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

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We investigate the finite nuclear mass corrections in the helium atom in order to resolve a significant disagreement between the $2\,^3S$-$2\,^3P$ and $2\,^3S$-$2\,^1S$ transition isotope shifts. These two transitions lead to discrepant results for the nuclear charge radii difference between ^{4}He and ^{3}He. The accurate treatment of the finite nuclear mass effects is quite complicated and requires the use of the quantum field theoretical approach. We derive the $\alpha^6\,m^2/M$ correction with the help of nonrelativistic QED and dimensional regularization of the three-body Coulombic system and present accurate numerical results for low-lying states. The previously reported $4\,\sigma$ discrepancy in the nuclear charge radius difference between ^{3}He and ^{4}He from two different atomic isotope shift transitions is confirmed, which calls for verification of experimental transition frequencies.

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I. INTRODUCTION

The atomic spectroscopy of light atoms has reached the level of precision that allows the determination of nuclear parameters from measured transition frequencies, in particular the nuclear charge radius. The best-known example is the hydrogen spectroscopy from which one obtains the proton mean-square charge radius of $r_p = 0.8758(77)$ fm, in agreement with the result derived from the electron-proton elastic scattering, 0.895(18) fm [1]. Both these values are in significant disagreement with the result derived from the muonic hydrogen Lamb shift, $r_p = 0.840\,87(39)$ fm [2,3]. This discrepancy attracted much attention from the scientific community and became known as the proton charge radius puzzle [4]. Up to now the determination of nuclear charge radii from light atoms other than hydrogen has been limited by the lack of sufficiently accurate theory. It was only possible to find the nuclear charge radii differences from the isotope shifts of atomic transition frequencies [5]. Bearing in mind the discrepancy between the electronic and the muonic hydrogen determinations of the proton charge radius, we investigate the isotopic differences in the nuclear charge radii in order to explore other potential discrepancies. Indeed, the nuclear charge radii difference δr^2 between ^{4}He and ^{3}He was determined to be 1.069(3) fm^2 from the $2\,^3S$-$2\,^3P$ transition [6] and 1.027(11) fm^2 from the $2\,^3S$-$2\,^1S$ transition [7]. The 4σ discrepancy between these two results could be explained by a 8.8-kHz shift in the $2\,^3S$-$2\,^1S$ transition, a small correction which in principle might have been overlooked in previous calculations. The corresponding shift in the $2\,^3S$-$2\,^3P$ transition would have to be much larger, 49.7 kHz, and thus is less probable. In this work we calculate the last unknown correction, of order $\alpha^6 m^2/M$, which might contribute at this level of accuracy. We find out that the result for the isotope shift of the $2\,^3S$-$2\,^1S$ transition almost coincides with our previous estimate [7], namely 2.73 kHz versus 2.75(69) kHz. Since we do not see any possibility to miss a 8.8-kHz effect in our theoretical predictions, we are in a position to claim a discrepancy between the isotope shift in the $2\,^3S$-$2\,^3P$ [8–10] and $2\,^3S$-$2\,^1S$ [11] transition frequencies.

II. NOTATIONS

In this work we closely follow our previous paper devoted to nuclear recoil effects for triplet states of helium [6] and use the same notations. The reader may consider checking that paper first, but nevertheless we repeat here the main principles. The operators, energies, and wave functions for a nucleus with a finite mass M are marked with indices "M": X_M, E_M, and ϕ_M. The operators, energies, and wave functions in the infinite nuclear mass limit are without indices: X, E, and ϕ. The recoil corrections to the operators and energies are denoted by $\delta_M X$ and $\delta_M E$:

$$X_M \equiv X + \frac{m}{M}\delta_M X + O\Big(\frac{m}{M}\Big)^2, \tag{1}$$

$$E_M = E + \frac{m}{M}\,\delta_M E + O\Big(\frac{m}{M}\Big)^2. \tag{2}$$

We also introduce the following shorthand notations:

$$\langle X\rangle_M \equiv \langle\phi_M|X|\phi_M\rangle \tag{3}$$

and

$$\delta_M\,\langle X\rangle \equiv \langle\phi|\frac{\vec{P}_I^2}{2}\frac{1}{(E-H)'}\,X|\phi\rangle + \langle\phi|X\,\frac{1}{(E-H)'}\,\frac{\vec{P}_I^2}{2}|\phi\rangle, \tag{4}$$

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 wave function in the infinite nuclear mass limit.

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

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

where $E_M^{(n)}$ 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:

$$E_M^{(n)} = E^{(n)} + \frac{m}{M}\,\delta_M E^{(n)} + O\Big(\frac{m}{M}\Big)^2. \tag{6}$$

We are interested here in $E_M^{(6)}$, which can be expressed as

$$E_M^{(6)} = \Big\langle H_M^{(4)}\,\frac{1}{(E_M - H_M)'}\,H_M^{(4)}\Big\rangle_M + \big\langle H_M^{(6)}\big\rangle_M = A_M + B_M, \tag{7}$$

where the last equation is a definition of A_M and B_M. In this paper we derive the recoil part of this correction $\delta_M E^{(6)}$ for singlet states in helium. The computational approach is similar to the one used for triplet states in Ref. [6] and to the nonrecoil $\alpha^6 m$ correction for singlet states in Ref. [12].

III. DIMENSIONAL REGULARIZATION

Since individual terms in $E^{(6)}$ are divergent they have to be regularized. We found in Ref. [12] that the most convenient regularization is the dimensional one, although it seems to be very exotic for atomic systems. In this regularization, the dimension of space is assumed to be $d = 3 - 2\epsilon$. The photon propagator, and thus the Coulomb interaction, preserves its form in the momentum representation, while in the coordinate representation the Coulomb potential is

$$\int \frac{d^d k}{(2\pi)^d}\,\frac{4\pi}{k^2}\,e^{i\vec k\cdot\vec r} = \pi^{\epsilon-1/2}\,\Gamma(1/2-\epsilon)\,r^{2\epsilon-1} \equiv \frac{C_1}{r^{1-2\epsilon}}. \tag{8}$$

The elimination of singularities is performed in atomic units by the transformation

$$\vec r \to (m\alpha)^{-1/(1+2\epsilon)}\,\vec r \tag{9}$$

and pulling common 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 $H^{(6)}$, respectively. The nonrelativistic Hamiltonian of hydrogenlike systems is

$$H = \frac{\vec p^{\,2}}{2} - Z\,\frac{C_1}{r^{1-2\epsilon}} \tag{10}$$

and that of heliumlike systems is

$$H = \frac{\vec p_1^{\,2}}{2} + \frac{\vec p_2^{\,2}}{2} + V, \tag{11}$$

where

$$V = -Z\frac{C_1}{r_1^{1-2\epsilon}} - Z\frac{C_1}{r_2^{1-2\epsilon}} + \frac{C_1}{r_{12}^{1-2\epsilon}} \equiv \Big[-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r}\Big]_\epsilon. \tag{12}$$

We calculate further integrals involving the photon propagator in the Coulomb gauge as follows:

$$\int \frac{d^d k}{(2\pi)^d}\,\frac{4\pi}{k^4}\,\Big(\delta^{ij} - \frac{k^i\,k^j}{k^2}\Big)\,e^{i\vec k\cdot\vec r} = \pi^{\epsilon-1/2}\,r^{-1+2\epsilon}\Big[\frac{3}{16}\,\delta^{ij}\,\Gamma(-1/2-\epsilon)\,r^2 + \frac{1}{8}\,\Gamma(1/2-\epsilon)\,r^i\,r^j\Big] \equiv \Big[\frac{1}{8r}\,(r^i\,r^j - 3\,\delta^{ij}\,r^2)\Big]_\epsilon, \tag{13}$$

and

$$\int \frac{d^d k}{(2\pi)^d}\,\frac{4\pi}{k^2}\,\Big(\delta^{ij} - \frac{k^i\,k^j}{k^2}\Big)\,e^{i\vec k\cdot\vec r} = \pi^{\epsilon-1/2}\,r^{-3+2\epsilon}\Big[\frac{1}{2}\delta^{ij}\,\Gamma(1/2-\epsilon)\,r^2 + \Gamma(3/2-\epsilon)\,r^i\,r^j\Big] \equiv \frac{1}{2}\Big[\frac{\delta^{ij}}{r} + \frac{r^i\,r^j}{r^3}\Big]_\epsilon. \tag{14}$$

The solution of the stationary Schrödinger equation $H\,\phi = E\,\phi$ is denoted by ϕ, and we will never need its explicit (and unknown) form in d dimensions.

IV. EFFECTIVE HAMILTONIAN IN *d* DIMENSIONS

We pass now to the effective Hamiltonian terms in Eq. (7). The Breit-Pauli Hamiltonian $H_M^{(4)}$ [12,13] is split into two parts (with $r_{12} \equiv r$, $r_{aI} \equiv r_a$, and $\vec P \equiv \vec p_1 + \vec p_2$):

$$H_M^{(4)} = H_A^M + H_C^M, \tag{15}$$

where

$$\begin{aligned} H_A^M =& -\frac{1}{8}\,(p_1^4 + p_2^4) + \frac{Z\,\pi}{2}\,[\delta^d(r_1) + \delta^d(r_2)] + \pi\,(d-2)\,\delta^d(r) - \frac{1}{2}\,p_1^i\,\Big[\frac{\delta^{ij}}{r} + \frac{r^i\,r^j}{r^3}\Big]_\epsilon\,p_2^j \\ &- \frac{Z}{2}\,\frac{m}{M}\,\Big\{p_1^i\Big[\frac{\delta^{ij}}{r_1} + \frac{r_1^i\,r_1^j}{r_1^3}\Big]_\epsilon + p_2^i\Big[\frac{\delta^{ij}}{r_2} + \frac{r_2^i\,r_2^j}{r_2^3}\Big]_\epsilon\Big\}\,P^j \end{aligned} \tag{16}$$

and

$$H_C^M = \Big[\frac{Z}{4}\Big(\frac{\vec r_1}{r_1^3}\times\vec p_1 - \frac{\vec r_2}{r_2^3}\times\vec p_2\Big) + \frac{1}{4}\,\frac{\vec r}{r^3}\times(\vec p_1 + \vec p_2) + \frac{Z}{2}\,\frac{m}{M}\,\Big(\frac{\vec r_1}{r_1^3} - \frac{\vec r_2}{r_2^3}\Big)\times\vec P\Big]\cdot\frac{\vec\sigma_1 - \vec\sigma_2}{2}. \tag{17}$$

H_M^C in the above is represented in $d=3$ as it does not lead to any singularities. The other terms in $H_M^{(4)}$ do not contribute to energies of singlet states. The corresponding second-order correction is

$$A_M = \left\langle H_A^M \frac{1}{(E_M - H_M)'} H_A^M \right\rangle_M + \left\langle H_C^M \frac{1}{(E_M - H_M)'} H_C^M \right\rangle_M , \tag{18}$$

whereas the first-order contribution is given by

$$B_M = \left\langle \sum_{i=1,12} H_i^M \right\rangle_M , \tag{19}$$

where, following Ref. [6], H_i^M in arbitrary d dimensions are as follows:

$$H_1^M = \frac{p_1^6}{16} + \frac{p_2^2}{16}, \tag{20}$$

$$H_2^M = \frac{(\nabla_1 V)^2 + (\nabla_2 V)^2}{8} + \frac{5}{128}\big([p_1^2,[p_1^2,V]] + [p_2^2,[p_2^2,V]]\big) - \frac{3}{64}\big(\{p_1^2,\nabla_1^2 V\} + \{p_2^2,\nabla_2^2 V\}\big), \tag{21}$$

$$H_3^M = \frac{1}{64}\left(-4\pi\,\nabla^2\delta^3(r) + \frac{16\pi}{d(d-1)}\sigma_1^{kl}\sigma_2^{kl}\,p_1^i\left[\frac{2}{3}\delta^{ij}4\pi\,\delta^3(r) + \frac{1}{r^5}(3r^i r^j - \delta^{ij}r^2)\right]_\epsilon p_2^j\right), \tag{22}$$

$$H_4^M = \frac{1}{2}\left(p_1^2+p_2^2\right)p_1^i\left[\frac{1}{2r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)\right]_\epsilon p_2^j + \frac{(p_1^2+p_2^2)}{8}\,\frac{\sigma_1\,\sigma_2}{d}\,4\pi\,\delta^3(r)$$
$$+\frac{Z}{2M}\left(p_1^2\,p_1^i\left[\frac{1}{2r_1}\left(\delta^{ij}+\frac{r_1^i r_1^j}{r_1^2}\right)\right]_\epsilon P^j + p_2^2\,p_2^i\left[\frac{1}{2r}\left(\delta^{ij}+\frac{r_2^i r_2^j}{r_2^2}\right)\right]_\epsilon P^j\right), \tag{23}$$

$$H_5^M = \frac{\sigma_1^{ij}\sigma_2^{ij}}{2d}\left(-\frac{1}{2}\left[\frac{\vec r}{r^3}\right]_\epsilon(\nabla_1 V + \nabla_2 V) + \frac{1}{16}\left(\left[\left[\left[\frac{1}{r}\right]_\epsilon, p_1^2\right], p_1^2\right] + \left[\left[\left[\frac{1}{r}\right]_\epsilon, p_2^2\right], p_2^2\right]\right)\right), \tag{24}$$

$$H_6^M = \frac{1}{8}\,p_1^i\,\frac{1}{r^2}\left(\delta^{ij}+3\,\frac{r^i r^j}{r^2}\right)p_1^j + \frac{1}{8}\,p_2^i\,\frac{1}{r^2}\left(\delta^{ij}+3\,\frac{r^i r^j}{r^2}\right)p_2^j + \frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon$$
$$+\frac{Z}{4}\frac{m}{M}\left[p_2^i\left(\frac{\delta^{ij}}{r}+\frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_1}+\frac{r_1^j r_1^k}{r_1^3}\right)P^k + (1\leftrightarrow 2)\right] + \frac{Z^2}{8}\,\frac{m}{M}$$
$$\times\left[p_1^i\left(\frac{\delta^{ij}}{r_1}+3\,\frac{r_1^i r_1^j}{r_1^3}\right)p_1^k + p_2^i\left(\frac{\delta^{ij}}{r_2}+3\,\frac{r_2^i r_2^j}{r_2^3}\right)p_2^k + 2\,p_1^i\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_2}+\frac{r_2^j r_2^k}{r_2^3}\right)p_2^k\right.$$
$$\left.+\frac{\sigma_1^{ij}\sigma_1^{ij}}{d}\left[\frac{1}{r_1^4}\right]_\epsilon + \frac{\sigma_2^{ij}\sigma_2^{ij}}{d}\left[\frac{1}{r_2^4}\right]_\epsilon + 2\,\frac{\sigma_1^{ij}\sigma_2^{ij}}{d}\,\frac{\vec r_1}{r_1^3}\,\frac{\vec r_2}{r_2^3}\right], \tag{25}$$

$$H_{7a}^M = -\frac{1}{8}\left\{[p_1^i,V]\,\frac{r^i r^j - 3\,\delta^{ij} r^2}{r}\,[V,p_2^j] + [p_1^i,V]\left[\frac{p_2^2}{2},\frac{r^i r^j - 3\,\delta^{ij} r^2}{r}\right]p_2^j\right.$$
$$\left.+\;p_1^i\left[\frac{r^i r^j - 3\,\delta^{ij} r^2}{r},\frac{p_1^2}{2}\right][V,p_2^j] + p_1^i\left[\frac{p_2^2}{2},\left[\frac{r^i r^j - 3\,\delta^{ij} r^2}{r},\frac{p_1^2}{2}\right]\right]p_2^j\right\}, \tag{26}$$

$$H_{7c}^M = \frac{\sigma_1^{ij}\sigma_2^{ij}}{16d}\left[p_1^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right], \tag{27}$$

$$H_{7d}^M = \frac{i\,Z}{8}\,\frac{m}{M}\left(\nabla_1^i V + \nabla_2^i V\right)\left(\left[H-E\,,\,\frac{r_1^i r_1^j - 3\,\delta^{ij} r_1^2}{r_1}\,p_1^j\right] + \left[H-E\,,\,\frac{r_2^i r_2^j - 3\,\delta^{ij} r_2^2}{r_2}\,p_2^j\right]\right). \tag{28}$$

H_{7b}^M would contain the spin-orbit type of interaction, but it vanishes for singlet states. Further terms come from high-energy photons and are known as pure, radiative, and radiative recoil corrections, which are the same as in hydrogenic systems [14]:

$$H_8^M = Z^3\,\frac{m}{M}\left(4\,\ln 2 - \frac{7}{2}\right)[\delta^3(r_1)+\delta^3(r_2)], \tag{29}$$

$$H_9^M = Z^2\,\frac{m}{M}\left(\frac{35}{36} - \frac{448}{27\pi^2} - 2\ln(2) + \frac{6\zeta(3)}{\pi^2}\right)[\delta^3(r_1)+\delta^3(r_2)], \tag{30}$$

$$H_{10}^M = \pi\, Z^2 \left(\frac{427}{96} - 2\,\ln(2)\right)[\delta^3(r_1)+\delta^3(r_2)] + \pi\,\left(\frac{6\zeta(3)}{\pi^2} - \frac{697}{27\pi^2} - 8\ln(2) + \frac{1099}{72}\right)\delta^3(r), \tag{31}$$

$$H_{11}^M = \pi\, Z\,\left(-\frac{2179}{648\pi^2} - \frac{10}{27} + \frac{3}{2}\,\ln(2) - \frac{9\zeta(3)}{4\pi^2}\right)[\delta^3(r_1)+\delta^3(r_2)] + \pi\,\left(\frac{15\zeta(3)}{2\pi^2} + \frac{631}{54\pi^2} - 5\ln(2) + \frac{29}{27}\right)\delta^3(r). \tag{32}$$

The last term comes from the hard three-photon exchange between electrons. It was originally calculated for positronium in Ref. [15], and for electrons its sign is reversed, see H_H in Ref. [12]:

$$H_{12}^M = \left(-\frac{1}{\epsilon} - 4\ln\alpha - \frac{39\,\zeta(3)}{\pi^2} + \frac{32}{\pi^2} - 6\ln(2) + \frac{7}{3}\right)\frac{\pi\,\delta^d(r)}{4}, \tag{33}$$

where by convention we pull out the common factor $\left[(4\pi)^\epsilon\,\Gamma(1+\epsilon)\right]^2$ from all matrix elements.

V. ELIMINATION OF SINGULARITIES

The principal problem of this approach is that both the first-order and the second-order contributions in Eq. (7) are divergent and the divergence cancels out only in the sum. To achieve the explicit cancellation of the divergences, we (i) regularize the divergent contributions by applying dimensional regularization with $d = 3 - 2\epsilon$, (ii) move singularities from the second-order contributions to the first-order ones, and (iii) cancel algebraically the $1/\epsilon$ terms.

In the following we first consider the recoil correction coming from the second-order matrix elements, i.e., the first term in Eq. (7), which is denoted by A_M. The recoil correction from the second term in Eq. (7), denoted by B_M, is examined next. It is the second-order contribution due to H_A^M which is divergent and therefore is treated in d dimensions. To pull out divergences we rewrite H_A^M as

$$H_A^M = H_R^M + \{H_M - E_M, Q_M\}, \tag{34}$$

where $Q_M = Q + \delta_M Q$ and

$$Q = -\frac{1}{4}\left[\frac{Z}{r_1} + \frac{Z}{r_2}\right]_\epsilon + \frac{(d-1)}{4}\left[\frac{1}{r}\right]_\epsilon, \tag{35}$$

$$\delta_M Q = \frac{3}{4}\left[\frac{Z}{r_1} + \frac{Z}{r_2}\right]_\epsilon. \tag{36}$$

The operator Q_M is the same as that in Ref. [12] with the exception that it also includes the recoil part $\delta_M Q$. The regular part of operator H_A^M can be evaluated in three dimensions to yield

$$H_R^M = H_R + \frac{m}{M}\delta_M H_R, \tag{37}$$

$$H_R\,|\phi\rangle = \left\{-\frac{1}{2}(E-V)^2 - \frac{Z}{4}\frac{\vec r_1\cdot\vec\nabla_1}{r_1^3} - \frac{Z}{4}\frac{\vec r_2\cdot\vec\nabla_2}{r_2^3} + \frac{1}{4}\nabla_1^2\,\nabla_2^2 - p_1^i\,\frac{1}{2\,r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)p_2^j\right\}|\phi\rangle, \tag{38}$$

$$\delta_M H_R\,|\phi\rangle = \left\{(E-V)\left(\frac{\vec P^2}{2} - \left\langle\frac{\vec P^2}{2}\right\rangle\right) + \frac{3Z}{4}\frac{\vec r_1\cdot\vec\nabla_2}{r_1^3} + \frac{3Z}{4}\frac{\vec r_2\cdot\vec\nabla_1}{r_2^3} - \frac{Z}{2}\,p_1^i\,\frac{1}{r_1}\left(\delta^{ij} + \frac{r_1^i r_1^j}{r_1^2}\right)P^j - \frac{Z}{2}\,p_2^i\,\frac{1}{r_2}\left(\delta^{ij} + \frac{r_2^i r_2^j}{r_2^2}\right)P^j\right\}|\phi\rangle, \tag{39}$$

where

$$V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r}, \tag{40}$$

and the kinetic energy of the nucleus is $\langle\vec P^2/2\rangle = \delta_M E$. After the transformation in Eq. (34) A_M takes the form

$$A_M = \sum_{a=R,C}\left\langle H_a^M\,\frac{1}{(E_M - H_M)'}\,H_a^M\right\rangle_M + \langle Q_M\,(H_M - E_M)\,Q_M\rangle_M + 2\,E_M^{(4)}\,\langle Q_M\rangle_M - 2\left\langle H_M^{(4)}\,Q_M\right\rangle_M = A_1^M + A_2^M, \tag{41}$$

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. As a result $\delta_M A_1$ becomes

$$\delta_M A_1 = \sum_{a=R,C}\left\langle H_a\frac{1}{(E-H)'}\left[\frac{\vec P^2}{2} - \delta_M E\right]\frac{1}{(E-H)'}\,H_a\right\rangle + 2\left\langle H_a\,\frac{1}{(E-H)'}\,[H_a - \langle H_a\rangle]\,\frac{1}{(E-H)'}\,\frac{\vec P^2}{2}\right\rangle + 2\left\langle\delta_M H_a\frac{1}{(E-H)'}H_a\right\rangle, \tag{42}$$

while the first-order terms are

$$A_2^M = \langle Q\,(H_M - E_M)\,Q\rangle_M + 2\,E_M^{(4)}\langle Q\rangle_M - 2\big\langle H_M^{(4)}\,Q\big\rangle_M + \frac{m}{M}\,\{2\,\langle Q\,(H-E)\,\delta_M Q\rangle + 2E^{(4)}\langle \delta_M Q\rangle - 2\,\langle H_A\,\delta_M Q\rangle\}. \tag{43}$$

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

$$\begin{aligned}
\delta_M A_2 = \delta_M\,\bigg\langle &-\frac{3}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{(d-1)(d-5)}{16}\left[\frac{1}{r^4}\right]_\epsilon + \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} + 2\,E^{(4)}\,Q\\
&+\frac{Z(Z-2)}{4}\pi\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^ir^j}{r^2}\right)p_2^j\\
&+\frac{(d-1)}{4}\left[p_1^i,\left[p_2^j,\left[\frac{1}{r}\right]_\epsilon\right]\right]\left[\frac{1}{2\,r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)\right]_\epsilon + (E-V)^2\,Q + \frac{1}{8}\,p_1^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)p_2^2\\
&-\frac{(d-1)}{8}\,p_1^2\left[\frac{1}{r}\right]_\epsilon p_2^2 - \frac{(d-1)}{16}\big[p_1^2,[p_2^2,V]\big] + \frac{Z\,\pi}{2}\left(\frac{\delta^3(r)}{r_1}+\frac{\delta^3(r)}{r_2}\right)\bigg\rangle + \delta_M E^{(4)}\left(E+\left\langle\frac{1}{2r}\right\rangle\right)\\
&+\bigg\langle\frac{11}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon - \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} - 3\,E E^{(4)} + \frac{3}{4}\,(E-V)^2\left[\frac{Z}{r_1}+\frac{Z}{r_2}\right]_\epsilon\\
&-\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^ir^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}+2\,E+2\,Z^2\right) + \frac{\pi\,Z}{4}\delta^3(r_2)\left(\frac{Z-6}{r_1}+2\,E+2\,Z^2\right)\\
&+\vec P\left[\frac{E}{4}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right) - \frac{E}{2r} + \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\\
&-\frac{Z}{4}\left[P^i\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^ir_1^j}{r_1^3}\right)\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{2}{r}\right)p_1^j + (1\leftrightarrow 2)\right] - \frac{3}{2}\pi\,Z\left(\frac{\delta^3(r)}{r_1}+\frac{\delta^3(r)}{r_2}\right)\bigg\rangle.
\end{aligned} \tag{44}$$

We examine now the recoil correction coming from B_M in Eq. (19). 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) the perturbation of the nonrelativistic wave function, of 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; therefore we have moved its description to Appendix B and present here only the final result for the recoil correction

$$\begin{aligned}
\delta_M B = \delta_M\,\bigg\langle &\frac{7}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon - \frac{13}{64}\left(\frac{Z\vec r_1}{r_1^3}-\frac{Z\vec r_2}{r_2^3}\right)\cdot\frac{\vec r}{r^3} + \frac{1}{4}\left(\frac{Z\vec r_1}{r_1^3}-\frac{Z\vec r_2}{r_2^3}\right)\cdot\frac{\vec r}{r^2} - \frac{1}{4}\left[\frac{1}{r^3}\right]_\epsilon\\
&+\frac{23}{32}\left[\frac{1}{r^4}\right]_\epsilon + \frac{7}{64}\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right] + \frac{1}{2}\,(E-V)^3 - \frac{3}{8}\,p_1^2\,(E-V)\,p_2^2\\
&-\frac{3}{8}\pi\,Z\left[2\left(E+\frac{Z-1}{r_2}\right)\delta^3(r_1) + 2\left(E+\frac{Z-1}{r_1}\right)\delta^3(r_2) - p_1^2\,\delta^3(r_2) - p_2^2\,\delta^3(r_1)\right]\\
&+\left(1-E-\frac{Z}{r_1}-\frac{Z}{r_2}-\frac{5\,\vec P^2}{48}\right)\pi\,\delta^3(r) - \frac{1}{2}\left[\frac{1}{2\,r}\left(\delta^{ij}+\frac{r^i\,r^j}{r^2}\right)\right]_\epsilon \nabla^i\,\nabla^j\left[\frac{1}{r}\right]_\epsilon\\
&+\frac{1}{2}\,p_1^i\,(E-V)\,\frac{1}{r}\left(\delta^{ij}+\frac{r^ir^j}{r^2}\right)p_2^j - \frac{1}{8}\,\frac{Z^2\,r_1^ir_2^j}{r_1^3r_2^3}\left(\frac{r^ir^j}{r}-3\,\delta^{ij}r\right)\\
&-\frac{Z}{8}\left[\frac{r_1^i}{r_1^3}\,p_2^k\left(\delta^{jk}\frac{r^i}{r}-\delta^{ik}\frac{r^j}{r}-\delta^{ij}\frac{r^k}{r}-\frac{r^ir^jr^k}{r^3}\right)p_2^j + (1\leftrightarrow 2)\right]\\
&+\frac{1}{8}\,p_1^k\,p_2^l\left[-\frac{\delta^{il}\delta^{jk}}{r}+\frac{\delta^{ik}\delta^{jl}}{r}-\frac{\delta^{ij}\delta^{kl}}{r}-\frac{\delta^{jl}r^ir^k}{r^3}-\frac{\delta^{ik}r^jr^l}{r^3}+3\,\frac{r^ir^jr^kr^l}{r^5}\right]p_1^i\,p_2^j\\
&+\frac{1}{4}\left(\vec p_1\,\frac{1}{r^2}\,\vec p_1 + \vec p_2\,\frac{1}{r^2}\,\vec p_2\right) - \frac{1}{64}\,P^i\,P^j\,\frac{3\,r^i\,r^j-\delta^{ij}\,r^2}{r^5} + H_{10} + H_{11} + H_{12}\bigg\rangle
\end{aligned}$$

$$+ \left\langle \frac{3}{2}\,\delta_M E\,(E-V)^2 - \frac{3}{4}\,\vec{P}\,(E-V)^2\,\vec{P} - \frac{3}{8}\,\delta_M E\,p_1^2\,p_2^2 + \frac{3}{16}\,P^2 p_1^2 p_2^2 \right.$$
$$- \frac{3}{4}\left(\delta_M E + 3\,E + \frac{3\,(Z-1)}{r_2} - \vec{p}_1\cdot\vec{p}_2\right)\pi\,Z\,\delta^3(r_1) + (1\leftrightarrow 2)$$
$$+ \frac{1}{2}\,\delta_M E\,p_1^i\,\frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j - \frac{1}{4}\,\vec{P}^2\,p_1^i\,\frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j + \frac{13}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon$$
$$\left. + \frac{13}{16}\,\frac{Z^2\,\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3} - \pi\,\delta^3(r)\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\right\rangle + \langle\delta_M H^{(6)}\rangle, \tag{45}$$

where

$$\langle\delta_M H^{(6)}\rangle = \left\langle \frac{Z}{2}\left[p_1^i\,(E-V)\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right) + p_2^i\,(E-V)\left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)\right]P^j \right.$$
$$- \frac{Z}{4}\left[p_1^i\,p_2^k\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)p_2^k\,P^j + p_2^i\,p_1^k\left(\frac{\delta^{ij}}{r_2}+\frac{r_2^i r_2^j}{r_2^3}\right)p_1^k\,P^j\right] - \frac{Z^2}{2}\,\frac{\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}$$
$$+ \frac{Z}{4}\left[p_2^i\left(\frac{\delta^{ij}}{r}+\frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_1}+\frac{r_1^j r_1^k}{r_1^3}\right) + p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_2}+\frac{r_2^j r_2^k}{r_2^3}\right)\right]P^k$$
$$+ \frac{Z^2}{4}\left[\vec{p}_1\,\frac{1}{r_1^2}\,\vec{p}_1 + \vec{p}_2\,\frac{1}{r_2^2}\,\vec{p}_2 + p_1^i\left(\frac{\delta^{ij}}{r_1}+\frac{r_1^i r_1^j}{r_1^3}\right)\left(\frac{\delta^{jk}}{r_2}+\frac{r_2^j r_2^k}{r_2^3}\right)p_2^k\right]$$
$$+ \frac{Z^3\,\vec{r}_1\cdot\vec{r}_2}{4 r_1^3 r_2^2} + \frac{Z^3\,\vec{r}_1\cdot\vec{r}_2}{4 r_1^2 r_2^3} + \frac{Z^2}{8}\left(\frac{r_1^i}{r_1^3}+\frac{r_2^i}{r_2^3}\right)\left(\frac{r_1^i r_1^j - 3\,\delta^{ij}\,r_1^2}{r_1} - \frac{r_2^i r_2^j - 3\,\delta^{ij}\,r_2^2}{r_2}\right)\frac{r^j}{r^3}$$
$$+ \frac{Z^2}{8}\left[p_2^k\,\frac{r_1^i}{r_1^3}\left(-\delta^{ik}\frac{r_2^j}{r_2} + \delta^{jk}\frac{r_2^i}{r_2} - \delta^{ij}\frac{r_2^k}{r_2} - \frac{r_2^i r_2^j r_2^k}{r_2^3}\right)p_2^j + (1\leftrightarrow 2)\right]$$
$$\left. + \frac{1}{4}\left[\frac{Z^3}{r_1^3}+\frac{Z^3}{r_2^3}\right]_\epsilon - \frac{1}{8}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon - \frac{3\,Z^3}{2}[\pi\,\delta^3(r_1)+\pi\,\delta^3(r_2)] + \delta_M H_8 + \delta_M H_9 \right\rangle, \tag{46}$$

and where H_8 and H_9 are presented in Eqs. (29) and (30), respectively.

VI. TOTAL RECOIL CORRECTION

The final results are split into five parts: (i) the second-order and third-order matrix elements containing H_R, (iii) the second-order and third-order matrix elements containing H_C, (v) the first-order matrix elements between 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-loops radiative corrections. The final formula for singlet states of helium is then

$$\delta_M E^{(6)} = E_{\rm i} + E_{\rm iii} + E_{\rm v} + E_{\rm vi} + E_{\rm vii}, \tag{47}$$

where

$$E_{\rm i} = \left\langle H_R\,\frac{1}{(E-H)'}\left(\frac{\vec{P}^2}{2}-\delta_M E\right)\frac{1}{(E-H)'}\,H_R\right\rangle$$
$$+ 2\left\langle H_R\,\frac{1}{(E-H)'}\,[H_R-\langle H_R\rangle]\,\frac{1}{(E-H)'}\,\frac{\vec{P}^2}{2}\right\rangle + 2\left\langle\delta_M H_R\,\frac{1}{(E-H)'}\,H_R\right\rangle, \tag{48}$$

$$E_{\rm iii} = \left\langle H_C\,\frac{1}{(E-H)}\left(\frac{\vec{P}^2}{2}-\delta_M E\right)\frac{1}{(E-H)}\,H_C\right\rangle$$
$$+ 2\left\langle H_C\,\frac{1}{(E-H)}\,H_C\,\frac{1}{(E-H)}\,\frac{\vec{P}^2}{2}\right\rangle + 2\left\langle\delta_M H_C\,\frac{1}{(E-H)}\,H_C\right\rangle, \tag{49}$$

and where H_R is defined in Eq. (38), $\delta_M H_R$ in Eq. (39), and H_C and $\delta_M H_C$ in Eq. (17). The terms $E_{\rm ii}$ and $E_{\rm iv}$ vanish for singlets. The first-order terms $\delta_M A_2$ and $\delta_M B$ become the sum of $E_{\rm v}$, $E_{\rm vi}$, and $E_{\rm vii}$. In order to explicitly cancel out $1/\epsilon$ terms and simplify

TABLE I. Expectation values of operators Q_i with $i = 1, \dots, 30$ for the $1\,^1S_0$, $2\,^1S_0$, and $2\,^1P_1$ states.

	$1\,^1S_0$	$2\,^1S_0$	$2\,^1P_1$
$Q_1 = 4\pi\,\delta^3(r_1)$	22.750 526	16.455 169	16.014 493
$Q_2 = 4\pi\,\delta^3(r)$	1.336 375	0.108 679	0.009 238
$Q_3 = 4\pi\,\delta^3(r_1)/r_2$	33.440 565	5.593 743	3.934 081
$Q_4 = 4\pi\,\delta^3(r_1)\,p_2^2$	49.160 046	7.578 158	3.866 237
$Q_5 = 4\pi\,\delta^3(r)/r_1$	5.019 713	0.440 864	0.012 785
$Q_6 = 4\pi\,\delta^3(r)\,P^2$	18.859 765	1.800 294	0.070 787
$Q_7 = 1/r$	0.945 818	0.249 683	0.245 024
$Q_8 = 1/r^2$	1.464 771	0.143 725	0.085 798
$Q_9 = 1/r^3$	0.989 274	0.067 947	0.042 405
$Q_{10} = 1/r^4$	− 3.336 384	− 0.312 402	0.008 956
$Q_{11} = 1/r_1^2$	6.017 409	4.146 939	4.043 035
$Q_{12} = 1/(r_1 r_2)$	2.708 655	0.561 861	0.491 245
$Q_{13} = 1/(r_1 r)$	1.920 944	0.340 634	0.285 360
$Q_{14} = 1/(r_1 r_2 r)$	4.167 175	0.398 366	0.159 885
$Q_{15} = 1/(r_1^2 r_2)$	9.172 094	1.472 014	1.063 079
$Q_{16} = 1/(r_1^2 r)$	8.003 454	1.348 761	1.002 157
$Q_{17} = 1/(r_1 r^2)$	3.788 791	0.337 891	0.105 081
$Q_{18} = (\vec{r}_1\cdot\vec{r})/(r_1^3 r^3)$	3.270 472	0.278 353	0.010 472
$Q_{19} = (\vec{r}_1\cdot\vec{r})/(r_1^3 r^2)$	1.827 027	0.159 078	0.043 524
$Q_{20} = r_1^i r_2^j (r^i r^j - 3\delta^{ij} r^2)/(r_1^3 r_2^3 r)$	0.784 425	0.063 677	−0.004 747
$Q_{21} = p_2^2/r_1^2$	14.111 960	2.064 285	1.127 058
$Q_{22} = \vec{p}_1/r_1^2\,\vec{p}_1$	21.833 598	16.459 209	16.067 214
$Q_{23} = \vec{p}_1/r^2\,\vec{p}_1$	4.571 652	0.499 768	0.190 797
$Q_{24} = p_1^i\,(r^i r^j + \delta^{ij} r^2)/(r_1 r^3)\,p_2^j$	0.811 933	0.065 354	0.053 432
$Q_{25} = P^i\,(3r^i r^j - \delta^{ij} r^2)/r^5\,P^j$	−3.765 488	−0.252 967	0.013 743
$Q_{26} = p_2^k\,r_1^i/r_1^3(\delta^{jk} r^i/r - \delta^{ik} r^j/r - \delta^{ij} r^k/r - r^i r^j r^k/r^3)\,p_2^j$	−0.266 894	−0.038 928	−0.039 976
$Q_{27} = p_1^2\,p_2^2$	7.133 710	1.428 213	0.973 055
$Q_{28} = p_1^2/r_1\,p_2^2$	37.010 643	5.955 767	3.102 248
$Q_{29} = \vec{p}_1\times\vec{p}_2/r\,\vec{p}_1\times\vec{p}_2$	4.004 703	0.638 960	0.216 869
$Q_{30} = p_1^k\,p_2^l\,(-\delta^{jl} r^i r^k/r^3 - \delta^{ik} r^j r^l/r^3 + 3 r^i r^j r^k r^l/r^5)\,p_1^i\,p_2^j$	− 1.591 864	− 0.252 663	− 0.126 416

the final result we perform the following further transformations:

$$\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right] = \left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - 2\left[\frac{1}{r^4}\right]_\epsilon + P^i P^j\,\frac{3r^i r^j - \delta^{ij} r^2}{r^5} - \frac{4}{3}\pi\,\delta^d(r) P^2, \tag{50}$$

$$\left[\frac{1}{r^4}\right]_\epsilon = \left[\frac{1}{r^3}\right]_\epsilon + \frac{1}{2}\left(\vec{p}_1\,\frac{1}{r^2}\,\vec{p}_1 + \vec{p}_2\,\frac{1}{r^2}\,\vec{p}_2\right) - \left(E + \frac{Z}{r_1} + \frac{Z}{r_2}\right)\frac{1}{r^2} - \frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\frac{1}{r^2}, \tag{51}$$

$$\left[\frac{Z^2}{r_1^4}\right]_\epsilon = \vec{p}_1\,\frac{Z^2}{r_1^2}\,\vec{p}_1 - 2\left(E + \frac{Z}{r_2} - \frac{1}{r}\right)\frac{Z^2}{r_1^2} + p_2^2\,\frac{Z^2}{r_1^2} - 2\left[\frac{Z^3}{r_1^3}\right]_\epsilon - 2\,\frac{m}{M}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\frac{Z^2}{r_1^2}, \tag{52}$$

$$p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j = -2\,H_M^{(4)} - (E-V)^2 + \frac{1}{2}\,p_1^2\,p_2^2 + Z\pi\,[\delta^3(r_1)+\delta^3(r_2)] + 2\,\pi\,\delta^3(r)$$
$$-2\,\frac{m}{M}\left[(E-V)\left(\delta_M E - \frac{\vec{P}^2}{2}\right) - \delta_M H^{(4)}\right], \tag{53}$$

$$\vec{p}_1\cdot\vec{p}_2\left[\frac{1}{r}\right]_\epsilon \vec{p}_1\cdot\vec{p}_2 = p_1^2\left[\frac{1}{r}\right]_\epsilon p_2^2 - \vec{p}_1\times\vec{p}_2\,\frac{1}{r}\,\vec{p}_1\times\vec{p}_2 - 2\pi\,\delta^d(r) P^2. \tag{54}$$

TABLE II. Expectation values of operators Q_i with $i = 31, \ldots, 50$, nonrelativistic energy E, the expectation value of the Breit Hamiltonian $E^{(4)}$, and the first-order corrections $\delta_M E$ and $\delta_M E^{(4)}$ for the $1\,{}^1S_0$, $2\,{}^1S_0$, and $2\,{}^1P_1$ states.

	$1\,{}^1S_0$	$2\,{}^1S_0$	$2\,{}^1P_1$
$Q_{31} = 4\pi\delta^3(r_1)\,\vec p_1\cdot\vec p_2$	5.610 577	0.485 629	0.281 360
$Q_{32} = (\vec r_1\cdot\vec r_2)/(r_1^3 r_2^3)$	− 0.683 465	− 0.054 344	0.005 113
$Q_{33} = \vec p_1\cdot\vec p_2$	0.159 069	0.009 504	0.046 045
$Q_{34} = \vec P\,/r_1\,\vec P$	10.586 465	5.103 771	4.890 226
$Q_{35} = \vec P\,/r\,\vec P$	7.020 556	1.367 497	1.129 114
$Q_{36} = \vec P\,/r_1^2\,\vec P$	38.918 728	18.764 418	17.426 840
$Q_{37} = \vec P\,/(r_1 r_2)\,\vec P$	17.360 500	3.093 110	2.275 085
$Q_{38} = \vec P\,/(r_1 r)\,\vec P$	14.417 322	2.139 854	1.339 969
$Q_{39} = \vec P\,/r^2\,\vec P$	13.995 389	1.425 735	0.444 219
$Q_{40} = p_1^2\,p_2^2\,P^2$	244.833 024	39.737 868	20.202 142
$Q_{41} = P^2\,p_1^i\,(r^i r^j + \delta^{ij} r^2)/r^3\,p_2^j$	12.204 592	1.693 435	0.490 552
$Q_{42} = p_1^i\,\big(r_1^i r_1^j + \delta^{ij} r_1^2\big)/r_1^4\,P^j$	45.454 198	33.063 647	32.258 198
$Q_{43} = p_1^i\,\big(r_1^i r_1^j + \delta^{ij} r_1^2\big)/\big(r_1^3 r_2\big)\,P^j$	16.864 462	3.053 603	2.163 635
$Q_{44} = p_1^i\,p_2^k\,\big(r_1^i r_1^j + \delta^{ij} r_1^2\big)/r_1^3\,p_2^k\,P^j$	26.906 923	4.533 118	2.283 665
$Q_{45} = p_2^i(r^i r^j + \delta^{ij} r^2)\big(r_1^j r_1^k + \delta^{jk} r_1^2\big)/\big(r_1^3 r^3\big)\,P^k$	12.589 902	1.471 046	0.550 295
$Q_{46} = p_1^i\big(r_1^i r_1^j + \delta^{ij} r_1^2\big)\big(r_2^j r_2^k + \delta^{jk} r_2^2\big)/\big(r_1^3 r_2^3\big)\,p_2^k$	1.225 423	0.096 713	0.111 613
$Q_{47} = (\vec r_1\cdot\vec r_2)/\big(r_1^3 r_2^2\big)$	− 0.275 868	− 0.021 822	0.001 588
$Q_{48} = r_1^i r^j\big(r_1^i r_1^j - 3\delta^{ij} r_1^2\big)/\big(r_1^4 r^3\big)$	− 2.285 118	− 0.185 238	− 0.034 770
$Q_{49} = r_1^i r^j\big(r_2^i r_2^j - 3\delta^{ij} r_2^2\big)/\big(r_1^3 r_2 r^3\big)$	− 3.574 722	− 0.306 798	− 0.074 979
$Q_{50} = p_2^k\,r_1^i/r_1^3\,\big(\delta^{jk} r_2^i/r_2 - \delta^{ik} r_2^j/r_2 - \delta^{ij} r_2^k/r_2 - r_2^i r_2^j r_2^k/r_2^3\big)\,p_2^j$	− 0.071 814	0.014 329	0.041 860
E	− 2.903 724 377	− 2.145 974 046	− 2.123 843 086
$E^{(4)}$	− 1.951 754 768	− 2.034 167 340	− 2.040 025 575
$\delta_M E$	3.062 793 852	2.155 477 910	2.169 887 611
$\delta_M E^{(4)}$	− 2.159 371 705	− 0.069 625 849	− 0.058 484 955

The final result for $E_{\rm v}$ and $E_{\rm vi}$ in terms of Q_i operators defined in Tables I–III is

$$\begin{aligned}E_{\rm v} = &-\frac{E}{8}\,Z\,\delta_M\langle Q_1\rangle + \frac{1}{8}\,\delta_M\langle Q_2\rangle + \frac{1}{8}\,Z\,(1-2\,Z)\,\delta_M\langle Q_3\rangle + \frac{3}{16}\,Z\,\delta_M\langle Q_4\rangle - \frac{Z}{4}\,\delta_M\langle Q_5\rangle\\ &+\frac{1}{24}\,\delta_M\langle Q_6\rangle + \frac{E^2+2\,E^{(4)}}{4}\,\delta_M\langle Q_7\rangle - \frac{E}{2}\,\delta_M\langle Q_8\rangle + \frac{1}{4}\,\delta_M\langle Q_9\rangle + \frac{E}{2}\,Z^2\,\delta_M\langle Q_{11}\rangle\\ &+E\,Z^2\,\delta_M\langle Q_{12}\rangle - E\,Z\,\delta_M\langle Q_{13}\rangle - Z^2\,\delta_M\langle Q_{14}\rangle + Z^3\,\delta_M\langle Q_{15}\rangle - \frac{Z^2}{2}\,\delta_M\langle Q_{16}\rangle\\ &-\frac{Z}{2}\,\delta_M\langle Q_{17}\rangle + \frac{Z}{16}\,\delta_M\langle Q_{18}\rangle + \frac{Z}{2}\,\delta_M\langle Q_{19}\rangle - \frac{Z^2}{8}\,\delta_M\langle Q_{20}\rangle + \frac{Z^2}{4}\,\delta_M\langle Q_{21}\rangle\\ &+\frac{Z^2}{4}\,\delta_M\langle Q_{22}\rangle + \delta_M\langle Q_{23}\rangle + \frac{Z}{2}\,\delta_M\langle Q_{24}\rangle - \frac{1}{32}\,\delta_M\langle Q_{25}\rangle - \frac{Z}{4}\,\delta_M\langle Q_{26}\rangle\\ &-\frac{E}{8}\,\delta_M\langle Q_{27}\rangle - \frac{Z}{2}\,\delta_M\langle Q_{28}\rangle + \frac{1}{4}\,\delta_M\langle Q_{29}\rangle + \frac{1}{8}\,\delta_M\langle Q_{30}\rangle + \delta_M E_H,\end{aligned} \tag{55}$$

where $\delta_M E_H$ is the remainder from H_{12} in Eq. (33) after cancellation of $1/\epsilon$ singularities,

$$\delta_M E_H = \left(-4\ln\alpha - \frac{39\,\zeta(3)}{\pi^2} + \frac{32}{\pi^2} - 6\ln(2) + \frac{7}{3}\right)\frac{\delta_M\langle Q_2\rangle}{16}, \tag{56}$$

and

$$\begin{aligned}E_{\rm vi} = \bigg\langle &-\frac{3}{2}\,E^3 - 3\,E\,E^{(4)} - 2\,E^2\,\delta_M E - \frac{3\,E + \delta_M E + 4\,Z^2}{8}\,Z\,Q_1 - \frac{Z\,(8\,Z-3)}{8}\,Q_3\\ &-\frac{3}{4}\,Z\,Q_5 + \frac{1}{8}\,Q_6 + \frac{3\,E^2 + 2\,E\,\delta_M E + 6\,E^{(4)} + 2\,\delta_M E^{(4)}}{4}\,Q_7 - \frac{1}{2}\,\delta_M E\,Q_8\\ &+\frac{2\,E + \delta_M E}{2}\,Z^2\,Q_{11} + (3\,E + \delta_M E)\,(Z^2\,Q_{12} - Z\,Q_{13}) - 3\,Z^2\,Q_{14} + \frac{5}{2}\,Z^3\,Q_{15}\\ &-Z^2\,Q_{16} + \frac{3}{2}\,Z\,Q_{17} + Z^2\,Q_{21} + \frac{3}{2}\,Z^2\,Q_{22} + \frac{3}{2}\,Z\,Q_{24} - \frac{1}{8}\,\delta_M E\,Q_{27} - \frac{3}{4}\,Z\,Q_{28}\end{aligned}$$

$$+\frac{3}{8}\,Z\,Q_{31}+\frac{Z^2}{8}\,Q_{32}-\frac{3}{2}\,E\,Z\,Q_{34}+\frac{E}{2}\,Q_{35}-\frac{3}{4}\,Z^2\,Q_{36}-Z^2\,Q_{37}+\frac{3}{2}\,Z\,Q_{38}$$
$$+\frac{3}{16}\,Q_{40}-\frac{1}{4}\,Q_{41}+\frac{Z^2}{2}\,Q_{42}+\frac{Z^2}{2}\,Q_{43}-\frac{Z}{2}\,Q_{44}+\frac{Z}{2}\,Q_{45}+\frac{Z^2}{4}\,Q_{46}+\frac{Z^3}{2}\,Q_{47}$$
$$+\frac{Z^2}{4}\,Q_{48}-\frac{Z^2}{4}\,Q_{49}+\frac{Z^2}{4}\,Q_{50}\Big\rangle. \tag{57}$$

Finally,

$$E_{\rm vii}=\langle\delta_M H_8+\delta_M H_9\rangle+\delta_M\langle H_{10}+H_{11}\rangle. \tag{58}$$

VII. NUMERICAL RESULTS

The numerical calculations of the nonrelativistic energy and wave function were performed in the explicitly correlated exponential basis with nonlinear parameters generated randomly within variationally optimized intervals, a method described in the literature by Korobov [16]. The method is very efficient and allows getting accuracy for energies as high as 16 digits with a basis as small as 1500 functions. The evaluation of second-order matrix elements is more complicated and requires large values of nonlinear parameters for obtaining accurate results. In order to avoid numerical problems related to linear dependence in the basis set, all the calculations are performed in octuple precision arithmetics.

Table I presents our results for the expectation values of operators $Q_{i=1,\ldots,30}$ which appear in the evaluation of the nonrecoil $\alpha^6 m$ corrections for singlet states of helium. Table II presents results for the expectation values of additional operators $Q_{i=31,\ldots,50}$ which appear in the recoil correction to order $\alpha^6 m^2/M$. Table III presents results for the matrix elements of $Q_{i=1,\ldots,30}$ perturbed by the nuclear kinetic energy operator. These are all matrix elements that are needed to obtain energy shifts of order $\alpha^6 m$ and $\alpha^6 m^2/M$. Table IV presents the results for the individual contributions to the recoil $\alpha^6 m^2/M$ correction. We notice that the photon exchange contributions $E_{\rm i}+E_{\rm iii}+E_{\rm v}+E_{\rm vi}$ tend to cancel each other and their net effect is relatively small in comparison to $E_{\rm vii}$. Only for the $2\,^1P_1$ state are both parts of the same order. Table VI presents our summary of all contributions to the isotope shift in the $2\,^1S$-$2\,^3S$ transition for a point nucleus. It includes two additional contributions. The first one is a small shift due to the nuclear polarizability. The second contribution is due to the hyperfine mixing of $2\,^1S$ and $2\,^3S$ levels, which is a nominally $\alpha^6 m^3/M^2$ correction, but is enhanced by a small energy difference between these states.

In Table V we present the status of the theoretical prediction of the $2\,^1S$-$2\,^3S$ transition energy of ^{4}He. All contributions listed in the table are numerically exact [17], except for $\alpha^7 m$. Following Ref. [17], this contribution is estimated based on the known hydrogenic result. Due to a strong cancellation of the estimate between the $2\,^1S$ and $2\,^3S$ states, the uncertainty of the difference is difficult to guess, so we assume 50% of the whole contribution. We observe a fair agreement with the experimental value from Ref. [12]. In fact, the difference with

TABLE III. Expectation values of operators $\delta_M\langle Q_i\rangle$ with $i=1,\ldots,30$ for the $1\,^1S_0$, $2\,^1S_0$, and $2\,^1P_1$ states.

	$1\,^1S_0$	$2\,^1S_0$	$2\,^1P_1$
$\delta_M\langle Q_1\rangle$	−69.398 419	−49.370 647	−47.548 301
$\delta_M\langle Q_2\rangle$	−4.164 065	−0.303 860	−0.071 149
$\delta_M\langle Q_3\rangle$	−140.863 781	−22.886 485	−17.954 636
$\delta_M\langle Q_4\rangle$	−264.235 067	−39.376 218	−23.782 626
$\delta_M\langle Q_5\rangle$	−21.752 541	−1.810 273	−0.115 562
$\delta_M\langle Q_6\rangle$	−104.659 635	−9.811 620	−0.734 559
$\delta_M\langle Q_7\rangle$	−0.884 405	−0.254 546	−0.394 523
$\delta_M\langle Q_8\rangle$	−2.818 398	−0.266 907	−0.305 911
$\delta_M\langle Q_9\rangle$	−1.015 798	−0.042 815	−0.216 329
$\delta_M\langle Q_{10}\rangle$	14.670 321	1.241 088	−0.016 021
$\delta_M\langle Q_{11}\rangle$	−12.344 317	−8.297 087	−8.038 384
$\delta_M\langle Q_{12}\rangle$	−5.755 090	−1.156 557	−1.274 719
$\delta_M\langle Q_{13}\rangle$	−3.923 779	−0.687 748	−0.772 874
$\delta_M\langle Q_{14}\rangle$	−13.208 243	−1.217 078	−0.704 072
$\delta_M\langle Q_{15}\rangle$	−29.209 816	−4.532 140	−3.865 798
$\delta_M\langle Q_{16}\rangle$	−25.139 317	−4.116 908	−3.618 037
$\delta_M\langle Q_{17}\rangle$	−11.755 788	−0.997 079	−0.498 120
$\delta_M\langle Q_{18}\rangle$	−14.692 291	−1.220 964	−0.076 044
$\delta_M\langle Q_{19}\rangle$	−6.384 958	−0.549 039	−0.222 341
$\delta_M\langle Q_{20}\rangle$	−5.471 095	−0.509 842	−0.028 997
$\delta_M\langle Q_{21}\rangle$	−61.053 735	−8.609 657	−5.848 982
$\delta_M\langle Q_{22}\rangle$	−89.811 452	−65.992 539	−64.011 907
$\delta_M\langle Q_{23}\rangle$	−19.418 528	−2.078 930	−1.071 679
$\delta_M\langle Q_{24}\rangle$	−6.349 789	−0.818 061	−0.508 001
$\delta_M\langle Q_{25}\rangle$	20.318 585	1.280 443	−0.069 997
$\delta_M\langle Q_{26}\rangle$	0.019 487	0.013 046	0.262 948
$\delta_M\langle Q_{27}\rangle$	−31.111 811	−5.980 380	−5.023 306
$\delta_M\langle Q_{28}\rangle$	−199.698 515	−31.075 150	−19.296 491
$\delta_M\langle Q_{29}\rangle$	−21.211 342	−3.263 956	−1.458 861
$\delta_M\langle Q_{30}\rangle$	9.913 115	1.535 897	0.868 894

TABLE IV. Results for the $\alpha^6 m^2/M$ contribution to ionization energies of the $1\,^1S_0$, $2\,^1S_0$, and $2\,^1P_1$ states of helium.

$\alpha^6 m^2/M$	$1\,^1S_0$	$2\,^1S_0$	$2\,^1P_1$
$E_{\rm i}$	−2.676 12(3)	−0.245 21	−0.482 76(12)
$E_{\rm iii}$	7.337 46	0.680 17	−3.419 39
$E_{\rm v}$	−48.911 81	−52.988 42	−53.940 11
$E_{\rm vi}$	60.445 89	53.983 65	54.110 62
Subtotal	16.195 42(3)	1.430 19	−3.731 64(12)
$E_{\rm vii}$	−152.161 17	−9.857 35	2.630 40
$\delta_M E^{(6)}$	−135.965 75(3)	−8.427 16	−1.101 24(12)
$\delta_M E^{(6)}$(kHz h)	−347.79	−21.56	−2.82

TABLE V. Breakdown of theoretical contributions to the $2\,^1S$-$2\,^3S$ centroid transition frequencies in ^{4}He, in MHz.

	$(m/M)^0$	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum
α^2	192 490 838.755	– 24 529.467	– 6.511	0.004	192 466 302.781
α^4	45 657.859	– 7.628	0.003	–	45 650.234
α^5	– 1 243.670	0.173	–	–	– 1 243.497
α^6	– 6.947	0.008	–	–	– 6.939
α^7	1.4 (0.7)	–	–	–	1.4 (0.7)
FNS	– 0.607	–	–	–	– 0.607
Total					192 510 703.4 (0.7)
Exp. [12]					192 510 702.145 6 (1 8)

the experiment will be ten times smaller if we neglect the $\alpha^7 m$ contribution completely, so we may have overestimated its magnitude.

VIII. NUCLEAR CHARGE RADIUS DIFFERENCE

We now turn to the determination of the nuclear charge radii difference from the isotope shift. Table VI presents theoretical results for individual contributions to the isotope shift in the $2\,^1S$-$2\,^3S$ transition, for the point nucleus. The contribution of the higher-order $\alpha^7 m^2/M$ QED effects was estimated on the basis of the double logarithmic contribution to the Lamb shift in hydrogen, which for helium takes the form [14]

$$E^{(7)} \approx -Z^3\,\alpha^7\,\ln^2(Z\alpha)^{-2}\,m\,\langle\delta^3(r_1)+\delta^3(r_2)\rangle_M, \qquad (59)$$

and we ascribe a 50% uncertainty to this estimate. The total uncertainty of the theoretical prediction amounts to just 0.2 kHz, which is an order of magnitude smaller than the present experimental error (see Table VII).

By comparing the theoretical (point-nucleus) and experimental values of the centroid energies of a transition in ^{3}He and ^{4}He, we extract the difference in the squares of the nuclear charge radii, $\delta r^2 = r^2(^3\mathrm{He}) - r^2(^4\mathrm{He})$. The difference between the theoretical point-nucleus result and the measured isotope shift frequency can be ascribed solely to the finite nuclear size shift, which can be parametrized as $E_{\rm fs} = C r^2$, with C being a parameter calculated numerically. Using the experimental results for the $2\,^1S$-$2\,^3S$ transition energies in ^{3}He and ^{4}He from Ref. [11] and taking into account the experimental hyperfine shift of the $2\,^3S_1$ state, we obtain δr^2 as described in Table VII, with the result $\delta r^2 = 1.027(11)$ fm^2. It does not agree with the δr^2 values obtained in Refs. [6,7] from the isotope shift in the $2\,^3P$-$2\,^3S$ transition, namely $\delta r^2 = 1.069(3)$ fm^2 [8,9] and $\delta r^2 = 1.061(3)$ fm^2 [10]. We observe that the two results from the $2\,^3P$-$2\,^3S$ transitions are in only slight disagreement with each other but both deviate significantly from the result obtained from the $2\,^1S$-$2\,^3S$ transition.

IX. SUMMARY

The 4σ discrepancy for δr^2 is very puzzling, since we cannot explain it by any missed corrections in the theoretical predictions. All significant theoretical contributions have been calculated and the theoretical uncertainty is orders of magnitude smaller than the deviation. This discrepancy calls for the verification of the experimental transition frequencies (first of all, $2\,^1S$-$2\,^3S$) by independent measurements. Moreover, it can be also accessed by isotope shift measurements in muonic helium. Hopefully, this might be accomplished in the next measurement of the Lamb shift in muonic helium at the Paul Scherrer Institute by the CREMA Collaboration [21]. This experiment will provide an independent determination of the charge radii of helium isotopes, thus shedding light on the proton charge radius puzzle and on the discrepancy for the helium nuclear charge radius difference.

TABLE VI. Breakdown of theoretical contributions to the ^{3}He-^{4}He isotope shift of the $2\,^1S$-$2\,^3S$ centroid transition frequencies, for the point nucleus, in kHz. EMIX is the contribution due to hyperfine mixing of the $2\,^1S$ and $2\,^3S$ states, the related uncertainty of $\alpha^6(m/M)^2$ term due to hyperfine mixing with the other states is estimated by 0.15 kHz.

	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum
α^2	– 8 026 758.52	– 4 958.33	5.07	– 8 031 711.78
α^4	– 2 496.23	2.08	–	– 2 494.15
α^5	56.61	–	–	56.61
α^6	2.73	0.00(15)	–	2.73(15)
α^7	– 0.21(11)			– 0.21(11)
NPOL [18]	0.20(2)	–	–	0.20(2)
EMIX	–	80.69	–	80.69
Present theory				– 8 034 065.91(19)

TABLE VII. Determination of the nuclear charge difference δr^2 from the measurement by van Rooij *et al.* in Ref. [11], in kHz.

$E(^3\mathrm{He},2\,^1S^{F=1/2}\text{-}2\,^3S^{F=3/2}) - E(^4\mathrm{He},2\,^1S\text{-}2\,^3S)$	− 5 787 719.2(2.4)	Ref. [11]
$\delta E_{\mathrm{hfs}}(2\,^3S^{3/2})$	− 2 246 567.059(5)	Refs. [19,20]
$-\delta E_{\mathrm{iso}}(2\,^1S\text{-}2\,^3S)$ (point nucleus)	8 034 065.91(19)	Theory, Table VI
δE	− 220.4(2.4)	
C	− 214.66(2) kHz/fm^2	Ref. [7]
$\delta r^2 = r^2(^3\mathrm{He}) - r^2(^4\mathrm{He})$	1.027(11) fm^2	

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APPENDIX A: DERIVATION OF $\delta_M A_2$

A_2^M is split into six parts in the order that they appear in Eq. (43):

$$A_2^M = A_{2a}^M + A_{2b}^M + A_{2c}^M + A_{2d}^M + A_{2e}^M + A_{2f}^M. \tag{A1}$$

The first three terms contain both recoil and nonrecoil parts while the latter three contain only recoil terms. Individual parts are transformed as follows:

$$\begin{aligned} A_{2a}^M &= \langle Q\,(H_M - E_M)\,Q\rangle_M = \frac{1}{2}\,\langle [Q,[H_M - E_M,Q]]\rangle_M = \frac{1}{2}\,\langle (\nabla_1 Q)^2 + (\nabla_2 Q)^2\rangle_M + \frac{1}{4}\frac{m}{M}\langle [Q,[\vec{P}^2,Q]]\rangle \\ &= \left\langle \frac{1}{32}\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon + \frac{(d-1)^2}{16}\left[\frac{1}{r^4}\right]_\epsilon - \frac{Z}{8}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle_M + \frac{m}{M}\left\langle \frac{1}{32}\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon + \frac{1}{16}\frac{Z^2\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right\rangle, \end{aligned} \tag{A2}$$

$$A_{2b}^M = 2\,E^{(4)}\langle Q\rangle_M + 2\,\delta_M E^{(4)}\left(\frac{E}{2} + \left\langle\frac{1}{4r}\right\rangle\right), \tag{A3}$$

$$A_{2c}^M = -2\left\langle H_M^{(4)}\,Q\right\rangle_M = X_1 + X_2 + X_3 + X_4, \tag{A4}$$

where

$$\begin{aligned} X_4 &= -2\,\langle \delta_M H^{(4)}\,Q\rangle \\ &= \sum_a \left\langle -\frac{Z}{4}\,P^i\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)p_a^j - \frac{Z}{4}\left[\frac{1}{2\,r_a}\left(\delta^{ij} + \frac{r_a^i r_a^j}{r_a^2}\right)\right]_\epsilon \left[p_a^i,\left[p_a^j,\left[\frac{Z}{r_a}\right]_\epsilon\right]\right]\right\rangle \\ &= \sum_a \left\langle -\frac{Z}{4}\,P^i\left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i r_a^j}{r_a^3}\right)\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)p_a^j + \frac{1}{4}\left[\frac{Z^2}{r_a^4}\right]_\epsilon + \frac{Z^3}{2}\,\pi\,\delta^3(r_a)\right\rangle. \end{aligned} \tag{A5}$$

In the above the term with the Dirac delta function was obtained by using dimensionally regularized representation of the Coulomb potential. Further, using the identity $\langle\,\delta^d(x)\,\frac{1}{x}\,\rangle = 0$,

$$X_3 = -\,\langle [Z\,\pi\,\delta^3(r_1) + Z\,\pi\,\delta^3(r_2) + 2\,\pi\,\delta^3(r)]\,Q\rangle_M = \left\langle \frac{Z\,(Z-2)\,\pi}{4}\left(\frac{\delta^3(r_1)}{r_2} + \frac{\delta^3(r_2)}{r_1}\right) + \frac{Z\,\pi}{2}\left(\frac{\delta^3(r)}{r_1} + \frac{\delta^3(r)}{r_2}\right)\right\rangle_M, \tag{A6}$$

$$\begin{aligned} X_2 &= \left\langle p_1^i\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j)}{r^2}\right)\,p_2^j\,Q\right\rangle_M \\ &= \left\langle -\frac{1}{4}\,p_1^i\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{2}{r}\right)\frac{1}{r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\,p_2^j + \frac{d-1}{4}\left[p_1^i,\left[p_2^j,\left[\frac{1}{r}\right]_\epsilon\right]\right]\left[\frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\right]_\epsilon\right\rangle_M, \end{aligned} \tag{A7}$$

$$\begin{aligned} X_1 &= \frac{1}{4}\,\langle [(p_1^2 + p_2^2) - 2\,p_1^2 p_2^2]\,Q\rangle_M \\ &= \frac{1}{4}\left\langle (p_1^2 + p_2^2)\,Q\,(p_1^2 + p_2^2) + \frac{1}{2}\,[p_1^2 + p_2^2,[Q,p_1^2 + p_2^2]] - 2\,p_1^2\,Q\,p_2^2 - [p_1^2,[p_2^2,Q]]\right\rangle_M \\ &= X_{1A} + X_{1B} + X_{1C} + X_{1D}. \end{aligned} \tag{A8}$$

Here

$$X_{1A} = \langle (E-V)^2\, Q\rangle_M + 2\,\frac{m}{M}\left\langle (E-V)\,Q\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\right\rangle$$
$$= \langle (E-V)^2\, Q\rangle_M + \frac{m}{M}\left\langle 2\,\delta_M E\,(E-V)\,Q - \vec{P}\,(E-V)\,Q\vec{P} - \frac{1}{2}\,[\vec{P},[\vec{P},(E-V)\,Q]]\right\rangle, \tag{A9}$$

$$X_{1B} = -\frac{1}{4}\left\langle\left[V + \frac{m}{M}\,\frac{\vec{P}^2}{2},\left[p_1^2+p_2^2,\,Q\right]\right]\right\rangle_M$$
$$= \left\langle -\frac{1}{8}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon\right\rangle_M + \frac{m}{M}\left\langle \frac{1}{8}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{1}{4}\,\frac{Z^2\,\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right\rangle, \tag{A10}$$

$$X_{1C} = \left\langle \frac{1}{8}\,p_1^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)p_2^2 - \frac{(d-1)}{8}\,p_1^2\left[\frac{1}{r}\right]_\epsilon p_2^2\right\rangle_M, \tag{A11}$$

$$X_{1D} = \left\langle -\frac{(d-1)}{16}\left[p_1^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right\rangle_M. \tag{A12}$$

The remaining A terms are

$$A_{2d}^M = \frac{m}{M}\,\langle [Q,[H-E,\delta_M Q]]\rangle$$
$$= \frac{m}{M}\,\langle (\nabla_1 Q)(\nabla_1 \delta_M Q) + (\nabla_2 Q)(\nabla_2 \delta_M Q)\rangle$$
$$= \frac{m}{M}\left\langle -\frac{3}{16}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle, \tag{A13}$$

$$A_{2e}^M = \frac{m}{M}\left(\frac{3}{2}\,E^{(4)}\left\langle\frac{1}{r}\right\rangle - 3\,E\,E^{(4)}\right), \tag{A14}$$

$$A_{2f}^M = -2\,\frac{m}{M}\,\langle H_A\,\delta_M Q\rangle = F_1 + F_2 + F_3, \tag{A15}$$

where

$$F_3 = -\frac{m}{M}\left\langle \frac{3\,Z^2\,\pi}{4}\left(\frac{\delta^3(r_1)}{r_2}+\frac{\delta^3(r_2)}{r_1}\right) + \frac{3}{2}\pi\,Z\left(\frac{\delta^3(r)}{r_1}+\frac{\delta^3(r)}{r_2}\right)\right\rangle, \tag{A16}$$

$$F_2 = \frac{m}{M}\left\langle \frac{3}{4}\,p_1^i\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\frac{1}{r}\left(\delta^{ij}+\frac{r^i r^j}{r^2}\right)p_2^j\right\rangle, \tag{A17}$$

$$F_1 = \frac{1}{4}\,\frac{m}{M}\,\langle\left[\left(p_1^2+p_2^2\right)^2 - 2\,p_1^2 p_2^2\right]\delta Q\rangle$$
$$= \frac{1}{4}\,\frac{m}{M}\,\langle\left(p_1^2+p_2^2\right)\delta Q\left(p_1^2+p_2^2\right) + \frac{1}{2}\left[p_1^2+p_2^2,\left[p_1^2+p_2^2,\delta Q\right]\right] - 2\,p_1^2\,\delta Q\,p_2^2\rangle$$
$$= F_{1A} + F_{1B} + F_{1C}, \tag{A18}$$

and where

$$F_{1A} = \frac{m}{M}\left\langle \frac{3}{4}\,(E-V)^2\left[\frac{Z}{r_1}+\frac{Z}{r_2}\right]_\epsilon\right\rangle, \tag{A19}$$

$$F_{1B} = \frac{m}{M}\left\langle \frac{3}{8}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon - \frac{3}{8}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle, \tag{A20}$$

$$F_{1C} = -\frac{m}{M}\left\langle \frac{3}{8}\,p_1^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)p_2^2\right\rangle. \tag{A21}$$

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

$$\delta_M A_{2a} = \delta_M\left\langle \frac{1}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{(d-1)^2}{16}\left[\frac{1}{r^4}\right]_\epsilon - \frac{Z}{8}\left(\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3}\right\rangle + \left\langle \frac{1}{32}\left(\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right) + \frac{1}{16}\,\frac{Z^2\,\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right\rangle, \tag{A22}$$

$$\delta_M A_{2b} = 2E^{(4)}\delta_M\langle Q\rangle + 2\delta_M E^{(4)}\left(\frac{E}{2}+\left\langle\frac{1}{4r}\right\rangle\right), \tag{A23}$$

$$\delta_M A_{2c} = \delta_M \bigg\langle \frac{Z(Z-2)\pi}{4}\bigg(\frac{\delta^3(r_1)}{r_2}+\frac{\delta^3(r_2)}{r_1}\bigg) + \frac{Z\pi}{2}\bigg(\frac{\delta^3(r)}{r_1}+\frac{\delta^3(r)}{r_2}\bigg) - \frac{1}{4}\,p_1^i\bigg(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{2}{r}\bigg)\frac{1}{r}\bigg(\delta^{ij}+\frac{r^i r^j}{r^2}\bigg)\,p_2^j$$
$$+\frac{(d-1)}{4}\bigg[p_1^i,\bigg[p_2^j,\bigg[\frac{1}{r}\bigg]_\epsilon\bigg]\bigg]\bigg[\frac{1}{2r}\bigg(\delta^{ij}+\frac{r^i r^j}{r^2}\bigg)\bigg]_\epsilon + (E-V)^2\,Q - \frac{1}{8}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon$$
$$+\frac{3}{8}\bigg(\frac{Z\vec r_1}{r_1^3}-\frac{Z\vec r_2}{r_2^3}\bigg)\cdot\frac{\vec r}{r^3} - \frac{(d-1)}{4}\bigg[\frac{1}{r^4}\bigg]_\epsilon + \frac{1}{8}\,p_1^2\bigg(\frac{Z}{r_1}+\frac{Z}{r_2}\bigg)\,p_2^2 - \frac{(d-1)}{8}\,p_1^2\bigg[\frac{1}{r}\bigg]_\epsilon\,p_2^2 - \frac{(d-1)}{16}\bigg[p_1^2,\bigg[p_2^2,\bigg[\frac{1}{r}\bigg]_\epsilon\bigg]\bigg]\bigg\rangle$$
$$+\bigg\langle -\frac{Z}{4}\sum_a P^i\bigg(\frac{\delta^{ij}}{r_a}+\frac{r_a^i r_a^j}{r_a^3}\bigg)\bigg(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{2}{r}\bigg)\,p_a^j + \frac{3}{8}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon$$
$$+\frac{Z^3}{2}[\pi\,\delta^3(r_1)+\pi\,\delta^3(r_2)] + 2\delta_M E\,(E-V)\,Q - \vec P\,(E-V)\,Q\vec P - \frac{1}{2}\,[\vec P,[\vec P,(E-V)\,Q]] + \frac{1}{4}\,\frac{Z^2\,\vec r_1\cdot\vec r_2}{r_1^3 r_2^3}\bigg\rangle, \quad \text{(A24)}$$

$$\delta_M A_{2d} = \bigg\langle -\frac{3}{16}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon + \frac{3}{8}\bigg(\frac{Z\vec r_1}{r_1^3}-\frac{Z\vec r_2}{r_2^3}\bigg)\cdot\frac{\vec r}{r^3}\bigg\rangle, \quad \text{(A25)}$$

$$\delta_M A_{2e} = \frac{3}{2}\,E^{(4)}\bigg\langle\frac{1}{r}\bigg\rangle - 3\,E\,E^{(4)}, \quad \text{(A26)}$$

$$\delta_M A_{2f} = \bigg\langle -\frac{3\,Z^2\pi}{4}\bigg(\frac{\delta^3(r_1)}{r_2}+\frac{\delta^3(r_2)}{r_1}\bigg) + \frac{3}{4}\,p_1^i\bigg(\frac{Z}{r_1}+\frac{Z}{r_2}\bigg)\frac{1}{r}\bigg(\delta^{ij}+\frac{r^i r^j}{r^2}\bigg)\,p_2^j + \frac{3}{4}\,(E-V)^2\bigg[\frac{Z}{r_1}+\frac{Z}{r_2}\bigg]_\epsilon$$
$$+\frac{3}{8}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon - \frac{3}{8}\bigg(\frac{Z\vec r_1}{r_1^3}-\frac{Z\vec r_2}{r_2^3}\bigg)\cdot\frac{\vec r}{r^3} - \frac{3}{8}\,p_1^2\bigg(\frac{Z}{r_1}+\frac{Z}{r_2}\bigg)\,p_2^2 - \frac{3}{2}\pi\,Z\bigg(\frac{\delta^3(r)}{r_1}+\frac{\delta^3(r)}{r_2}\bigg)\bigg\rangle. \quad \text{(A27)}$$

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

$$[\vec P,[\vec P,(E-V)\,Q]] = \frac{1}{2}\,\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon + \frac{Z^2\,\vec r_1\cdot\vec r_2}{r_1^3 r_2^3} - \bigg(E+\frac{2\,Z-3}{r_2}\bigg)\pi\,Z\,\delta^3(r_1) - \bigg(E+\frac{2\,Z-3}{r_1}\bigg)\pi\,Z\,\delta^3(r_2), \quad \text{(A28)}$$

we get the final result in Eq. (44).

APPENDIX B: DERIVATION OF $\delta_M B$

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

$$B_i^M = \langle H_i^M\rangle_M, \quad \text{(B1)}$$

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

$$H_1^M = \tfrac{1}{16}\,(p_1^6+p_2^6) \quad \text{(B2)}$$

is

$$B_1^M = \frac{1}{16}\,\big\langle (p_1^2+p_2^2)^3 - 3\,p_1^2 p_2^2\,(p_1^2+p_2^2)\big\rangle_M$$
$$= \bigg\langle \frac{1}{8}\bigg[V+\frac{m}{M}\frac{\vec P^2}{2},[p_1^2+p_2^2,V]\bigg] + \frac{1}{2}\bigg[E-V+\frac{m}{M}\bigg(\delta_M E-\frac{\vec P^2}{2}\bigg)\bigg]^3 - \frac{3}{8}\,p_1^2\,p_2^2\bigg[E-V+\frac{m}{M}\bigg(\delta_M E-\frac{\vec P^2}{2}\bigg)\bigg]\bigg\rangle_M$$
$$= \bigg\langle \frac{1}{4}\,[(\nabla_1 V)^2+(\nabla_2 V)^2] + \frac{1}{2}\,(E-V)^3 - \frac{3}{8}\,p_1^2\,(E-V)\,p_2^2 + \frac{3}{16}\,[p_1^2,[p_2^2,V]]\bigg\rangle_M$$
$$+\frac{m}{M}\bigg\langle \frac{3}{2}\,(E-V)^2\bigg(\delta_M E-\frac{\vec P^2}{2}\bigg) - \frac{3}{8}\,p_1^2 p_2^2\bigg(\delta_M E-\frac{\vec P^2}{2}\bigg) - \frac{1}{2}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon - \frac{Z^2\,\vec r_1\cdot\vec r_2}{r_1^3 r_2^3}\bigg\rangle. \quad \text{(B3)}$$

Recoil correction $\delta_M B_1$ is then

$$\delta_M B_1 = \delta_M\bigg\langle \frac{1}{4}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon - \frac{1}{2}\bigg(\frac{Z\vec r_1}{r_1^3}-\frac{Z\vec r_2}{r_2^3}\bigg)\cdot\frac{\vec r}{r^3} + \frac{1}{2}\bigg[\frac{1}{r^4}\bigg]_\epsilon + \frac{1}{2}\,(E-V)^3 + \frac{3}{16}\bigg[p_1^2,\bigg[p_2^2,\bigg[\frac{1}{r}\bigg]_\epsilon\bigg]\bigg] - \frac{3}{8}\,p_1^2\,(E-V)\,p_2^2\bigg\rangle$$
$$+\bigg\langle \frac{3}{2}\,\delta_M E\,(E-V)^2 - \frac{3}{4}\,\vec P\,(E-V)^2\,\vec P + \frac{1}{4}\bigg[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\bigg]_\epsilon + \frac{1}{2}\,\frac{Z^2\,\vec r_1\cdot\vec r_2}{r_1^3 r_2^3}$$
$$-3\,\bigg(E+\frac{Z-1}{r_2}\bigg)\,\pi\,Z\,\delta^3(r_1) + (1\leftrightarrow 2) - \frac{3}{8}\,p_1^2 p_2^2\,\bigg(\delta_M E-\frac{\vec P^2}{2}\bigg)\bigg\rangle. \quad \text{(B4)}$$

Here we used the identity

$$[\vec{P},[\vec{P},(E-V)^2]] = -2\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon - 4\,\frac{Z^2\,\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3} + 2\,(E-V)\,[4\pi\,Z\delta^3(r_1)+4\pi\,Z\delta^3(r_2)]. \tag{B5}$$

The operator H_2^M is

$$H_2^M = \sum_{a=1,2}\frac{(\nabla_a V)^2}{8} + \frac{5}{128}\left[p_a^2,\left[p_a^2,V\right]\right] - \frac{3}{64}\left\{p_a^2,\nabla_a^2 V\right\}. \tag{B6}$$

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

$$\begin{aligned}B_2^M &= \left\langle \tfrac{1}{8}\,[(\nabla_1 V)^2+(\nabla_2 V)^2] + \tfrac{5}{128}\left(\left[p_1^2,\left[p_1^2,V\right]\right]+\left[p_2^2,\left[p_2^2,V\right]\right]\right) - \tfrac{3}{32}\left(p_1^2\,\nabla_1^2 V + p_2^2\,\nabla_2^2 V\right)\right\rangle_M\\ &= B_{2a}^M + B_{2b}^M + B_{2c}^M.\end{aligned} \tag{B7}$$

The term

$$B_{2a}^M = \tfrac{1}{8}\langle(\nabla_1 V)^2+(\nabla_2 V)^2\rangle_M \tag{B8}$$

needs no further reduction. The remaining terms could be simplified to

$$\begin{aligned}B_{2b}^M &= \frac{5}{128}\left\langle\left[p_1^2+p_2^2,\left[p_1^2,V\right]\right]+\left[p_1^2+p_2^2,\left[p_2^2,V\right]\right]-2\left[p_1^2,\left[p_2^2,V\right]\right]\right\rangle_M\\ &= -\frac{5}{64}\left\langle\left[V+\frac{m}{M}\frac{\vec{P}^2}{2},\left[p_1^2+p_2^2,V\right]\right]+\left[p_1^2,\left[p_2^2,V\right]\right]\right\rangle_M,\end{aligned} \tag{B9}$$

$$\begin{aligned}B_{2c}^M &= -\frac{3}{32}\left\langle\left(p_1^2+p_2^2\right)\nabla_1^2 V + \left(p_1^2+p_2^2\right)\nabla_2^2 V - p_2^2\,\nabla_1^2 V - p_1^2\,\nabla_2^2 V\right\rangle_M\\ &= -\frac{3}{8}\,\pi\left\langle 2\left[E-V+\frac{m}{M}\left(\delta_M E-\frac{\vec{P}^2}{2}\right)\right][Z\,\delta^3(r_1)+Z\,\delta^3(r_2)-\delta^3(r)] - p_1^2\,Z\,\delta^3(r_2) - p_2^2\,Z\,\delta^3(r_1)\right\rangle_M.\end{aligned} \tag{B10}$$

Taking now only the recoil parts of individual terms we get

$$\delta_M B_{2a} = \frac{1}{8}\,\delta_M\,\langle(\nabla_1 V)^2+(\nabla_2 V)^2\rangle, \tag{B11}$$

$$\delta_M B_{2b} = -\frac{5}{32}\,\delta_M\left\langle(\nabla_1 V)^2+(\nabla_2 V)^2+\frac{1}{2}\left[p_1^2,\left[p_2^2,V\right]\right]\right\rangle + \frac{5}{64}\,\langle[V,[\vec{P}^2,V]]\rangle, \tag{B12}$$

$$\begin{aligned}\delta_M B_{2c} = &-\frac{3}{8}\,\pi\,\delta_M\left\langle 2\left(E+\frac{Z-1}{r_2}\right)Z\,\delta^3(r_1) + 2\left(E+\frac{Z-1}{r_1}\right)Z\,\delta^3(r_2)\right.\\ &\left.-2\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right)\delta^3(r) - p_1^2\,Z\,\delta^3(r_2) - p_2^2\,Z\,\delta^3(r_1)\right\rangle\\ &-\frac{3}{4}\,\pi\left\langle\left(\delta_M E-\frac{\vec{P}^2}{2}\right)[Z\,\delta^3(r_1)+Z\,\delta^3(r_2)-\delta^3(r)]\right\rangle.\end{aligned} \tag{B13}$$

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

$$\begin{aligned}\delta_M B_2 = \delta_M&\left\langle -\frac{1}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{1}{16}\left(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{1}{16}\left[\frac{1}{r^4}\right]_\epsilon - \frac{5}{64}\left[p_1^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right.\\ &-\frac{3}{8}\,\pi\left[2\left(E+\frac{Z-1}{r_2}\right)Z\,\delta^3(r_1) + 2\left(E+\frac{Z-1}{r_1}\right)Z\,\delta^3(r_2) - 2\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}\right)\delta^3(r)\right.\\ &\left.\left. - p_1^2\,Z\,\delta^3(r_2) - p_2^2\,Z\,\delta^3(r_1)\right]\right\rangle + \left\langle\frac{5}{32}\left[\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right]_\epsilon + \frac{5}{16}\,\frac{Z^2\,\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right.\\ &\left.-\frac{3}{4}\,\pi\left\{\left(\delta_M E - E + \frac{1-Z}{r_2} - \vec{p}_1\cdot\vec{p}_2\right)Z\,\delta^3(r_1) + (1\leftrightarrow 2) - \left(\delta_M E-\frac{\vec{P}^2}{2}\right)\delta^3(r)\right\}\right\rangle.\end{aligned} \tag{B14}$$

The operator H_3^M is

$$H_3^M = -\frac{\pi}{16}\,\nabla^2\delta^3(r) - \frac{\pi}{16}\,\delta_\perp^{ij}\,P^i\,P^j + \frac{\pi}{4}\,\delta_\perp^{ij}\,p^i\,p^j, \tag{B15}$$

and its expectation value is

$$B_3^M = \left\langle -\frac{\pi}{8}\,\nabla^2\delta^3(r) - \frac{1}{64}\,P^i\,P^j\,\frac{3r^3\,r^j - \delta^{ij}\,r^2}{r^5} - \frac{\pi}{24}\,\delta^3(r)\vec{P}^2 - \frac{1}{64}\left(\frac{Z\,\vec{r}_1}{r_1^3} - \frac{Z\,\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r} + \frac{1}{32}\left[\frac{1}{r^4}\right]_\epsilon\right\rangle_M, \tag{B16}$$

where we use the identities

$$4\,\pi\,\delta_\perp^{ij}\,P^i\,P^j = P^i\,P^j\,\frac{3r^3\,r^j - \delta^{ij}\,r^2}{r^5} + \frac{8\,\pi}{3}\,\delta^3(r)\vec{P}^2, \tag{B17}$$

$$4\,\pi\,\delta_\perp^{ij}\,p^i\,p^j = -\pi\,\nabla^2\delta^3(r) - \frac{1}{4}\left(\frac{Z\,\vec{r}_1}{r_1^3} - \frac{Z\,\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r} + \frac{1}{2}\left[\frac{1}{r^4}\right]_\epsilon. \tag{B18}$$

Further, with the help of identity valid for singlet states

$$\langle\,\nabla^2\delta^3(r)\rangle_M = -2\left\langle\,\delta^3(r)\left[E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{\vec{P}^2}{4} + \frac{m}{M}\left(\delta_M\,E - \frac{\vec{P}^2}{2}\right)\right]\right\rangle_M, \tag{B19}$$

we get the following recoil correction $\delta_M B_3$:

$$\begin{aligned}\delta_M B_3 = \delta_M\,&\left\langle\frac{\pi}{4}\,\delta^3(r)\left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{\vec{P}^2}{4}\right) - \frac{1}{64}\,P^i\,P^j\,\frac{3r^3\,r^j - \delta^{ij}\,r^2}{r^5} - \frac{\pi}{24}\,\delta^3(r)\,\vec{P}^2\right.\\ &\left.- \frac{1}{64}\left(\frac{Z\,\vec{r}_1}{r_1^3} - \frac{Z\,\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r} + \frac{1}{32}\left[\frac{1}{r^4}\right]_\epsilon\right\rangle + \left\langle\frac{\pi}{4}\,\delta^3(r)\left(\delta_M\,E - \frac{\vec{P}^2}{2}\right)\right\rangle.\end{aligned} \tag{B20}$$

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 B_{4a}^M, and the expectation value of the recoil part $\delta_M\,H_4$, which we denote B_{4b}^M. The nonrecoil part of the operator H_4^M is

$$H_4 = \frac{1}{4}\left(p_1^2 + p_2^2\right)\,p_1^i\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\,p_2^j - \frac{1}{4}\left(p_1^2 + p_2^2\right)4\,\pi\,\delta^3(r). \tag{B21}$$

The expectation value of this is

$$\begin{aligned}B_{4a}^M &= \frac{1}{2}\left\langle(E - V)\,p_1^i\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\,p_2^j - \frac{1}{2}\,(E - V)\,4\,\pi\,\delta^3(r)\right\rangle_M\\ &\quad+ \frac{m}{M}\left\langle\frac{1}{2}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\,p_1^i\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\,p_2^j - \frac{1}{2}\left(\delta_M\,E - \frac{\vec{P}^2}{2}\right)4\,\pi\,\delta^3(r)\right\rangle\\ &= \left\langle\frac{1}{2}\,p_1^i\,(E - V)\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\,p_2^j - \frac{1}{2}\left[\frac{1}{2r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\right]_\epsilon\,\nabla^i\,\nabla^j\left[\frac{1}{r}\right]_\epsilon - \frac{1}{2}\,(E - V)\,4\,\pi\,\delta^3(r)\right\rangle_M\\ &\quad+ \frac{m}{M}\left\langle\frac{1}{2}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\,p_1^i\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\,p_2^j - \frac{1}{2}\left(\delta_M\,E - \frac{\vec{P}^2}{2}\right)4\,\pi\,\delta^3(r)\right\rangle.\end{aligned} \tag{B22}$$

The recoil correction $\delta_M\,B_{4a}$ is then

$$\begin{aligned}\delta_M\,B_{4a} = \delta_M\,&\left\langle\frac{1}{2}\,p_1^i\,(E - V)\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)p_2^j\; - \frac{1}{2}\left[\frac{1}{2r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\right]_\epsilon\,\nabla^i\,\nabla^j\left[\frac{1}{r}\right]_\epsilon\right.\\ &\left.- \frac{1}{2}\,(E - V)\,4\,\pi\,\delta^3(r)\right\rangle + \left\langle\frac{1}{2}\left(\delta_M E - \frac{\vec{P}^2}{2}\right)\,p_1^i\,\frac{1}{r}\left(\delta^{ij} + \frac{r^i\,r^j}{r^2}\right)\,p_2^j - \frac{1}{2}\left(\delta_M\,E - \frac{\vec{P}^2}{2}\right)4\,\pi\,\delta^3(r)\right\rangle.\end{aligned} \tag{B23}$$

The recoil part of H_4^M is

$$\delta_M\,H_4 = \frac{Z}{4}\left[p_1^2\,p_1^i\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)\,P^j + p_2^2\,p_2^i\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)\,P^j\right]. \tag{B24}$$

The expectation value of this operator can then be reduced to

$$\begin{aligned}\delta_M\,B_{4b} &= \frac{Z}{4}\left\langle 2(E - V)\left[p_1^i\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)P^j + p_2^i\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)P^j\right] - \left[p_2^2\,p_1^i\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)P^j + p_1^2 p_2^i\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)\,P^j\right]\right\rangle\\ &= \left\langle\,\frac{Z}{2}\left[\,p_1^i\,(E - V)\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)\,P^j + p_2^i\,(E - V)\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)\,P^j\right] - \frac{1}{2}\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon - Z^3[\pi\,\delta^3(r_1) + \pi\,\delta^3(r_2)]\right.\\ &\quad\left.- \frac{Z}{4}\left[\,p_1^i\,p_2^k\,\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)\,p_2^k\,P^j + p_2^i\,p_1^k\,\left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i r_2^j}{r_2^3}\right)\,p_1^k\,P^j\,\right]\right\rangle.\end{aligned} \tag{B25}$$

The operator H_5^M is

$$H_5^M = \frac{1}{2}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{(d-1)}{2}\left[\frac{1}{r^4}\right]_\epsilon - \frac{(d-1)}{32}\left(\left[p_1^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right] + \left[p_2^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right), \tag{B26}$$

and its expectation value is

$$B_5^M = \left\langle\frac{1}{2}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{(d-1)}{2}\left[\frac{1}{r^4}\right]_\epsilon + \frac{(d-1)}{16}\left(\left[V,\left[p_1^2+p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right] + \left[p_1^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right)\right\rangle_M. \tag{B27}$$

The recoil correction is then

$$\delta_M B_5 = \delta_M\left\langle\frac{1}{4}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^3} - \frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon + \frac{(d-1)}{16}\left[p_1^2,\left[p_2^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right\rangle. \tag{B28}$$

The operator H_6^M contains the recoil part $\delta_M H_6$ and we thus again split the calculation into two parts: the recoil correction due to H_6, which we denote 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

$$H_6 = \frac{1}{8}\,p_1^i\,\frac{1}{r^2}\left(\delta^{ij} + 3\,\frac{r^i r^j}{r^2}\right)p_1^j + \frac{1}{8}\,p_2^i\,\frac{1}{r^2}\left(\delta^{ij} + 3\,\frac{r^i r^j}{r^2}\right)p_2^j + \frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon, \tag{B29}$$

and the recoil correction due to it is simply

$$\delta_M B_{6a} = \delta_M\left\langle\frac{1}{8}\,p_1^i\,\frac{1}{r^2}\left(\delta^{ij} + 3\,\frac{r^i r^j}{r^2}\right)p_1^j + \frac{1}{8}\,p_2^i\,\frac{1}{r^2}\left(\delta^{ij} + 3\frac{r^i r^j}{r^2}\right)p_2^j + \frac{(d-1)}{4}\left[\frac{1}{r^4}\right]_\epsilon\right\rangle. \tag{B30}$$

The expectation value of $\delta_M H_6$ is

$$\begin{aligned}\delta_M B_{6b} = \bigg\langle &\frac{Z}{4}\left[p_2^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_1} + \frac{r_1^j r_1^k}{r_1^3}\right) + p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)\left(\frac{\delta^{jk}}{r_2} + \frac{r_2^j r_2^k}{r_2^3}\right)\right]P^k \\ &+ \frac{1}{4}\left(\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon - 2\,\frac{Z^2\,\vec{r}_1\cdot\vec{r}_2}{r_1^3 r_2^3}\right) + \frac{Z^3}{2}[\pi\,\delta^3(r_1) + \pi\,\delta^3(r_2)] \\ &+ \frac{Z^2}{8}\left[p_1^i\,\frac{1}{r_1^2}\left(\delta^{ij} + 3\,\frac{r_1^i r_1^j}{r_1^2}\right)p_1^j + p_2^i\,\frac{1}{r_2^2}\left(\delta^{ij} + 3\,\frac{r_2^i r_2^j}{r_2^2}\right)p_2^j + 2\,p_1^i\left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i r_1^j}{r_1^3}\right)\left(\frac{\delta^{jk}}{r_2} + \frac{r_2^j r_2^k}{r_2^3}\right)p_2^k\right]\bigg\rangle.\end{aligned} \tag{B31}$$

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

$$\begin{aligned}H_{7a}^M = -\frac{1}{8}\bigg\{&[p_1^i,V]\left(\frac{r^i r^j}{r} - 3\,\delta^{ij} r\right)[V,p_2^j] + [p_1^i,V]\left[\frac{p_2^2}{2},\frac{r^i r^j}{r} - 3\,\delta^{ij} r\right]p_2^j \\ &+ p_1^i\left[\frac{r^i r^j}{r} - 3\,\delta^{ij} r,\frac{p_1^2}{2}\right][V,p_2^j] + p_1^i\left[\frac{p_2^2}{2},\left[\frac{r^i r^j}{r} - 3\,\delta^{ij} r,\frac{p_1^2}{2}\right]\right]p_2^j\bigg\}.\end{aligned} \tag{B32}$$

The recoil correction due to this operator is

$$\begin{aligned}\delta_M B_{7a} = \delta_M\bigg\langle &-\frac{1}{8}\frac{Zr_1^i}{r_1^3}\frac{Zr_2^j}{r_2^3}\left(\frac{r^i r^j}{r} - 3\delta^{ij} r\right) + \frac{1}{4}\left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3}\right)\cdot\frac{\vec{r}}{r^2} - \frac{1}{4}\left[\frac{1}{r}\right]_\epsilon^3 \\ &- \frac{Z}{8}\left[\frac{r_1^i}{r_1^3}\,p_2^k\left(\delta^{jk}\frac{r^i}{r} - \delta^{ik}\frac{r^j}{r} - \delta^{ij}\frac{r^k}{r} - \frac{r^i r^j r^k}{r^3}\right)p_2^j + (1\leftrightarrow 2)\right] \\ &+ \frac{1}{8}\left[p_2^j\,\frac{1}{r^4}(\delta^{jk} r^2 - 3r^j r^k)p_2^k + (1\leftrightarrow 2)\right] + \frac{1}{4}\left[\frac{1}{r^4}\right]_\epsilon + \pi\,\delta^3(r) \\ &+ \frac{1}{8}\,p_1^k\,p_2^l\left[-\frac{\delta^{il}\delta^{jk}}{r} + \frac{\delta^{ik}\delta^{jl}}{r} - \frac{\delta^{ij}\delta^{kl}}{r} - \frac{\delta^{jl} r^i r^k}{r^3} - \frac{\delta^{ik} r^j r^l}{r^3} + 3\,\frac{r^i r^j r^k r^l}{r^5}\right]p_1^i\,p_2^j\bigg\rangle.\end{aligned} \tag{B33}$$

The operator H_{7c}^M is

$$H_{7c}^M = -\frac{(d-1)}{16}\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right], \tag{B34}$$

and the corresponding recoil correction is simply

$$\delta_M B_{7c} = \delta_M \left\langle -\frac{(d-1)}{16}\left[p_2^2,\left[p_1^2,\left[\frac{1}{r}\right]_\epsilon\right]\right]\right\rangle. \tag{B35}$$

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

$$\begin{aligned} H_{7d}^M &= i\,\frac{Z^2}{8M}\sum_{a,b}\frac{r_a^i}{r_a^3}\left[H-E,\frac{r_b^i r_b^j - 3\,\delta^{ij} r_b^2}{r_b}\,p_b^j\right] \\ &= i\,\frac{Z^2}{8M}\sum_{a,b}\frac{r_a^i}{r_a^3}\left\{\left[V,p_b^j\right]\frac{r_b^i r_b^j - 3\,\delta^{ij} r_b^2}{r_b} + \left[\frac{p_b^2}{2},\frac{r_b^i r_b^j - 3\,\delta^{ij} r_b^2}{r_b}\right]p_b^j\right\}. \end{aligned} \tag{B36}$$

The expectation value of this can then be written as

$$\delta_M B_{7d} = W_1 + W_2, \tag{B37}$$

where

$$\begin{aligned} W_1 &= \left\langle -\frac{Z^2}{8}\sum_{a,b,c\neq b}\frac{r_a^i}{r_a^3}\left(\frac{Z r_b^j}{r_b^3} - \frac{r_{bc}^j}{r_{bc}^3}\right)\frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b} - \frac{7\,Z^3}{4}\pi\,\delta^3(r_b)\right\rangle \\ &= \left\langle \frac{1}{4}\left[\frac{Z}{r_1}\right]_\epsilon^3 + \frac{1}{4}\left[\frac{Z}{r_2}\right]_\epsilon^3 + \frac{Z^3\,\vec{r}_1\cdot\vec{r}_2}{4 r_1^3 r_2^2} + \frac{Z^3\,\vec{r}_1\cdot\vec{r}_2}{4 r_1^2 r_2^3} - \frac{7\,Z^3}{4}[\pi\,\delta^3(r_1) + \pi\,\delta^3(r_2)] + \frac{Z^2}{8}\sum_{b,c\neq b}\left(\frac{r_1^i}{r_1^3} + \frac{r_2^i}{r_2^3}\right)\frac{r_b^i r_b^j - 3\delta^{ij} r_b^2}{r_b}\,\frac{r_{bc}^j}{r_{bc}^3}\right\rangle, \end{aligned} \tag{B38}$$

and

$$\begin{aligned} W_2 &= \left\langle \langle i\,\frac{Z^2}{16}\left(\sum_{a\neq b}\frac{r_a^i}{r_a^3}\left[p_b^2,\frac{r_b^i r_b^j - 3\,\delta^{ij} r_b^2}{r_b}\right]p_b^j + \sum_b\frac{r_b^i}{r_b^3}\left[p_b^2,\frac{r_b^i r_b^j - 3\,\delta^{ij} r_b^2}{r_b}\right]p_b^j\right)\right\rangle \\ &= \left\langle \frac{Z^2}{8}\sum_{a\neq b}p_b^k\,\frac{r_a^i}{r_a^3}\left(-\delta^{ik}\frac{r_b^j}{r_b} + \delta^{jk}\frac{r_b^i}{r_b} - \delta^{ij}\frac{r_b^k}{r_b} - \frac{r_b^i r_b^j r_b^k}{r_b^3}\right)p_b^j \right. \\ &\quad \left. + \frac{1}{8}\left[\frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4}\right]_\epsilon + \frac{3\,Z^3}{4}[\pi\,\delta^3(r_1) + \pi\,\delta^3(r_2)] + \frac{Z^2}{8}\sum_b p_b^j\,\frac{1}{r_b^4}\left(\delta^{jk} r_b^2 - 3 r_b^j r_b^k\right)p_b^k\right\rangle. \end{aligned} \tag{B39}$$

Summing all of the recoils parts $\delta_M B_i$ we get the result in Eq. (45).

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