nabla_a V)^2}{8} + \frac{5}{128}[p_a^2, [p_a^2, V]] - \frac{3}{64}\{p_a^2, \nabla_a^2 V\}. \tag{C6}$$

For the sake of simplicity we split its expectation value into three parts,

$$B_2^M = \Bigg\langle \frac{1}{8}[(\nabla_1 V)^2 + (\nabla_2 V)^2] + \frac{5}{128}\left([p_1^2, [p_1^2, V]] + [p_2^2, [p_2^2, V]]\right) - \frac{3}{32}\left(p_1^2 \nabla_1^2 V + p_2^2 \nabla_2^2 V\right)\Bigg\rangle_M = B_{2a}^M + B_{2b}^M + B_{2c}^M. \tag{C7}$$

Term $B_{2a}^M = \frac{1}{8}\langle(\nabla_1 V)^2 + (\nabla_2 V)^2\rangle_M$ needs no further reduction. The remaining terms could be simplified to

$$\begin{aligned}
B_{2b}^M &= \frac{5}{128}\langle[p_1^2 + p_2^2, [p_1^2, V]] + [p_1^2 + p_2^2, [p_2^2, V]] - 2[p_1^2, [p_2^2, V]]\rangle_M \\
&= -\frac{5}{64}\Bigg\langle\left[V + \frac{m}{M}\frac{\vec{P}^2}{2}, [p_1^2 + p_2^2, V]\right] + [p_1^2, [p_2^2, V]]\Bigg\rangle_M,
\end{aligned} \tag{C8}$$

$$\begin{aligned}
B_{2c}^M &= -\frac{3}{32}\langle(p_1^2 + p_2^2)\nabla_1^2 V + (p_1^2 + p_2^2)\nabla_2^2 V - p_2^2\nabla_1^2 V - p_1^2\nabla_2^2 V\rangle_M \\
&= -\frac{3}{8}\pi Z\Bigg\langle 2\left[E - V + \frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\right][\delta^3(r_1) + \delta^3(r_2)] - p_1^2\delta^3(r_2) - p_2^2\delta^3(r_1)\Bigg\rangle_M.
\end{aligned} \tag{C9}$$

Taking now only the recoil parts of individual terms we get

$$\delta_M B_{2a} = \frac{1}{8} \delta_M \langle (\boldsymbol{\nabla}_1 V)^2 + (\boldsymbol{\nabla}_2 V)^2 \rangle, \tag{C10}$$

$$\delta_M B_{2b} = -\frac{5}{32} \delta_M \left\langle (\boldsymbol{\nabla}_1 V)^2 + (\boldsymbol{\nabla}_2 V)^2 + \frac{1}{2} \left[p_1^2, [p_2^2, V] \right] \right\rangle + \frac{5}{64} \langle [V, [\vec{P}^2, V]] \rangle, \tag{C11}$$

$$\delta_M B_{2c} = -\frac{3}{8} \pi Z \delta_M \left\langle 2 \left(E + \frac{Z-1}{r_2} \right) \delta^3(r_1) + 2 \left(E + \frac{Z-1}{r_1} \right) \delta^3(r_2) - p_1^2 \delta^3(r_2) - p_2^2 \delta^3(r_1) \right\rangle$$

$$- \frac{3}{4} \left\langle \left(\delta_M E - \frac{\vec{P}^2}{2} \right) \pi Z [\delta^3(r_1) + \delta^3(r_2)] \right\rangle. \tag{C12}$$

The term $\delta_M B_2$ is then the sum of these three terms and takes the form

$$\delta_M B_2 = \delta_M \left\langle -\frac{1}{32} \left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4} \right) + \frac{1}{16} \left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3} \right) \cdot \frac{\vec{r}}{r^3} - \frac{1}{16r^4} - \frac{5}{64} \left[p_1^2, \left[p_2^2, \frac{1}{r} \right] \right] \right.$$

$$- \frac{3}{8} \pi Z \left[2 \left(E + \frac{Z-1}{r_2} \right) \delta^3(r_1) + 2 \left(E + \frac{Z-1}{r_1} \right) \delta^3(r_2) - p_1^2 \delta^3(r_2) - p_2^2 \delta^3(r_1) \right] \right\rangle$$

$$+ \left\langle \frac{5}{32} \left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4} \right) + \frac{5}{16} \frac{Z^2 \vec{r}_1 \cdot \vec{r}_2}{r_1^3 r_2^3} - \frac{3}{4} \left(\delta_M E - E + \frac{1-Z}{r_2} - \vec{p}_1 \cdot \vec{p}_2 \right) \pi Z \delta^3(r_1) + (1 \leftrightarrow 2) \right\rangle. \tag{C13}$$

The operator H_3^M is

$$H_3^M = \frac{1}{64} \left\{ -4\pi \nabla^2 \delta^3(r) + \frac{4}{3} p_1^i \left[\frac{2}{3} \delta^{ij} 4\pi \delta^3(r) + \frac{1}{r^5} (3r^i r^j - \delta^{ij} r^2) \right] p_2^j \right\}. \tag{C14}$$

Here we used the identity valid for triplets,

$$\sigma_1^{ij} \sigma_2^{ij} = 2\vec{\sigma}_1 \cdot \vec{\sigma}_2 = 2, \tag{C15}$$

to evaluate the spin product in H_3^M. Since there is no singular term, we can use $d = 3$ representation and the scalar product in the evaluation of the spin part. This will be assumed also in all the other terms where the spin product appears. In the case where the term containing the spin product is singular and one has to use its d-dimensional form to evaluate such term, it will be explicitly stated. The expectation value of H_3^M is

$$B_3^M = \left\langle -\frac{1}{16} \pi \nabla^2 \delta^3(r) + \frac{1}{48} p_1^i \left[\frac{2}{3} \delta^{ij} 4\pi \delta^3(r) + \frac{1}{r^5} (3r^i r^j - \delta^{ij} r^2) \right] p_2^j \right\rangle_M$$

$$= \left\langle -\frac{1}{48} p_1^i \frac{1}{r^5} (\delta^{ij} r^2 - 3r^i r^j) p_2^j - \frac{13}{144} \pi \nabla^2 \delta^3(r) \right\rangle_M, \tag{C16}$$

where we used the expectation value identity

$$\langle \vec{p}_1 \delta^3(r) \vec{p}_2 \rangle = -\frac{1}{2} \langle \nabla^2 \delta^3(r) \rangle. \tag{C17}$$

Further, with the help of identity

$$p_1^i \frac{1}{r^5} (\delta^{ij} r^2 - 3r^i r^j) p_2^j = -\frac{1}{4} \left[p_1^2, \left[p_2^2, \frac{1}{r} \right] \right] - \frac{\pi}{3} \nabla^2 \delta^3(r), \tag{C18}$$

we get the resulting recoil correction $\delta_M B_3$

$$\delta_M B_3 = \delta_M \left\langle \frac{1}{192} \left[p_1^2, \left[p_2^2, \frac{1}{r} \right] \right] - \frac{\pi}{12} \nabla^2 \delta^3(r) \right\rangle. \tag{C19}$$

We split the correction due to operator $H_4^M = H_4 + \frac{m}{M} \delta_M H_4$ into two parts: the recoil correction to operator H_4, which we denote as B_{4a}^M, and the expectation value of the recoil part $\delta_M H_4$, which we denote as B_{4b}^M. The nonrecoil part of the operator H_4^M is (omitting the part with $\delta^3(r)$, which does not contribute for triplet states)

$$H_4 = \frac{1}{4} (p_1^2 + p_2^2) p_1^i \frac{1}{r} \left(\delta^{ij} + \frac{r^i r^j}{r^2} \right) p_2^j. \tag{C20}$$

The expectation value of this is

$$
\begin{aligned}
B_{4a}^{M} &= \frac{1}{2}\left\langle (E-V)p_1^i \frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j \right\rangle_M + \frac{m}{2M}\left\langle \left(\delta_M E - \frac{\vec{P}^2}{2}\right)p_1^i \frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j \right\rangle \\
&= \frac{1}{2}\left\langle p_1^i (E-V)\frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j - \frac{1}{2r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)\left[p_1^i,\left[p_2^j,\frac{1}{r}\right]\right] \right\rangle_M + \frac{m}{2M}\left\langle \left(\delta_M E - \frac{\vec{P}^2}{2}\right)p_1^i \frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j \right\rangle .
\end{aligned}
\tag{C21}
$$

Recoil correction $\delta_M B_{4a}$ is then

$$
\delta_M B_{4a} = \delta_M \left\langle \frac{1}{2}p_1^i (E-V)\frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j - \frac{1}{2r^4} \right\rangle + \left\langle \frac{1}{2}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)p_1^i \frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j \right\rangle .
\tag{C22}
$$

The recoil part of H_4^M is

$$
\delta_M H_4 = \frac{Z}{4}\left[p_1^2 p_1^i \left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)P^j + p_2^2 p_2^i \left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)P^j \right].
\tag{C23}
$$

The expectation value of this operator can then be reduced to

$$
\begin{aligned}
\delta_M B_{4b} &= \frac{Z}{4}\left\langle 2(E-V)\left[p_1^i\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)P^j + p_2^i\left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)P^j \right] - \left[p_2^2 p_1^i\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)P^j + p_1^2 p_2^i\left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)P^j \right] \right\rangle \\
&= \left\langle \frac{Z}{2}\left[p_1^i(E-V)\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)P^j + p_2^i(E-V)\left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)P^j \right] - \frac{1}{2}\left(\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right) - Z^3[\pi\delta^3(r_1)+\pi\delta^3(r_2)] \right. \\
&\quad \left. - \frac{Z}{4}\left[p_1^i p_2^k\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)p_2^k P^j + p_2^i p_1^k\left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)p_1^k P^j \right] \right\rangle .
\end{aligned}
\tag{C24}
$$

When commuting $E-V$ we used Eq. (A25) of Appendix A, in particular,

$$
\left\langle \frac{Z}{4}\left[p_a^i,[P^j,E-V]\right]\left(\frac{\delta^{ij}}{r_a}+\frac{r_a^i r_a^j}{r_a^3}\right) \right\rangle = \left\langle -\frac{1}{2}\frac{Z^2}{r_a^4} - Z^3\pi\delta^3(r_a) \right\rangle .
\tag{C25}
$$

The operator H_5^M is

$$
H_5^M = -\frac{1}{6}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + \frac{1}{3r^4} + \frac{1}{48}\left(\left[p_1^2,\left[p_1^2,\frac{1}{r}\right]\right]+\left[p_2^2,\left[p_2^2,\frac{1}{r}\right]\right]\right),
\tag{C26}
$$

where the spin product was again resolved using identity (C15). The expectation value is

$$
B_5^M = \left\langle -\frac{1}{6}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + \frac{1}{3r^4} - \frac{1}{24}\left(\left[V,\left[p_1^2+p_2^2,\frac{1}{r}\right]\right]+\left[p_1^2,\left[p_2^2,\frac{1}{r}\right]\right]\right) \right\rangle_M .
\tag{C27}
$$

The recoil correction is then

$$
\delta_M B_5 = \delta_M \left\langle -\frac{1}{12}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} + \frac{1}{6r^4} - \frac{1}{24}\left[p_1^2,\left[p_2^2,\frac{1}{r}\right]\right] \right\rangle .
\tag{C28}
$$

The operator H_6^M contains the recoil part $\delta_M H_6$, so we again split the calculation into two parts: the recoil correction due to H_6, denoted as $\delta_M B_{6a}$, and the expectation value of $\delta_M H_6$, which we denote as $\delta_M B_{6b}$. The nonrecoil part of the operator H_6^M is

$$
H_6 = \frac{1}{8}p_1^i \frac{1}{r^2}\left(\delta^{ij}+3\frac{r^i r^j}{r^2}\right)p_1^j + \frac{1}{8}p_2^i \frac{1}{r^2}\left(\delta^{ij}+3\frac{r^i r^j}{r^2}\right)p_2^j + \frac{1}{2r^4},
\tag{C29}
$$

where we used the identity from Eq. (A29). The recoil correction due to this operator is simply

$$
\delta_M B_{6a} = \delta_M \left\langle \frac{1}{8}p_1^i \frac{1}{r^2}\left(\delta^{ij}+3\frac{r^i r^j}{r^2}\right)p_1^j + \frac{1}{8}p_2^i \frac{1}{r^2}\left(\delta^{ij}+3\frac{r^i r^j}{r^2}\right)p_2^j + \frac{1}{2r^4} \right\rangle .
\tag{C30}
$$

The recoil part of operator H_6^M contains a singular term with spin product, which we have to evaluate using dimensional regularization. In particular, we use Eq. (A28) to get

$$
\left\langle \frac{\sigma_a^{ij}\sigma_a^{ij}}{24}\frac{Z^2}{r_a^4} \right\rangle = \left\langle \frac{1}{4}\frac{Z^2}{r_a^4} + \frac{Z^3}{2}\pi\delta^3(r_a) \right\rangle .
\tag{C31}
$$

Using this and (C15), the expectation value of $\delta_M H_6$ can be evaluated to

$$\delta_M B_{6b} = \left\langle \frac{Z}{4} \left[p_2^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) \left(\frac{\delta^{jk}}{r_1} + \frac{r_1^j r_1^k}{r_1^3} \right) + p_1^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) \left(\frac{\delta^{jk}}{r_2} + \frac{r_2^j r_2^k}{r_2^3} \right) \right] P^k \right.$$

$$+ \frac{1}{4} \left(\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4} + \frac{2}{3} \frac{Z^2 \vec{r}_1 \cdot \vec{r}_2}{r_1^3 r_2^3} \right) + \frac{Z^3}{2} [\pi \delta^3(r_1) + \pi \delta^3(r_2)]$$

$$\left. + \frac{Z^2}{8} \left[p_1^i \frac{1}{r_1^2} \left(\delta^{ij} + 3 \frac{r_1^i r_1^j}{r_1^2} \right) p_1^j + p_2^i \frac{1}{r_2^2} \left(\delta^{ij} + 3 \frac{r_2^i r_2^j}{r_2^2} \right) p_2^j + 2 p_1^i \left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3} \right) \left(\frac{\delta^{jk}}{r_2} + \frac{r_2^j r_2^k}{r_2^3} \right) p_2^k \right] \right\rangle. \quad \text{(C32)}$$

Finally, we calculate correction due to the operator $H_7^M = H_{7a}^M + H_{7c}^M + H_{7d}^M$. We split it correspondingly into three parts, $B_7^M = B_{7a}^M + B_{7c}^M + B_{7d}^M$. The operator H_{7a}^M reads

$$H_{7a}^M = -\frac{1}{8} \left\{ [p_1^i, V] \left(\frac{r^i r^j}{r} - 3\delta^{ij} r \right) [V, p_2^j] + [p_1^i, V] \left[\frac{p_2^2}{2}, \frac{r^i r^j}{r} - 3\delta^{ij} r \right] p_2^j \right.$$

$$\left. + p_1^i \left[\frac{r^i r^j}{r} - 3\delta^{ij} r, \frac{p_1^2}{2} \right] [V, p_2^j] + p_1^i \left[\frac{p_2^2}{2}, \left[\frac{r^i r^j}{r} - 3\delta^{ij} r, \frac{p_1^2}{2} \right] \right] p_2^j \right\}. \quad \text{(C33)}$$

The recoil correction due to this operator is

$$\delta_M B_{7a} = \delta_M \left\langle -\frac{1}{8} \frac{Z r_1^i}{r_1^3} \frac{Z r_2^j}{r_2^3} \left(\frac{r^i r^j}{r} - 3\delta^{ij} r \right) + \frac{1}{4} \left(\frac{Z \vec{r}_1}{r_1^3} - \frac{Z \vec{r}_2}{r_2^3} \right) \cdot \frac{\vec{r}}{r^2} - \frac{1}{4r^3} \right.$$

$$- \frac{Z}{8} \left[\frac{r_1^i}{r_1^3} p_2^k \left(\delta^{jk} \frac{r^i}{r} - \delta^{ik} \frac{r^j}{r} - \delta^{ij} \frac{r^k}{r} - \frac{r^i r^j r^k}{r^3} \right) p_2^j + (1 \leftrightarrow 2) \right] + \frac{1}{8} \left[p_2^j \frac{1}{r^4} (\delta^{jk} r^2 - 3 r^j r^k) p_2^k + (1 \leftrightarrow 2) \right] + \frac{1}{4r^4}$$

$$\left. + \frac{1}{8} p_1^k p_2^l \left[-\frac{\delta^{il} \delta^{jk}}{r} + \frac{\delta^{ik} \delta^{jl}}{r} - \frac{\delta^{ij} \delta^{kl}}{r} - \frac{\delta^{jl} r^i r^k}{r^3} - \frac{\delta^{ik} r^j r^l}{r^3} + 3 \frac{r^i r^j r^k r^l}{r^5} \right] p_1^i p_2^j \right\rangle. \quad \text{(C34)}$$

The operator H_{7c}^M is

$$H_{7c}^M = \frac{1}{24} \left[p_2^2, \left[p_1^2, \frac{1}{r} \right] \right], \quad \text{(C35)}$$

where we used (C15) for the spin part. The corresponding recoil correction is simply

$$\delta_M B_{7c} = \delta_M \left\langle \frac{1}{24} \left[p_2^2, \left[p_1^2, \frac{1}{r} \right] \right] \right\rangle. \quad \text{(C36)}$$

Finally, the operator H_{7d}^M is

$$H_{7d}^M = i \frac{Z^2}{8M} \sum_{a,b} \frac{r_a^i}{r_a^3} \left[H - E, \frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b} p_b^j \right] = i \frac{Z^2}{8M} \sum_{a,b} \frac{r_a^i}{r_a^3} \left\{ [V, p_b^j] \frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b} + \left[\frac{p_b^2}{2}, \frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b} \right] p_b^j \right\}. \quad \text{(C37)}$$

The expectation value of this can then be written as

$$\delta_M B_{7d} = W_1 + W_2, \quad \text{(C38)}$$

where

$$W_1 = \left\langle -\frac{Z^2}{8} \sum_{a,b,c \neq b} \frac{r_a^i}{r_a^3} \left(\frac{Z r_b^j}{r_b^3} - \frac{r_{bc}^j}{r_{bc}^3} \right) \frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b} - \frac{7Z^3}{4} \pi \delta^3(r_b) \right\rangle$$

$$= \left\langle \frac{Z^3}{4r_1^3} + \frac{Z^3}{4r_2^3} + \frac{Z^3 \vec{r}_1 \cdot \vec{r}_2}{4r_1^3 r_2^2} + \frac{Z^3 \vec{r}_1 \cdot \vec{r}_2}{4r_1^2 r_2^3} - \frac{7Z^3}{4} [\pi \delta^3(r_1) + \pi \delta^3(r_2)] + \frac{Z^2}{8} \sum_{b,c \neq b} \left(\frac{r_1^i}{r_1^3} + \frac{r_2^i}{r_2^3} \right) \frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b} \frac{r_{bc}^j}{r_{bc}^3} \right\rangle. \quad \text{(C39)}$$

Here we used the identity (A26) to rewrite the singular term as

$$\left\langle -Z \frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{8r_b} \left(\nabla_b^i \frac{Z}{r_b} \right) \left(\nabla_b^j \frac{Z}{r_b} \right) \right\rangle = \left\langle \frac{1}{4} \frac{Z^3}{r_b^3} - \frac{7Z^3}{4} \pi \delta^3(r_b) \right\rangle. \quad \text{(C40)}$$

Further,

$$
\begin{aligned}
W_2 &= \left\langle i\frac{Z^2}{16}\left(\sum_{a\neq b}\frac{r_a^i}{r_a^3}\left[p_b^2, \frac{r_b^i r_b^j - 3\delta^{ij}r_b^2}{r_b}\right]p_b^j + \sum_b \frac{r_b^i}{r_b^3}\left[p_b^2, \frac{r_b^i r_b^j - 3\delta^{ij}r_b^2}{r_b}\right]p_b^j\right)\right\rangle \\
&= \left\langle \frac{Z^2}{8}\sum_{a\neq b}p_b^k\frac{r_a^i}{r_a^3}\left(-\delta^{ik}\frac{r_b^j}{r_b} + \delta^{jk}\frac{r_b^i}{r_b} - \delta^{ij}\frac{r_b^k}{r_b} - \frac{r_b^i r_b^j r_b^k}{r_b^3}\right)p_b^j\right\rangle \\
&\quad + \frac{Z^2}{8r_1^4} + \frac{Z^2}{8r_2^4} + \frac{3Z^3}{4}[\pi\delta^3(r_1) + \pi\delta^3(r_2)] + \frac{Z^2}{8}\sum_b p_b^j\frac{1}{r_b^4}\left(\delta^{jk}r_b^2 - 3r_b^j r_b^k\right)p_b^k\right\rangle,
\end{aligned}
\tag{C41}
$$

where for the reduction of the singular term we used the identity (A27) from Appendix A, in particular,

$$
i\frac{Z^2}{16}\left\langle\frac{r_b^i}{r_b^3}\left[p_b^2, \frac{r_b^i r_b^j - 3\delta^{ij}r_b^2}{r_b}\right]p_b^j\right\rangle = \left\langle\frac{1}{8}\frac{Z^2}{r_b^4} + \frac{3Z^3}{4}\pi\delta^3(r_b) + \frac{Z^2}{8}p_b^j\frac{1}{r_b^4}\left(\delta^{jk}r_b^2 - 3r_b^j r_b^k\right)p_b^k\right\rangle.
\tag{C42}
$$

APPENDIX D: HYDROGEN LIMIT

In this section we perform the reduction of our general formulas to the hydrogenic limit for the S states, in order to demonstrate that the method reproduces the known results in agreement with the Dirac equation and with the hydrogenic recoil corrections. First we treat the infinite nucleus mass limit and then the recoil correction.

1. Infinite nucleus mass limit

We obtain the hydrogenic limit by sending $r_2 \to \infty$ and consequently $\vec{p}_2 \to 0$ and $r \to \infty$. The effective operator $H^{(6)}$ reduces in the hydrogenic limit to (writing $r_1 \equiv r$)

$$
H^{(6)} = \frac{p^6}{16} + \frac{1}{8}(\nabla V)^2 + \frac{5}{128}[p^2,[p^2,V]] - \frac{3}{32}p^2\nabla^2 V.
\tag{D1}
$$

The first-order contribution to energy $B = \langle H^{(6)}\rangle$ is then

$$
\begin{aligned}
B &= \left\langle\frac{1}{4}(E-V)p^2(E-V) + \frac{1}{8}\frac{Z^2}{r^4} + \frac{5}{64}[E-V,[p^2,V]] - \frac{3}{16}(E-V)\nabla^2 V\right\rangle \\
&= \left\langle\frac{1}{8}[V,[p^2,V]] + \frac{1}{2}(E-V)^3 + \frac{1}{8}\frac{Z^2}{r^4} - \frac{5}{32}\frac{Z^2}{r^4} - \frac{3E}{16}4\pi Z\delta^3(r)\right\rangle \\
&= \left\langle\frac{7}{32}\frac{Z^2}{r^4} - \frac{5}{2}E^3 + \frac{3E}{2}\frac{Z^2}{r^2} + \frac{1}{2}\frac{Z^3}{r^3} - \frac{3E}{16}4\pi Z\delta^3(r)\right\rangle.
\end{aligned}
\tag{D2}
$$

The operator $H^{(4)}$ reduces in the hydrogenic case to

$$
H^{(4)} = -\frac{p^4}{8} + \frac{Z\pi}{2}\delta^3(r),
\tag{D3}
$$

which we again regularize as

$$
H^{(4)} = H_R + \{H-E,Q\},
\tag{D4}
$$

with $Q = -Z/(4r) = V/4$ and

$$
H_R = -\frac{1}{2}(E-V)^2 - \frac{Z}{4}\frac{\vec{r}\cdot\vec{\nabla}}{r^3}.
\tag{D5}
$$

The second-order contribution to energy is then

$$
\begin{aligned}
A &= \left\langle H_R\frac{1}{(E-H)'}H_R\right\rangle + \langle Q(H-E)Q\rangle + 2\langle H^{(4)}\rangle\langle Q\rangle - 2\langle QH^{(4)}\rangle \\
&= \left\langle H_R\frac{1}{(E-H)'}H_R\right\rangle + \frac{1}{32}\langle[V,[H-E,V]]\rangle + EE^{(4)} + \frac{1}{16}\langle Vp^4\rangle \\
&= \left\langle H_R\frac{1}{(E-H)'}H_R\right\rangle + \left\langle -\frac{3}{32}\frac{Z^2}{r^4} + EE^{(4)} + \frac{E^3}{2} - \frac{E}{2}\frac{Z^2}{r^2} - \frac{1}{4}\frac{Z^3}{r^3}\right\rangle,
\end{aligned}
\tag{D6}
$$

where we have used $\langle V \rangle = 2E$. The sum of first- and second-order contributions is

$$E^{(6)} = \left\langle H_R \frac{1}{(E-H)'} H_R \right\rangle + \left\langle \frac{1}{8} \frac{Z^2}{r^4} + \frac{1}{4} \frac{Z^3}{r^3} - 2E^3 + E E^{(4)} + E \frac{Z^2}{r^2} - \frac{3E}{16} 4\pi Z \delta^3(r) \right\rangle$$

$$= \left\langle H_R \frac{1}{(E-H)'} H_R \right\rangle + \left\langle \frac{1}{8} \vec{p} \frac{Z^2}{r^2} \vec{p} + \frac{3E}{4} \frac{Z^2}{r^2} - 2E^3 + E E^{(4)} - \frac{3E}{16} 4\pi Z \delta^3(r) \right\rangle, \tag{D7}$$

where we have used the identity

$$\frac{Z^2}{r^4} = \vec{p} \frac{Z^2}{r^2} \vec{p} - 2 \left(E + \frac{Z}{r} \right) \frac{Z^2}{r^2}. \tag{D8}$$

The expectation values of operators appearing in the final result are for S states

$$E = -\frac{Z^2}{2n^2}, \tag{D9}$$

$$E^{(4)} = \frac{3Z^4}{8n^4} - \frac{Z^4}{2n^3}, \tag{D10}$$

$$\left\langle \frac{Z^2}{r^2} \right\rangle = \frac{2Z^4}{n^3}, \tag{D11}$$

$$\left\langle \vec{p} \frac{Z^2}{r^2} \vec{p} \right\rangle = -\frac{2Z^6}{3n^5} + \frac{8Z^6}{3n^3}, \tag{D12}$$

$$\left\langle H_R \frac{1}{(E-H)'} H_R \right\rangle = Z^6 \left(-\frac{3}{8n^6} + \frac{23}{24n^5} - \frac{3}{8n^4} - \frac{11}{24n^3} \right), \tag{D13}$$

$$\langle 4\pi Z \delta^3(r) \rangle = \frac{4Z^4}{n^3}. \tag{D14}$$

Substituting these values into energy we get the result

$$E^{(6)} = Z^6 \left(-\frac{5}{16n^6} + \frac{3}{4n^5} - \frac{3}{8n^4} - \frac{1}{8n^3} \right), \tag{D15}$$

in agreement with the result from the Dirac equation obtained by expanding

$$E_D = \left\{ 1 + \frac{(Z\alpha)^2}{[n - 1 + \sqrt{1 - (Z\alpha)^2}]^2} \right\}^{-\frac{1}{2}} \tag{D16}$$

in the order α^6.

2. Recoil correction for hydrogenic limit

Here the perturbation of the nonrelativistic Hamiltonian reduces to $\vec{P}^2/2M = \vec{p}^2/2M$. This correction is then easily accounted for by making reduced mass rescaling $r \to \frac{r}{\mu}$ and expanding the reduced mass as $(\mu/m)^n \approx 1 - n\frac{m}{M}$. The total recoil correction will then be the sum of the correction due to reduced mass and the correction due to extra recoil operators in $H_M^{(6)}$ and $H_M^{(4)}$. First we examine the reduced mass correction.

Rescaling the first-order operator $H^{(6)}$ and expanding up to the first order in nuclear mass, we obtain the recoil correction (utilizing results from the infinite nucleus mass limit)

$$\delta_M B_1 = -5B + \left\langle -\frac{p^6}{16} + \frac{1}{8}(\nabla V)^2 \right\rangle = -5B + \left\langle -\frac{1}{8} \frac{Z^2}{r^4} + \frac{5E^3}{2} - \frac{3E}{2} \frac{Z^2}{r^2} - \frac{1}{2} \frac{Z^3}{r^3} \right\rangle. \tag{D17}$$

The second-order contribution due to reduced mass is

$$\delta_M A_1 = -5A + \left\langle \frac{p^4}{4} \frac{1}{(E-H)'} H^{(4)} \right\rangle = -5A + \left\langle (E-V)^2 \frac{1}{(E-H)'} H^{(4)} \right\rangle + \left\langle (E-V)(H-E) \frac{1}{(E-H)'} H^{(4)} \right\rangle$$

$$= -5A + \left\langle (E-V)^2 \frac{1}{(E-H)'} H_R \right\rangle + \left\langle -2E E^{(4)} - 3E^3 + 2E \frac{Z^2}{r^2} + \frac{3}{4} \frac{Z^3}{r^3} + \frac{1}{4} \frac{Z^2}{r^4} \right\rangle. \tag{D18}$$

Summing now both terms $\delta_M A_1$ and $\delta_M B_1$, we get the total recoil correction due to the reduced mass rescaling E_i,

$$E_i = \delta_M A_1 + \delta_M B_1 = -5E^{(6)} + \left\langle (E-V)^2 \frac{1}{(E-H)'} H_R \right\rangle + \left\langle -\frac{E^3}{2} - 2E E^{(4)} + \frac{E}{4} \frac{Z^2}{r^2} + \frac{1}{8} \vec{p} \frac{Z^2}{r^2} \vec{p} \right\rangle, \tag{D19}$$

where we have again used the identity (D8).

The next contribution comes from the extra recoil operators. The recoil correction to the Breit Hamiltonian $H^{(4)}$ is

$$\delta_M H^{(4)} = -\frac{Z}{2} p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) P^j, \tag{D20}$$

and the corresponding second-order correction to energy is

$$\delta_M A_2 = -Z \left\langle p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j \frac{1}{(E-H)'} H^{(4)} \right\rangle = -Z \left\langle p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j \frac{1}{(E-H)'} H_R \right\rangle$$

$$+ \left\langle -\frac{EZ}{2} p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j - \frac{Z^2}{4} p^i \left(\frac{\delta^{ij}}{r^2} + \frac{r^i r^j}{r^4} \right) p^j + \frac{1}{4} \frac{Z^2}{r^4} + \frac{Z^3}{2} \pi \delta^3(r) \right\rangle. \tag{D21}$$

The correction due to the extra first-order recoil operators is

$$\delta_M B_2 = \langle \delta_M H^{(6)} \rangle = \left\langle \frac{1}{4} \frac{Z^2}{r^4} + \frac{Z^3}{2} \pi \delta^3(r) + \frac{Z}{4} p^2 p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j + \frac{Z^2}{8} p^i \left(\frac{\delta^{ij}}{r^2} + 3\frac{r^i r^j}{r^4} \right) p^j \right.$$

$$\left. + i\frac{Z^2}{8} \frac{r^i}{r^3} \left[H - E, \frac{r^i r^j - 3\delta^{ij} r^2}{r} p^j \right] \right\rangle = \delta_M B_{2a} + \delta_M B_{2b} + \delta_M B_{2c} + \delta_M B_{2d} + \delta_M B_{2e}. \tag{D22}$$

The third and the fifth terms are

$$\delta_M B_{2c} = \left\langle \frac{Z}{2} (E-V) p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j \right\rangle = \left\langle \frac{Z}{2} p^i (E-V) \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j + \frac{Z^2}{4} \left[p^i, \left[p^j, \frac{1}{r} \right] \right] \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) \right\rangle$$

$$= \left\langle \frac{Z}{2} p^i \left(E + \frac{Z}{r} \right) \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j - \frac{1}{2} \frac{Z^2}{r^4} - Z^3 \pi \delta^3(r) \right\rangle, \tag{D23}$$

and

$$\delta_M B_{2e} = \left\langle i\frac{Z^2}{8} \frac{r^i}{r^3} \left\{ [V, p^j] \frac{r^i r^j - 3\delta^{ij} r^2}{r} + \left[\frac{p^2}{2}, \frac{r^i r^j - 3\delta^{ij} r^2}{r} \right] p^j \right\} \right\rangle$$

$$= \left\langle \frac{1}{4} \frac{Z^3}{r^3} + \frac{1}{8} \frac{Z^2}{r^4} - Z^3 \pi \delta^3(r) + \frac{Z^2}{8} p^i \frac{1}{r^4} (\delta^{ij} r^2 - 3 r^i r^j) p^j \right\rangle. \tag{D24}$$

The first-order contribution $\delta_M B_2$ is the sum of all terms $\delta_M B_{2a}, \ldots, \delta_M B_{2e}$ and is

$$\delta_M B_2 = \left\langle -\frac{1}{8} \frac{Z^2}{r^4} + \frac{1}{4} \frac{Z^3}{r^3} - \frac{3Z^3}{2} \pi \delta^3(r) + \frac{Z}{2} p^i \left(E + \frac{Z}{r} \right) \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j + \frac{1}{4} \vec{p} \frac{Z^2}{r^2} \vec{p} \right\rangle. \tag{D25}$$

The correction E_{ii} due to extra recoil operators is then the sum of $\delta_M B_2$ and $\delta_M A_2$,

$$E_{\text{ii}} = \delta_M A_2 + \delta_M B_2 = -Z \left\langle p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j \frac{1}{(E-H)'} H_R \right\rangle + \left\langle \frac{Z^2}{4} p^i \left(\frac{\delta^{ij}}{r^2} + \frac{r^i r^j}{r^4} \right) p^j - Z^3 \pi \delta^3(r) + \frac{3}{8} \vec{p} \frac{1}{r^2} \vec{p} - \frac{E}{4} \frac{Z^2}{r^2} \right\rangle. \tag{D26}$$

Finally, the total recoil correction for the S-state hydrogenic limit is the sum of the reduced mass scaling correction E_{i} and the correction due to extra operators E_{ii} and is

$$\delta_M E^{(6)} = E_{\text{i}} + E_{\text{ii}} = \left\langle (E-V)^2 \frac{1}{(E-H)'} H_R \right\rangle - Z \left\langle p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j \frac{1}{(E-H)'} H_R \right\rangle$$

$$- 5 E^{(6)} - \frac{E^3}{2} - 2 E E^{(4)} + \left\langle \frac{1}{2} \vec{p} \frac{Z^2}{r^2} \vec{p} + \frac{Z^2}{4} p^i \left(\frac{\delta^{ij}}{r^2} + \frac{r^i r^j}{r^4} \right) p^j - Z^3 \pi \delta^3(r) \right\rangle. \tag{D27}$$

In addition to the operators already used, the expectation values are

$$\left\langle Z^2 p^i \left(\frac{\delta^{ij}}{r^2} + \frac{r^i r^j}{r^4} \right) p^j \right\rangle = -\frac{4Z^6}{3n^5} + \frac{16Z^6}{3n^3}, \tag{D28}$$

$$\left\langle (E-V)^2 \frac{1}{(E-H)'} H_R \right\rangle = Z^6 \left(\frac{1}{2n^6} - \frac{9}{4n^5} + \frac{3}{2n^4} + \frac{3}{2n^3} \right), \tag{D29}$$

$$Z \left\langle p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j \frac{1}{(E-H)'} H_R \right\rangle = Z^6 \left(\frac{2}{n^6} - \frac{37}{6n^5} + \frac{3}{n^4} + \frac{11}{3n^3} \right). \tag{D30}$$

Using these expectation values, the final result is

$$\delta_M E^{(6)} = Z^6 \left(\frac{1}{2n^6} - \frac{1}{n^5} + \frac{3}{8n^4} + \frac{1}{8n^3} \right),$$

(D31)

in agreement with the result from the Dirac equation

$$\delta_M E_D = \frac{1 - E_D^2}{2}$$

(D32)

expanded in the order α^6. In particular, it vanishes for the hydrogenic ground state.

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[1] P. J. Mohr, D. B. Newell, and B. N. Taylor, Rev. Mod. Phys. **88**, 035009 (2016).

[2] K. Pachucki, Phys. Rev. A **74**, 022512 (2006).

[3] V. A. Yerokhin and K. Pachucki, Phys. Rev. A **81**, 022507 (2010).

[4] P. C. Pastor, G. Giusfredi, P. De Natale, G. Hagel, C. de Mauro, and M. Inguscio, Phys. Rev. Lett. **92**, 023001 (2004); P. C. Pastor, *ibid.* **97**, 139903 (2006).

[5] K. Pachucki and V. A. Yerokhin, J. Phys.: Conf. Ser. **264**, 012007 (2011).

[6] A. Antognini *et al.*, Can. J. Phys. **89**, 47 (2011).

[7] R. Pohl *et al.*, Nature (London) **466**, 213 (2010).

[8] A. Antognini *et al.*, Science **339**, 417 (2013).

[9] K. Pachucki and V. A. Yerokhin, J. Phys. Chem. Ref. Data **44**, 031206 (2015).

[10] W. Nörtershäuser (private communication).

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

[12] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957); H. Araki, Prog. Theor. Phys. **17**, 619 (1957); J. Sucher, Phys. Rev. **109**, 1010 (1957).

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

[14] K. Pachucki, J. Phys. B **31**, 5123 (1998).

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

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

[17] K. Pachucki and J. Sapirstein, J. Phys. B **36**, 803 (2003).

[18] M. I. Eides, H. Grotch, and V. A. Shelyuto, Phys. Rep. **342**, 63 (2001).

[19] V. I. Korobov, Phys. Rev. A **61**, 064503 (2000); **66**, 024501 (2002).

[20] V. A. Yerokhin and V. M. Shabaev, Phys. Rev. Lett. **115**, 233002 (2015).

[21] P. C. Pastor, L. Consolino, G. Giusfredi, P. D. Natale, M. Inguscio, V. A. Yerokhin, and K. Pachucki, Phys. Rev. Lett. **108**, 143001 (2012).

[22] D. Shiner, R. Dixon, and V. Vedantham, Phys. Rev. Lett. **74**, 3553 (1995).

[23] R. van Rooij, J. S. Borbely, J. Simonet, M. D. Hoogerland, K. S. E. Eikema, R. A. Rozendaal, and W. Vassen, Science **333**, 196 (2011).