Complete quantum electrodynamic $\alpha^6 m$ correction to energy levels of light atoms

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We derive a complete expression for the nonrecoil quantum electrodynamic $\alpha^6 m$ correction to the Lamb shift, the fine and hyperfine structure of light N-electron atoms. The derivation is performed in the framework of nonrelativistic quantum electrodynamics. The obtained formulas generalize previous ones derived for the specific cases of the helium atom, and the fine and hyperfine structure of lithium, and pave the way for improving the theory of light atoms with three and more electrons.

Accurate theoretical predictions of transition energies in simple atoms are used for high-precision tests of the Standard Model of fundamental interactions, and determinations of fundamental constants and of nuclear parameters. The highest theoretical precision is achieved for the simplest systems, like the hydrogen and the hydrogen-like ions [1]. However, comparison of the hydrogen theory with the existing experimental data is presently limited by the uncertainty from two conflicting values of the proton charge radius [2].

Modern theoretical descriptions of few-electron atoms gradually approach the level of accuracy of the hydrogen theory [3], with higher potential for discovery of new effects. It is because there are several transitions which have narrow linewidth. In particular, the calculation of the $\alpha^6 m^2/M$ correction in helium [4, 5] allowed us to extract the difference of the nuclear charge radii of two helium isotopes, revealing inconsistencies between different experimental transition energies [6], which remain to be explained. Furthermore, the ongoing project of the complete calculation of the $\alpha^7 m$ effects will allow the determination of the absolute value of the helium nuclear charge radius [7].

For atoms with three and more electrons, the dominant uncertainty of the theoretical energy levels presently comes from uncalculated quantum electrodynamic (QED) effects of order $\alpha^6 m$. This correction was derived and calculated numerically for helium in Refs. [8, 9] and later for helium-like ions in Ref. [10]. The goal of the present investigation is to extend the derivation of Refs. [8, 9] to the general case of an atom with an arbitrary number of electrons, which will open the way towards numerical calculations of these effects in light atoms, such as lithium, beryllium, boron, and the corresponding isoelectronic sequences.

I. NRQED EXPANSION

In order to calculate energy levels of a light atom we employ the so called nonrelativistic QED (NRQED), which is an effective quantum field theory that gives the same predictions as the full QED in the region of small momenta, *i.e.*, those of the order of the characteristic electron momentum in the atom.

The basic assumption of the NRQED is that the bound-state energy E can be expanded in powers of the fine-structure constant α,

$$E\Big(\alpha, \frac{m}{M}\Big) = \alpha^2\, E^{(2)}\Big(\frac{m}{M}\Big) + \alpha^4\, E^{(4)}\Big(\frac{m}{M}\Big) + \alpha^5\, E^{(5)}\Big(\frac{m}{M}\Big) + \alpha^6\, E^{(6)}\Big(\frac{m}{M}\Big) + \ldots \tag{1}$$

The coefficients of this expansion $E^{(i)}$ depend implicitly on the electron-to-nucleus mass ratio m/M and may contain finite powers of $\ln\alpha$. These coefficients may be further expanded in powers of m/M,

$$E^{(i)}\Big(\frac{m}{M}\Big) = E^{(i,0)} + \frac{m}{M}\, E^{(i,1)} + \Big(\frac{m}{M}\Big)^2 E^{(i,2)} + \ldots. \tag{2}$$

According to NRQED, the expansion coefficients in Eqs. (1) and (2) can be expressed as expectation values of some effective Hamiltonians with the nonrelativistic wave function. The derivation of these effective Hamiltonians is the central problem of the NRQED approach.

The leading term of the NRQED expansion, $E^{(2)}$, is of order $\alpha^2 m$ and is just the nonrelativistic energy as obtained from the Schrödinger equation. The next term, $E^{(4)}$, is the leading relativistic correction of order $\alpha^4 m$ and is given by the expectation value of the Breit Hamiltonian $H^{(4)}$. The next term represents the leading QED effect of order $\alpha^5 m$, derived many years ago by Araki and Sucher [11, 12].

The subject of the present work is the next correction of order $\alpha^6 m$, which will be considered in the non-recoil limit, $E^{(6,0)}$. For the helium atom, this correction was derived and calculated numerically by one of us (K.P.) [8, 9], see also the recent review [3]. For lithium, the $\alpha^6 m$ effects were so far calculated for the fine and hyperfine structure [13, 14]. In this work we generalize those studies and present derivation of complete formulas for the $\alpha^6 m$ effects valid for arbitrary states of a general N-electron atom.

We represent the $\alpha^6 m$ correction to the energy level of an atom as a sum of three parts,

$$E^{(6,0)} = E^{(6)}_{\rm Lamb} + E^{(6)}_{\rm fs} + E^{(6)}_{\rm hfs}\,. \tag{3}$$

The first term $E^{(6)}_{\rm Lamb}$ ("Lamb shift") is the correction to the nLS centroid energy (n denotes the principal quantum number, L and S are the angular momentum and the spin of the state under consideration). Energy centroid $E_{\rm Lamb}$ is defined as weighted average over the fine levels

$$E_{\rm Lamb}(nLS) = \frac{\sum_J (2J+1)\, E(nLSJ)}{(2S+1)(2L+1)}\,, \tag{4}$$

where J is the total angular momentum of the electronic state. In the presence of the nuclear spin I, each fine level is in turn an average over the hyperfine levels, namely

$$E(nLSJ) = \frac{\sum_F (2F+1)\, E(nLSJF)}{(2I+1)(2J+1)}\,, \tag{5}$$

where F is the total angular momentum of the whole atom. The second term $E^{(6)}_{\rm fs}$ is a correction to the fine structure, defined by the condition that its contribution to the nLS centroid energy vanishes,

$$\sum_J (2J+1)\, E^{(6)}_{\rm fs}(nLSJ) = 0\,. \tag{6}$$

Finally, the third term $E^{(6)}_{\rm hfs}$ is a contribution to the hyperfine structure, defined by the condition that its contribution to the $nLSJ$ energy centroid vanishes,

$$\sum_F (2F+1)\, E^{(6)}_{\rm hfs}(nLSJF) = 0\,. \tag{7}$$

We note that this definition of the hyperfine splitting leads to the appearance of nuclear-spin dependent contributions in the Lamb shift and in the fine structure (through second-order effects), see Ref. [15] for details. Such corrections are of order $\alpha^6\, m^2/M$ and thus are not relevant for the present investigation.

It should be mentioned that when considering the structure of atomic levels, it is sometimes required to treat several closely lying levels as quasi-degenerate (rather than to consider each of them separately as an isolated level), because of a strong mixing between them. In particular, this is the case for the hyperfine structure of the $2\,^3P$ level of ^{3}He, studied in Ref. [15]. In such cases, the scalar energy E in Eq. (1) needs to be replaced by a matrix of an effective Hamiltonian constructed in a subspace of quasi-degenerate states, and the energy levels are determined by diagonalizing this matrix, see Ref. [15] for details.

II. ENERGY CENTROID

The $\alpha^6\, m$ correction to the energy centroid $E^{(6)}_{\rm Lamb}$ is represented [8] as a sum of several terms,

$$E^{(6)}_{\rm Lamb} = \Big\langle \sum_{i=1}^{7} H_i + \sum_{i=1}^{2} H_{R,i} + H_H \Big\rangle + \Big\langle H^{(4)}\, \frac{1}{(E_0 - H_0)'}\, H^{(4)} \Big\rangle\,, \tag{8}$$

where H_i are the effective $\alpha^6\, m$ operators induced by the virtual photon exchange between the particles, $H_{R,i}$ are the operators representing the radiative corrections, H_H is the effective operator originating from the forward three-photon scattering amplitude, and E_0 and H_0 are the nonrelativistic energy and Hamiltonian for the infinitely heavy nucleus, respectively. The last term on the right-hand side of Eq. (8) is the second-order correction induced by the Breit Hamiltonian $H^{(4)}$,

$$H^{(4)} = H_A + H_B + H_C\,, \tag{9}$$

where

$$H_A = \sum_a \bigg[-\frac{p_a^4}{8} + \frac{\pi Z}{2}\delta^d(r_a)\bigg] + \sum_{a<b}\sum_b \bigg[(d-2)\pi\delta^d(r_{ab}) - \frac{1}{2}\, p_a^i \bigg[\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\bigg]_\epsilon\, p_b^j\bigg]\,, \tag{10}$$

$$H_B^{(4+)} = \frac{Z}{4}\sum_a (g-1)\, \frac{\vec r_a}{r_a^3}\times\vec p_a\cdot\vec\sigma_a + \frac{1}{4}\sum_{b\neq a}\sum_a \frac{1}{r_{ab}^3}\big[g\,\vec r_{ab}\times\vec p_b - (g-1)\,\vec r_{ab}\times\vec p_a\big]\cdot\vec\sigma_a\,, \tag{11}$$

$$H_C^{(4+)} = \frac{1}{4}\sum_{a<b}\sum_b \Big(\frac{g}{2}\Big)^2 \bigg(\frac{\vec\sigma_a\,\vec\sigma_b}{r_{ab}^3} - 3\,\frac{\vec\sigma_a\cdot\vec r_{ab}\,\vec\sigma_b\cdot\vec r_{ab}}{r_{ab}^5}\bigg)\,, \tag{12}$$

where g denotes the electron g-factor, $d = 3-2\epsilon$ is the extended space dimension, $\delta^d(r)$ is the Dirac delta function in d dimensions and $[x]_\epsilon$ stands for d-dimensional form of expression x. In the above, the spin-independent part of the Breit Hamiltonian H_A is written in d dimensions, since it leads to divergent terms $\sim 1/(d-3)$ in the second-order correction. The spin-dependent parts of $H^{(4)}$ are written in $d=3$ as they do not lead to any singularities. The upper index in $H_B^{(4+)}$ and $H_C^{(4+)}$ indicates that these operators are of order $\alpha^4\, m$ but contain, in addition, some higher-order terms due to the presence of anomalous magnetic moment. For further calculations we will also need the $g\to 2$ limit of these operators,

$$H_X \equiv \lim_{g\to 2} H_X^{(4+)} \tag{13}$$

with $X = B, C$.

The derivation of the effective $\alpha^6\, m$ operators H_i is described in Appendix A. It is performed in $d = 3-2\epsilon$ dimensions, following the approach developed in Ref. [8]. The results are

$$H_1 = \sum_a \frac{p_a^6}{16}\,, \qquad H_2 = \sum_a \biggl(\frac{(\nabla_a V)^2}{8} + \frac{5}{128}\,[p_a^2,[p_a^2,V]] - \frac{3}{64}\Bigl\{p_a^2\,,\,\nabla_a^2 V\Bigr\}\biggr)\,,$$

$$H_3 = \sum_{a<b}\sum_b \frac{1}{64}\biggl\{-4\,\pi\,\nabla^2\,\delta^d(r_{ab}) + \frac{4}{d(d-1)}\,\sigma_a^{ij}\sigma_b^{ij}\biggl(\frac{(d-1)}{d}\,\vec p_a\,4\,\pi\,\delta^d(r_{ab})\,\vec p_b - p_a^i\biggl[\frac{\delta^{ij}}{r_{ab}^3} - 3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^5}\biggr]_\epsilon p_b^j\biggr)\biggr\}\,,$$

$$H_4 = \frac{1}{8}\sum_{b\neq a}\sum_a\biggl(\biggl\{p_a^2\,,\,p_a^i\biggl[\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\biggr]_\epsilon p_b^j\biggr\} + \frac{\sigma_a^{ij}\,\sigma_b^{ij}}{2d}\Bigl\{p_a^2\,,\,4\,\pi\,\delta^d(r_{ab})\Bigr\}\biggr)\,,$$

$$H_5 = \sum_{b\neq a}\sum_a \frac{\sigma_a^{ij}\,\sigma_b^{ij}}{2d}\biggl(-\frac{1}{2}\biggl[\frac{\vec r_{ab}}{r_{ab}^3}\biggr]_\epsilon\cdot\vec\nabla_a V + \frac{1}{16}\biggl[\biggl[\biggl[\frac{1}{r_{ab}}\biggr]_\epsilon\,,\,p_a^2\biggr]\,,\,p_a^2\biggr]\biggr)\,,$$

$$H_6 = \sum_{b\neq a}\sum_{c\neq a}\sum_a\biggl(\frac{1}{8}\,p_b^i\biggl(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\biggr)\biggl(\frac{\delta^{jk}}{r_{ac}} + \frac{r_{ac}^j\,r_{ac}^k}{r_{ac}^3}\biggr)p_c^k + \frac{\sigma_b^{ij}\sigma_c^{ij}}{8d}\biggl[\frac{\vec r_{ab}}{r_{ab}^3}\cdot\frac{\vec r_{ac}}{r_{ac}^3}\biggr]_\epsilon\biggr)\,,$$

$$H_7 = H_{7a} + H_{7c}\,,$$

$$H_{7a} = \sum_{a<b}\sum_b\biggl(-\frac{1}{8}\biggr)\biggl\{\nabla_a^i V\biggl[\frac{r_{ab}^i\,r_{ab}^j - 3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\biggr]_\epsilon\nabla_b^j V - i\,\nabla_a^i V\biggl[\frac{p_b^2}{2},\biggl[\frac{r_{ab}^i\,r_{ab}^j - 3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\biggr]_\epsilon\biggr]p_b^j$$
$$+i\,p_a^i\biggl[\biggl[\frac{r_{ab}^i\,r_{ab}^j - 3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\biggr]_\epsilon,\frac{p_a^2}{2}\biggr]\nabla_b^j V + p_a^i\biggl[\frac{p_b^2}{2},\biggl[\biggl[\frac{r_{ab}^i\,r_{ab}^j - 3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\biggr]_\epsilon,\frac{p_a^2}{2}\biggr]\biggr]p_b^j\biggr\}\,,$$

$$H_{7c} = \sum_{a<b}\sum_b\frac{\sigma_a^{ij}\sigma_b^{ij}}{16d}\biggl[p_a^2,\biggl[p_b^2,\biggl[\frac{1}{r_{ab}}\biggr]_\epsilon\biggr]\biggr]\,, \tag{14}$$

where $[.\,,.]$ and $\{.\,,.\}$ denote the commutator and the anticommutator, respectively, and V is the nonrelativistic potential,

$$V = -\sum_a\biggl[\frac{Z}{r_a}\biggr]_\epsilon + \sum_{a<b}\sum_b\biggl[\frac{1}{r_{ab}}\biggr]_\epsilon\,. \tag{15}$$

In the case of a two-electron atom, the operators H_i agree with those derived for helium in Ref. [8].

The effective operator originating from the forward three-photon scattering amplitude is deduced from the results derived in Ref. [16] for parapositronium, which yields

$$H_H = -\biggl(\frac{1}{\epsilon} + 4\ln\alpha\biggr)\sum_{a<b}\sum_b\frac{\pi}{4}\,\delta^d(r_{ab}) + H_H'\,, \tag{16}$$

where

$$H_H' = \biggl(-\frac{39\zeta(3)}{\pi^2} + \frac{32}{\pi^2} - 6\ln 2 + \frac{7}{3}\biggr)\sum_{a<b}\sum_b\frac{\pi}{4}\,\delta^3(r_{ab}) \tag{17}$$

and ζ is Riemann zeta function.

Radiative corrections to order $\alpha^6\,m$ are represented by the following one-loop and two-loop effective operators, which have been obtained originally for hydrogen and positronium spectra,

$$H_{R,1} = \biggl(\frac{472}{96} - 2\ln 2\biggr)\sum_a\pi\delta^3(r_a) \tag{18}$$
$$+\biggl(\frac{6\zeta(3)}{\pi^2} - \frac{697}{27\pi^2} - 8\ln 2 + \frac{1099}{72}\biggr)\sum_{a<b}\sum_b\pi\delta^3(r_{ab})\,,$$

$$H_{R,2} = \biggl(-\frac{9\zeta(3)}{4\pi^2} - \frac{2179}{648\pi^2} + \frac{3\ln 2}{2} - \frac{10}{27}\biggr)\sum_a\pi\delta^3(r_a)$$
$$+\biggl(\frac{15\zeta(3)}{2\pi^2} + \frac{631}{54\pi^2} - 5\ln 2 + \frac{29}{27}\biggr)\sum_{a<b}\sum_b\pi\delta^3(r_{ab})\,. \tag{19}$$

Both the first-order and second-order terms in Eq. (8) contain divergences, which need to be separated out and cancelled algebraically. We perform this in two steps. First, we identify divergences in the second-order corrections (last term in the right-hand side of Eq. (8)) and separate them out in terms of some effective first-order operators by the transformation (B2) as is described in detail in Appendix B. Second, we algebraically cancel singular terms proportional to $1/\epsilon$. This is done with help of various identities in d dimensions listed in Appendix C.

After performing all reductions and cancellations of singularities we get the final result

$$E^{(6)}_{\rm Lamb} = E_Q + E_H' + E_{\rm sec} + E_{R1} + E_{R2}$$
$$-\ln\alpha\,\Bigl\langle\sum_{a<b}\sum_b\pi\delta^3(r_{ab})\Bigr\rangle\,, \tag{20}$$

where $E_Q = \langle H_Q\rangle$ and $E_H' = \langle H_H'\rangle$. The first term in Eq. (20), E_Q, incorporates first-order operators remaining after the cancellation of divergences. With help of the identity $\sigma_a^{ij}\cdot\sigma_b^{ij} = 2\vec\sigma_a\cdot\vec\sigma_b$, we obtain the following formula for H_Q in terms of 45 operators Q_i listed in Table I. These operators are similar to those derived in [8] with two differences: (i) there are extra three-electron operators which are grouped together with corresponding similar one- and two-electron operators, and (ii) dependence on spin in form of product of σ matrices is now included in definition of Q operators. The result is

$$H_Q = -\frac{E_0^3}{2} - \frac{E_0 Z}{16} Q_1 + \frac{Q_2}{8} + \frac{Z(1-2Z)}{16} Q_3 + \frac{3Z}{32} Q_4 + \frac{Z}{16} Q_5 - \frac{Z}{8} Q_6 + \frac{Q_7}{24} + \frac{Q_8}{8} - \frac{Q_9}{96} + \frac{E_0^2 + 2E^{(4)}}{4} Q_{10}$$
$$-\frac{E_0}{32} Q_{11} + \frac{Q_{12}}{32} + \frac{Q_{13}}{32} + \frac{E_0 Z^2}{4} Q_{14} + E_0 Z^2 Q_{15} + \frac{3Z^3}{2} Q_{16} + \frac{Z^3}{2} Q_{17} - \frac{E_0 Z}{2} Q_{18} - Z^2 Q_{19} - \frac{Z}{32} Q_{20}$$
$$-\frac{Z^2}{4} Q_{21} + \frac{Z}{4} Q_{22} + \frac{Z}{2} Q_{23} - \frac{Z}{32} Q_{24} - \frac{Q_{25}}{2} + \frac{Q_{26}}{96} - \frac{Z^2}{8} Q_{27} - \frac{Z}{4} Q_{28} + \frac{Q_{29}}{8} + \frac{Z^2}{8} Q_{30} + \frac{Z^2}{8} Q_{31}$$
$$+\frac{Q_{32}}{32} + \frac{Q_{33}}{64} + \frac{Z}{4} Q_{34} - \frac{Q_{35}}{4} + \frac{Q_{36}}{192} + \frac{Q_{37}}{4} - \frac{Z}{4} Q_{38} + \frac{Q_{39}}{4} - \frac{E_0}{8} Q_{40} - \frac{Z}{4} Q_{41} + \frac{Q_{42}}{8} + \frac{Q_{43}}{4}$$
$$+\frac{Q_{44}}{8} + \frac{3}{16} Q_{45} \,. \tag{21}$$

Here, $E^{(4)} = \langle H^{(4)} \rangle$ is the expectation value of Breit Hamiltonian, and $E_0 = E^{(2)}$ is the nonrelativistic energy. In the case of operator Q_{12}, the expectation value of $1/r_{ab}^3$ is calculated in the sense of the following limit

$$\left\langle \frac{1}{r^3} \right\rangle = \lim_{a\to 0} \int d^3 r \phi^2(r) \biggl[\frac{1}{r^3}\, \Theta(r-a) + 4\pi \delta^3(r)(\gamma + \ln a) \biggr] . \tag{22}$$

In the case of Q_{36}, the matrix element is only conditionally convergent, so one has to integrate first over the angles and then over the radial r_{ab} variable.

$E_{\rm sec}$ in Eq. (20) incorporates what is left of the second-order correction after separation of divergences. It is given by

$$E_{\rm sec} = \langle H_{AR} \frac{1}{(E_0 - H_0)'} H_{AR} \rangle + \langle H_B \frac{1}{(E_0 - H_0)} H_B \rangle + \langle H_C \frac{1}{(E_0 - H_0)} H_C \rangle \,, \tag{23}$$

where H_{AR} is defined by Eq. (B2) and its action on a trial function ϕ is given by,

$$H_{AR} |\phi\rangle = \biggl[-\frac{1}{2} (E_0 - V)^2 + \frac{1}{4} \sum_{a<b} \sum_b \vec\nabla_a^2 \vec\nabla_b^2 - \frac{Z}{4} \sum_a \frac{\vec r_a \cdot \vec\nabla_a}{r_a^3} + \frac{1}{2} \sum_{a<b} \sum_b \nabla_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right) \nabla_b^j \biggr] |\phi\rangle \,, \tag{24}$$

with omitting $\delta^3(r_{ab})$ from differentiation. It is because $\delta^3(r_{ab})$ in the original H_A in Eq. (10) cancels out with that from $\vec\nabla_a^2 \, \vec\nabla_b^2$ differentiation.

III. FINE STRUCTURE CORRECTIONS

The fine-structure $\alpha^6\, m$ correction $E_{\rm fs}^{(6)}$ has the form similar to that for the Lamb shift,

$$E_{\rm fs}^{(6)} = \langle H_{\rm fs}^{(6)} \rangle + \langle H^{(4)} \frac{1}{(E_0 - H_0)'} H^{(4)} \rangle_{\rm fs} + E_{\rm fs,amm}^{(6)} \,. \tag{25}$$

The first term is given by the expectation value of the spin-dependent $\alpha^6\, m$ Hamiltonian $H_{\rm fs}^{(6)}$, whereas the second term is the second-order perturbative correction induced by the Breit Hamiltonian. The subscript "fs" in $\langle \ldots \rangle_{\rm fs}$ indicates that only the spin-dependent part of the correction should be taken. The last term is the anomalous magnetic moment ('amm') correction to the fine-structure from the amm-corrected Breit Hamiltonian, see Eqs. (11) and (12). This correction arises from the fact that the g-factor contains higher-order terms in α.

The Hamiltonian $H_{\rm fs}^{(6)}$ for helium atom was first obtained by Douglas and Kroll [17] in the framework of the Salpeter equation and later re-derived in a more simple way using the effective field theory in Refs. [18, 19]. In this work we use the general expression for $H_{\rm fs}^{(6)}$ valid for the N-electron atom which was derived in [20],

$$H_{\rm fs}^{(6)} = \sum_a \biggl\{ \frac{3}{16}\, p_a^2\, e\, \vec{\mathcal{E}}_a \times \vec p_a \cdot \vec\sigma_a + \frac{1}{4} \left(2\, p_a^2\, \vec p_a \cdot e\, \vec{\mathcal{A}}_a + p_a^2\, \vec\sigma_a \cdot \nabla_a \times e\, \vec{\mathcal{A}}_a \right) + \frac{1}{2}\, \vec\sigma_a \cdot e\, \vec{\mathcal{E}}_a \times e\, \vec{\mathcal{A}}_a$$
$$+ \frac{i\, e}{16} \left[\vec{\mathcal{A}}_a \times \vec p_a \cdot \vec\sigma_a - \vec\sigma_a \cdot \vec p_a \times \vec{\mathcal{A}}_a \,, p_a^2 \right] + \frac{1}{2}\, e^2\, \vec{\mathcal{A}}_a^2 \biggr\} + \sum_{b\neq a} \sum_a \biggl\{ -\frac{i\,\pi}{8}\, \vec\sigma_a \cdot \vec p_a \times \delta^3(r_{ab})\, \vec p_a$$

TABLE I. Definitions of operators Q_i, $\vec{P}_{ab}=\vec{p}_a+\vec{p}_b$, $\vec{p}_{ab}=\frac{1}{2}(\vec{p}_a-\vec{p}_b)$,

Q_1	$\sum_a 4\pi\delta^3(r_a)$
Q_2	$\sum_{a<b}\sum_b 4\pi\delta^3(r_{ab})$
Q_3	$\sum_{b\neq a}\sum_a 4\pi\delta^3(r_a)/r_b$
Q_4	$\sum_{b\neq a}\sum_a 4\pi\delta^3(r_a)\,p_b^2$
Q_5	$\sum_{b<c,b\neq a}\sum_{c\neq a}\sum_a 4\pi\delta^3(r_a)/r_{bc}$
Q_6	$\sum_{a<b}\sum_b\sum_c 4\pi\delta^3(r_{ab})/r_c$
Q_7	$\sum_{a<b}\sum_b 4\pi\,\delta^3(r_{ab})\,P_{ab}^2$
Q_8	$\sum_{c\neq a,b}\sum_{a<b}\sum_b 4\pi\,\delta^3(r_{ab})\,p_c^2$
Q_9	$\sum_{a<b}\sum_b(3+\vec{\sigma}_a\cdot\vec{\sigma}_b)\vec{p}_{ab}\,4\pi\delta^3(r_{ab})\,\vec{p}_{ab}$
Q_{10}	$\sum_{a<b}\sum_b 1/r_{ab}$
Q_{11}	$\sum_{a<b}\sum_b(31+5\vec{\sigma}_a\cdot\vec{\sigma}_b)1/r_{ab}^2$
Q_{12}	$\sum_{a<b}\sum_b(23+5\vec{\sigma}_a\cdot\vec{\sigma}_b)1/r_{ab}^3$
Q_{13}	$\sum_{a<b}\sum_b\sum_{c<d}\sum_{d,ab\neq cd}(31+5\vec{\sigma}_a\cdot\vec{\sigma}_b)1/(r_{ab}^2r_{cd})$
Q_{14}	$\sum_a 1/r_a^2$
Q_{15}	$\sum_{a<b}\sum_b 1/(r_ar_b)$
Q_{16}	$\sum_{a<b<c}1/(r_ar_br_c)$
Q_{17}	$\sum_{b\neq a}\sum_a 1/(r_a^2r_b)$
Q_{18}	$\sum_{a<b}\sum_b\sum_c 1/(r_{ab}r_c)$
Q_{19}	$\sum_{a<b}\sum_b\sum_{c<d}\sum_d 1/(r_{ab}r_cr_d)$
Q_{20}	$\sum_{a<b}\sum_b\sum_c(23+5\vec{\sigma}_a\cdot\vec{\sigma}_b)1/(r_{ab}^2r_c)$
Q_{21}	$\sum_{a<b}\sum_b\sum_c 1/(r_{ab}r_c^2)$
Q_{22}	$\sum_{a<b}\sum_b\sum_{c<d}\sum_{d,ab\neq cd}\sum_e 1/(r_{ab}r_{cd}r_e)$
Q_{23}	$\sum_{a<b}\sum_b\vec{r}_a\cdot\vec{r}_{ab}/(r_a^3r_{ab}^2)$
Q_{24}	$\sum_{a<b}\sum_b(13+5\vec{\sigma}_a\cdot\vec{\sigma}_b)\vec{r}_a\cdot\vec{r}_{ab}/(r_a^3r_{ab}^3)$
Q_{25}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b\vec{r}_{ac}\cdot\vec{r}_{ab}/(r_{ac}^3r_{ab}^2)$
Q_{26}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b(21+15\vec{\sigma}_a\cdot\vec{\sigma}_b+16\vec{\sigma}_b\cdot\vec{\sigma}_c)\vec{r}_{ac}\cdot\vec{r}_{ab}/(r_{ac}^3r_{ab}^3)$
Q_{27}	$\sum_{a<b}\sum_b r_a^ir_b^j(r_{ab}^ir_{ab}^j-3\delta^{ij}r_{ab}^2)/(r_a^3r_b^3r_{ab})$
Q_{28}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b r_a^ir_{cb}^j(r_{ab}^ir_{ab}^j-3\delta^{ij}r_{ab}^2)/(r_a^3r_{cb}^3r_{ab})$
Q_{29}	$\sum_{c\neq a,b}\sum_{d\neq a,b}\sum_{a<b}\sum_b r_{ac}^ir_{db}^j(r_{ab}^ir_{ab}^j-3\delta^{ij}r_{ab}^2)/(r_{ac}^3r_{db}^3r_{ab})$
Q_{30}	$\sum_{b\neq a}\sum_a p_b^2/r_a^2$
Q_{31}	$\sum_a\vec{p}_a/r_a^2\,\vec{p}_a$
Q_{32}	$\sum_{a<b}\sum_b(47+5\vec{\sigma}_a\cdot\vec{\sigma}_b)\vec{p}_a/r_{ab}^2\,\vec{p}_a$
Q_{33}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b(31+5\vec{\sigma}_a\cdot\vec{\sigma}_b)\vec{p}_c/r_{ab}^2\,\vec{p}_c$
Q_{34}	$\sum_{a<b}\sum_b\sum_c p_a^i(\delta^{ij}r_{ab}^2+r_{ab}^ir_{ab}^j)/(r_{ab}^3r_c)p_b^j$
Q_{35}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b p_a^ip_c^2(\delta^{ij}r_{ab}^2+r_{ab}^ir_{ab}^j)/r_{ab}^3p_b^j$
Q_{36}	$\sum_{a<b}\sum_b(-3+\vec{\sigma}_a\cdot\vec{\sigma}_b)P_{ab}^iP_{ab}^j(3r_{ab}^ir_{ab}^j-\delta^{ij}r_{ab}^2)/r_{ab}^5$
Q_{37}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b p_a^i(\delta^{ij}r_{ac}^2+r_{ac}^ir_{ac}^j)(\delta^{jk}r_{bc}+r_{bc}^jr_{bc}^k)/(r_{ac}^3r_{bc}^3)p_b^j$
Q_{38}	$\sum_{a<b}\sum_b p_b^kr_a^i/r_a^3(\delta^{jk}r_{ab}^i/r_{ab}-\delta^{ik}r_{ab}^j/r_{ab}-\delta^{ij}r_{ab}^k/r_{ab}-r_{ab}^ir_{ab}^jr_{ab}^k/r_{ab}^3)p_b^j$
Q_{39}	$\sum_{c\neq a,b}\sum_{a<b}\sum_b p_b^kr_{ac}^i/r_{ac}^3(\delta^{jk}r_{ab}^i/r_{ab}-\delta^{ik}r_{ab}^j/r_{ab}-\delta^{ij}r_{ab}^k/r_{ab}-r_{ab}^ir_{ab}^jr_{ab}^k/r_{ab}^3)p_b^j$
Q_{40}	$\sum_{a<b}\sum_b p_a^2p_b^2$
Q_{41}	$\sum_{a<b}\sum_b\sum_c p_a^2/r_cp_b^2$
Q_{42}	$\sum_{a<b}\sum_b\sum_{c<d}\sum_{d,ab\neq cd}p_a^2/r_{cd}p_b^2$
Q_{43}	$\sum_{a<b}\sum_b\vec{p}_a\times\vec{p}_b/r_{ab}\vec{p}_a\times\vec{p}_b$
Q_{44}	$\sum_{a<b}\sum_b p_a^kp_b^l(-\delta^{jl}r_{ab}^ir_{ab}^k/r_{ab}^3-\delta^{ik}r_{ab}^jr_{ab}^l/r_{ab}^3+3r_{ab}^ir_{ab}^jr_{ab}^kr_{ab}^l/r_{ab}^5)p_a^ip_b^j$
Q_{45}	$\sum_{a<b<c}p_a^2p_b^2p_c^2$

$$+\frac{1}{4}\left(-i\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2}\right]e\,\vec{\mathcal{E}}_b+\left[\frac{p_b^2}{2},\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2}\right]\right]\vec{p}_b\right)+\frac{1}{32}(\vec{\sigma}_a\times\vec{p}_a)^i\left[p_a^i,\left[\frac{1}{r_{ab}},p_b^j\right]\right](\vec{\sigma}_b\times\vec{p}_b)^j$$
$$+\frac{1}{64}\sigma_a^i\sigma_b^j\left[p_a^2,\left[p_b^2,\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right]\right]\bigg\}\,. \tag{26}$$

Here, $e\,\vec{\mathcal{E}}_a$ denotes the static electric field at the position of particle a

$$e\,\vec{\mathcal{E}}_a\equiv-\vec{\nabla}_a V=-Z\,\alpha\frac{\vec{r}_a}{r_a^3}+\sum_{b\neq a}\alpha\frac{\vec{r}_{ab}}{r_{ab}^3} \tag{27}$$

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

$$e\,\mathcal{A}_a^i\equiv\sum_{b\neq a}\left[\frac{\alpha}{2\,r_{ab}}\left(\delta^{ij}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)p_b^j+\frac{\alpha}{2}\frac{\left(\vec{\sigma}_b\times\vec{r}_{ab}\right)^i}{r_{ab}^3}\right]. \tag{28}$$

It is convenient to express $H_{\rm fs}^{(6)}$ in terms of the elementary spin-dependent operators R_i listed in Table II,

$$\begin{aligned}H_{\rm fs}^{(6)}=&-\frac{3}{16}ZR_1+\frac{3}{16}R_2-\frac{3}{8}R_3-\frac{1}{2}R_4-\frac{Z}{4}R_5-\frac{Z}{4}R_6\\&+\frac{1}{4}R_7+\frac{1}{4}R_8+\frac{1}{8}R_9-\frac{1}{8}R_{10}-\frac{1}{4}R_{11}-\frac{1}{4}R_{12}\\&-\frac{1}{8}R_{13}+\frac{Z}{4}R_{14}-\frac{Z}{4}R_{15}+\frac{3}{4}R_{16}-\frac{1}{4}R_{17}-\frac{1}{4}R_{18}\\&+\frac{1}{4}R_{19}-\frac{1}{4}R_{20}+\frac{Z}{4}R_{21}-\frac{1}{4}R_{22}-\frac{1}{8}R_{23}-\frac{1}{8}R_{24}\\&+\frac{1}{16}R_{25}-\frac{1}{32}R_{26}-\frac{3}{32}R_{27}\,.\end{aligned} \tag{29}$$

These operators are corresponding to operators derived previously for lithium in [23]. In particular, operators R_1-R_{20} correspond to operators Q_1-Q_{20} derived in that paper with the exception of R_{13} and R_{16}. Operator R_{13} corresponds to D_2 in [23] and operators $R_{21}-R_{24}$ correspond to P_1-P_4, albeit in slightly different form. The remaining operators $R_{25}-R_{27}$ along with R_{16} are equivalent to two-spin Douglas-Kroll operators [17].

The second-order term in Eq. (25) can be represented as

$$\begin{aligned}\left\langle H^{(4)}\frac{1}{(E_0-H_0)'}\,H^{(4)}\right\rangle_{\rm fs}=&\,2\left\langle H_A\frac{1}{(E_0-H_0)'}\left[H_B+H_C\right]\right\rangle\\&+\left\langle\left[H_B+H_C\right]\frac{1}{(E_0-H_0)'}\left[H_B+H_C\right]\right\rangle,\end{aligned} \tag{30}$$

where H_A, H_B, and H_C are parts of the Breit Hamiltonian given by Eq. (10) and the $g\to2$ limit of Eqs. (11), and (12), respectively.

Unlike the $\alpha^6\,m$ correction to the Lamb shift, all $\alpha^6\,m$ fine-structure corrections are finite and do not require any regularization. Numerical calculations of the $\alpha^6\,m$ effect to the helium fine structure were performed first by Lewis and Serafino [21] and more recently by other authors [18, 22]. For Li and Be$^+$, analogous calculations were carried out in Refs. [14, 23].

IV. HYPERFINE STRUCTURE

The $\alpha^6\,m$ corrections to the hyperfine structure was calculated for helium in Ref. [15]. Later, this treatment was extended to lithium in Ref. [13]. Here we reformulate results obtained in these studies in a general form valid for an N-electron atom.

The $\alpha^6\,m$ corrections to the hyperfine splitting has the same structure as the other $\alpha^6\,m$ corrections considered in the previous sections, namely,

$$E_{\rm hfs}^{(6)}=\left\langle H_{\rm hfs}^{(6)}\right\rangle+2\left\langle H^{(4)}\frac{1}{(E_0-H_0)'}\,H_{\rm hfs}^{(4)}\right\rangle+E_{\rm hfs,amm}^{(6)}\,, \tag{31}$$

where $H_{\rm hfs}^{(6)}$ is the effective $\alpha^6\,m$ operator proportional to the nuclear spin I, $H^{(4)}$ is the Breit Hamiltonian, and $H_{\rm hfs}^{(4)}$ is the nuclear-spin dependent $\alpha^4\,m$ correction to the Breit Hamiltonian, and $E_{\rm hfs,amm}^{(6)}$ is induced by the electron amm correction to $H_{\rm hfs}^{(4)}$.

The nuclear-spin dependent correction to the Breit Hamiltonian, with inclusion of the electron amm effects, is given by

$$H_{\rm hfs}^{(4+)}=-\sum_a\left[e\,\vec{p}_a\cdot\vec{A}(\vec{r}_a)+\frac{e}{2}\,\frac{g}{2}\,\vec{\sigma}_a\cdot\vec{B}(\vec{r}_a)\right], \tag{32}$$

where $\vec{A}$ and $\vec{B}$ correspond to the magnetic field of the nucleus,

$$e\,\vec{A}(\vec{r})=-Z\,\alpha\,\frac{g_N}{2\,M}\,\vec{I}\times\frac{\vec{r}}{r^3}\,, \tag{33}$$

$$\begin{aligned}e\,B^i(\vec{r})=&-Z\,\alpha\,\frac{g_N}{2\,M}\frac{8\pi}{3}\delta^3(r)\,I^i\\&+Z\,\alpha\,\frac{g_N}{2\,M}\frac{1}{r^3}\left(\delta^{ij}-3\frac{r^ir^j}{r^2}\right)I^j\,.\end{aligned} \tag{34}$$

Here, $\vec{I}$ denotes the nuclear spin operator, M is nuclear mass, and g_N is the nuclear g-factor defined as

$$g_N=\frac{M}{Zm_p}\,\frac{\mu}{\mu_N}\,\frac{1}{I}\,, \tag{35}$$

where m_p is the proton mass, μ is the nuclear magnetic moment, and $\mu_N=|e|/(2m_p)$ is the nuclear magneton.

One can express $H_{\rm hfs}^{(4)}$ in a more explicit form,

$$H_{\rm hfs}^{(4+)}=\varepsilon\sum_a\left(\frac{g}{2}\,\vec{I}\cdot\vec{\sigma}_a\,h_a+\vec{I}\cdot\vec{h}_a+\frac{g}{2}\,I^i\,\sigma_a^j\,h_a^{ij}\right), \tag{36}$$

where $\varepsilon=(m/M)\,g_{\rm N}/2$ and h_a operators are

$$h_a=\frac{4\,Z}{3}\,\pi\,\delta^3(r_a)\,, \tag{37}$$

TABLE II. Definitions of the fine-structure $\alpha^6\, m$ operators R_i.

R_1	$\sum_a \vec\sigma_a\, p_a^2\, \frac{\vec r_a}{r_a^3} \times \vec p_a$
R_2	$\sum_{b\neq a}\sum_a \vec\sigma_a\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_a$
R_3	$\sum_{b\neq a}\sum_a \vec\sigma_a\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_b$
R_4	$\sum_{b\neq a}\sum_a \vec\sigma_a\, p_b^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_b$
R_5	$\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{1}{r_{ab}}\, \frac{\vec r_a}{r_a^3} \times \vec p_b$
R_6	$\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{\vec r_a\times\vec r_{ab}}{r_a^3\, r_{ab}^3}\, (\vec r_{ab}\cdot\vec p_b)$
R_7	$\sum_{b\neq a}\sum_{c\neq a}\sum_a \vec\sigma_a\, \frac{1}{r_{ac}}\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_c$
R_8	$\sum_{b\neq a}\sum_{c\neq a}\sum_a \vec\sigma_a\, \frac{\vec r_{ab}\times\vec r_{ac}}{r_{ab}^3\, r_{ac}^3}\, (\vec r_{ac}\cdot\vec p_c)$
R_9	$\sum_{b\neq a}\sum_a i\,\vec\sigma_a\, p_a^2\, \frac{1}{r_{ab}}\, \vec p_a \times \vec p_b$
R_{10}	$\sum_{b\neq a}\sum_a i\,\vec\sigma_a\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times (\vec r_{ab}\cdot\vec p_b)\,\vec p_a$
R_{11}	$\sum_{c\neq b}\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{1}{r_{bc}}\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_c$
R_{12}	$\sum_{c\neq b}\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{\vec r_{ab}\times\vec r_{bc}}{r_{ab}^3 r_{bc}^3} (\vec r_{bc}\cdot\vec p_c)$
R_{13}	$\sum_{b\neq a}\sum_a i\,\vec\sigma_a\, \vec p_a \times \pi\delta^3(r_{ab})\vec p_a$
R_{14}	$\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{1}{r_{ab}}\, \frac{\vec r_b}{r_b^3} \times \vec p_a$
R_{15}	$\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{\vec r_b\times\vec r_{ab}}{r_b^3\, r_{ab}^3}\, (\vec r_{ab}\cdot\vec p_a)$
R_{16}	$\sum_{b\neq a}\sum_a \sigma_a^i\sigma_b^j\, p_a^2\, \frac{r_{ab}^i r_{ab}^j}{r_{ab}^5}$
R_{17}	$\sum_{c\neq b}\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{1}{r_{ab}}\, \frac{\vec r_{bc}}{r_{bc}^3} \times \vec p_a$
R_{18}	$\sum_{c\neq b}\sum_{b\neq a}\sum_a \vec\sigma_a\, \frac{\vec r_{ab}\times\vec r_{bc}}{r_{ab}^3\, r_{bc}^3}\, (\vec r_{ab}\cdot\vec p_a)$
R_{19}	$\sum_{b\neq a}\sum_a i\,\vec\sigma_a\, p_b^2\, \frac{1}{r_{ab}}\, \vec p_a \times \vec p_b$
R_{20}	$\sum_{b\neq a}\sum_a i\,\vec\sigma_a\, p_b^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times (\vec r_{ab}\cdot\vec p_a)\,\vec p_b$
R_{21}	$\sum_{b\neq a}\sum_a \sigma_a^i\sigma_b^j\, \frac{r_a^j r_{ab}^i}{r_a^3 r_{ab}^3}$
R_{22}	$\sum_{b\neq a}\sum_{c\neq a}\sum_a \sigma_a^i\sigma_b^j\, \frac{r_{ac}^j r_{ab}^i}{r_{ac}^3 r_{ab}^3}$
R_{23}	$\sum_{b\neq a}\sum_a i\,\sigma_a^i\sigma_b^j\, p_a^2\, \frac{r_{ab}^i}{r_{ab}^3} p_a^j$
R_{24}	$\sum_{b\neq a}\sum_{c\neq a}\sum_a \sigma_a^i\sigma_b^j\, \frac{r_{ac}^j r_{bc}^i}{r_{ac}^3 r_{bc}^3}$
R_{25}	$\sum_{b\neq a}\sum_a i\,\sigma_a^i\sigma_b^j\, p_a^2\, \frac{1}{r_{ab}^3}\Big(\delta^{ik} r_{ab}^j + \delta^{jk} r_{ab}^i - 3\frac{r_{ab}^i r_{ab}^j r_{ab}^k}{r_{ab}^2}\Big)\, p_b^k$
R_{26}	$\sum_{b\neq a}\sum_a \sigma_a^i\sigma_b^j\, \frac{1}{r_{ab}^3}\, p_a^j p_b^i$
R_{27}	$\sum_{b\neq a}\sum_a (\vec r_{ab}/r_{ab}^5)\times(\vec r_{ab}\times\vec p_a\cdot\vec\sigma_a)\,\vec p_b\cdot\vec\sigma_b$

$$\vec h_a = Z\,\frac{\vec r_a\times\vec p_a}{r_a^3}\,, \tag{38}$$

$$h_a^{ij} = -\frac{Z}{2}\,\frac{1}{r_a^3}\left(\delta^{ij} - 3\,\frac{r_a^i\, r_a^j}{r_a^2}\right). \tag{39}$$

We start the derivation of $\alpha^6\, m$ operators with the Breit-Pauli Hamiltonian $H_{\rm BP}$ of the atomic system in the external magnetic field,

$$H_{\rm BP} = \sum_a H_a + \sum_{a<b}\sum_b H_{ab}\,, \tag{40}$$

where

$$H_a = \frac{\vec\pi_a^2}{2\,m} - \frac{Z\,\alpha}{r_a} - \frac{e}{2\,m}\,\vec\sigma_a\cdot\vec B_a - \frac{\vec\pi_a^4}{8\,m^3} + \frac{\pi\, Z\,\alpha}{2\,m^2}\,\delta^3(r_a) + \frac{Z\,\alpha}{4\,m^2}\,\vec\sigma_a\cdot\frac{\vec r_a}{r_a^3}\times\vec\pi_a + \frac{e}{8\,m^3}\left(\vec\sigma_a\cdot\vec B_a\,\vec\pi_a^2 + \vec\pi_a^2\,\vec\sigma_a\cdot\vec B_a\right), \tag{41}$$

$$H_{ab} = \frac{\alpha}{r_{ab}} + \frac{\pi\,\alpha}{m^2}\,\delta^3(r_{ab}) - \frac{\alpha}{2\,m^2}\,\pi_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^2}\right)\pi_b^j + \frac{\alpha}{4\,m^2 r_{ab}^3}\left[\vec\sigma_a\cdot\vec r_{ab}\times(2\,\vec\pi_b-\vec\pi_a) - \vec\sigma_b\cdot\vec r_{ab}\times(2\,\vec\pi_a-\vec\pi_b)\right]$$
$$+\,\frac{\alpha}{4\,m^2}\,\frac{\sigma_a^i\,\sigma_b^j}{r_{ab}^3}\left(\delta^{ij} - 3\,\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^2}\right), \tag{42}$$

where $\vec\pi = \vec p - e\,\vec A$. Magnetic fields $\vec A$ and $\vec B$ induced by the nuclear magnetic moment are given in Eqs. (33) and

(34). The relativistic correction to the hyperfine interaction is obtained from the relativistic terms in the Breit-Pauli Hamiltonian $H_{\rm BP}$,

$$H^{(6)}_{\rm hfs} = \sum_a \frac{Z\,\alpha}{4\,m^2}\,\vec\sigma_a\cdot\frac{\vec r_a}{r_a^3}\times\big[-e\,\vec A(\vec r_a)\big] + \frac{e}{8\,m^3}\,\big(\vec\sigma_a\cdot\vec B_a\,\vec p_a^{\,2} + \vec p_a^{\,2}\,\vec\sigma_a\cdot\vec B_a\big) + \sum_{b\neq a}\sum_a \frac{\alpha}{4\,m^2 r_{ab}^3}\,\vec\sigma_a\cdot\vec r_{ab}\times\big[-2\,e\,\vec A(\vec r_b) + e\,\vec A(\vec r_a)\big]$$
$$+\frac{e}{4\,m^3}\,\sum_a\big[\vec p_a^{\,2}\,\vec p_a\cdot\vec A(\vec r_a) + \vec p_a\cdot\vec A(\vec r_a)\,\vec p_a^{\,2}\big] - \sum_{b\neq a}\sum_a \frac{\alpha}{2\,m^2}\,p_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)\big[-e\,A^j(\vec r_b)\big]\,. \tag{43}$$

Using $\vec A$ and $\vec B$ from Eqs. (33) and (34), the effective $\alpha^6\,m$ hfs operator $H^{(6)}_{\rm hfs}$ is [13, 15]

$$H^{(6)}_{\rm hfs} = \varepsilon\sum_a\big(\vec\sigma_a\cdot\vec I\,P_a - \vec I\cdot\vec P_a + \sigma_a^j\,I^i\,P_a^{ij}\big)\,, \tag{44}$$

$$P_a = \frac{Z^2}{6}\,\frac{1}{r_a^4} - \frac{Z}{12}\,\big\{p_a^2\,,\,4\,\pi\,\delta^3(r_a)\big\} + \sum_{b\neq a}\frac{Z}{6}\,\frac{\vec r_{ab}}{r_{ab}^3}\cdot\left(2\,\frac{\vec r_b}{r_b^3} - \frac{\vec r_a}{r_a^3}\right), \tag{45}$$

$$\vec P_a = \frac{Z}{2}\,p_a^2\,\frac{\vec r_a}{r_a^3}\times\vec p_a + \sum_{b\neq a}\frac{Z}{2}\,\frac{\vec r_b}{r_b^3}\times\left(\frac{1}{r_{ab}}\,\vec p_a + \frac{\vec r_{ab}}{r_{ab}^3}\,(\vec r_{ab}\cdot\vec p_a)\right), \tag{46}$$

$$P_a^{ij} = -\frac{Z}{4}\left(\frac{Z}{3r_a} + p_a^2\right)\left(3\,\frac{r_a^i r_a^j}{r_a^5} - \frac{\delta^{ij}}{r_a^3}\right) + \sum_{b\neq a}\frac{Z}{4}\left(3\,\frac{r_{ab}^j}{r_{ab}^3}\,\frac{r_a^i}{r_a^3} - \delta^{ij}\,\frac{\vec r_{ab}}{r_{ab}^3}\cdot\frac{\vec r_a}{r_a^3}\right). \tag{47}$$

Both the first-order and second-order terms in Eq. (31) are divergent and need to be regularized and transformed to an explicitly finite form. In order to do so, it is convenient to rewrite the hfs correction to the energy in terms of the hyperfine constant A defined as

$$E_{\rm hfs} = \vec I\cdot\vec J\,A\,, \tag{48}$$

where $\vec J$ is the total electronic angular momentum. Using the notation $H_{\rm hfs} = \vec I\cdot\vec H_{\rm hfs}$, we express A as

$$A = \frac{1}{J\,(J+1)}\,\langle\vec J\cdot\vec H_{\rm hfs}\rangle\,. \tag{49}$$

The expansion of A in α is of the form

$$A = \varepsilon\sum_{n=4}^{\infty}\alpha^n\,A^{(n)}\,, \tag{50}$$

where we are interested in the $\alpha^6\,m$ correction, $A^{(6)}$. Due to symmetry of the intermediate states in the second-order matrix elements, the A, B, and C parts of the hfs Hamiltonian $H^{(4)}_{\rm hfs}$ give nonvanishing contributions only when coupled to the corresponding A, B, and C parts of the Breit Hamiltonian $H^{(4)}$. So, the total result for $A^{(6)}$ can be expressed as

$$A^{(6)} = A^{(6)}_{AN} + A^{(6)}_B + A^{(6)}_C + A^{(6)}_R\,, \tag{51}$$

where

$$A^{(6)}_{AN} = \frac{2}{J\,(J+1)}\left\langle\sum_a\vec J\cdot\vec\sigma_a\,h_a\,\frac{1}{(E_0-H_0)'}\,H_A\right\rangle + \frac{1}{J\,(J+1)}\left\langle\sum_a\vec J\cdot\vec\sigma_a\,P_a - \vec J\cdot\vec P_a + \sigma_a^j J^i P_a^{ij}\right\rangle, \tag{52}$$

$$A^{(6)}_B = \frac{2}{J\,(J+1)}\left\langle\sum_a\vec J\cdot\vec h_a\,\frac{1}{(E_0-H_0)'}\,H_B\right\rangle, \tag{53}$$

$$A^{(6)}_C = \frac{2}{J\,(J+1)}\left\langle\sum_a J^i\,\sigma_a^j\,h_a^{ij}\,\frac{1}{(E_0-H_0)'}\,H_C\right\rangle, \tag{54}$$

$$A^{(6)}_R = \frac{1}{J\,(J+1)}\,\frac{4\,\pi\,Z^2}{3}\left\langle\sum_a\vec J\cdot\vec\sigma_a\,\delta^3(r_a)\right\rangle\left(\ln 2 - \frac{5}{2}\right), \tag{55}$$

and where $A^{(6)}_R$ is radiative correction known for the hydrogen atom [24].

We now separate divergencies from the above expressions. This is done with help of the following identities

$$4\,\pi\,\delta^3(r_a) = 4\,\pi\,[\delta^3(r_a)]_r - \sum_a\left\{\frac{2}{r_a}\,,\,E_0-H_0\right\}, \tag{56}$$

$$H_A = \widetilde H_{AR} + \frac{1}{4}\sum_a\left\{\frac{Z}{r_a}\,,\,E_0-H_0\right\}. \tag{57}$$

The regularized operators $[\delta^3(r_a)]_r$ and $\widetilde H_{AR}$ have exactly the same expectation value as the non-regularized operators $\delta^3(r_a)$ and H_A if the expectation values are calculated with the eigenstates of the Schrödinger Hamiltonian H_0. The difference between H_{AR} in Eq. (24) and $\widetilde H_{AR}$ in Eq. (57) is that in the latter case only electron-nucleus Dirac delta $\delta^3(r_a)$ needs to be regularized while in the former case we regularize also electron-electron delta $\delta^3(r_{ab})$. By applying the above identities, we make both the first and second-order matrix elements in $A^{(6)}_{AN}$ separately finite. The result is

$$A^{(6)}_{AN} = A^{(6)}_{A} + A^{(6)}_{N}\,, \tag{58}$$

$$A^{(6)}_{A} = \frac{2}{J\,(J+1)}\,\biggl\langle \sum_a \vec J\cdot\vec\sigma_a\, h_{aR}\,\frac{1}{(E_0-H_0)'}\,\widetilde H_{AR}\biggr\rangle\,, \tag{59}$$

$$\begin{aligned}A^{(6)}_{N} = {}& \frac{1}{J\,(J+1)}\,\biggl\langle \sum_a \vec J\cdot\vec\sigma_a\,\frac{Z}{6}\biggl\{\frac{1}{r_a}\sum_b p_b^4 - 4\,\pi\,\delta^3(r_a)\,p_a^2 + \sum_{b\neq a}\frac{\vec r_{ab}}{r_{ab}^3}\cdot\biggl(2\frac{\vec r_b}{r_b^3}-\frac{\vec r_a}{r_a^3}\biggr) + 4\,\pi\,Z\sum_{b\neq a}\biggl(\frac{\delta^3(r_a)}{r_b}-\frac{\delta^3(r_b)}{r_a}\biggr)\\ &-\frac{2}{r_a}\sum_{b>c}\sum_c 4\,\pi\,\delta^3(r_{bc}) + 4\sum_{b>c}\sum_c p_b^i\,\frac{1}{r_a}\biggl(\frac{\delta^{ij}}{r_{bc}}+\frac{r_{bc}^i\,r_{bc}^j}{r_{bc}^3}\biggr)p_c^j - 4\,\pi\,Z\,\delta^3(r_a)\,\biggl\langle\sum_b\frac{1}{r_b}\biggr\rangle + \frac{8}{r_a}\,\langle H_A\rangle\biggr\}\\ &-\vec J\cdot\vec P_a + \sigma_a^j J^i P_a^{ij}\biggr\rangle\,,\end{aligned} \tag{60}$$

where h_{aR} is obtained from h_a by the replacement $\delta^3(r_a)\to[\delta^3(r_a)]_r$. The above expression for $A^{(6)}_N$ still contains auxiliary singularities appearing on the level of individual operators. In order to remove them, we repeatedly use the Schrödinger equation, obtaining the identity

$$\begin{aligned}\biggl\langle\frac{1}{r_a}\sum_b p_b^4 - 4\,\pi\,\delta^3(r_a)\,p_a^2\biggr\rangle = {}&\biggl\langle -2\sum_{b\neq a}\frac{\vec r_{ab}}{r_{ab}^3}\cdot\frac{\vec r_a}{r_a^3} + \frac{4}{r_a}\biggl((E_0-V)^2-\frac{Z^2}{r_a^2}\biggr) - 2\sum_{b>c}\sum_c p_b^2\,\frac{1}{r_a}\,p_c^2 + 2\,Z\,\vec p_a\,\frac{1}{r_a^2}\,\vec p_a\\ &+\biggl(8\,\pi\,\delta^3(r_a)+\frac{4\,Z}{r_a^2}\biggr)\biggl(\sum_{b\neq a}\frac{p_b^2}{2}+V+\frac{Z}{r_a}-E_0\biggr)\biggr\rangle\,.\end{aligned} \tag{61}$$

After this transformation, all matrix elements are finite and can be calculated numerically.

As in the case of the Lamb shift and the fine structure, it is convenient to rewrite $A^{(6)}_N$ in terms of a set of elementary operators T_i defined in Table III:

$$\begin{aligned}J(J+1)\,A^{(6)}_N = {}& \frac{Z}{6}\biggl\langle -Q_{10}\,T_1 - 2\,T_2 - Z\,T_3 + T_4 + 2\,T_5 - Z\,T_6 + (8E^{(4)}+4E_0^2)\,T_7 + 4E_0Z\,T_8 + 8E_0Z\,T_9\\ &-8E_0\,T_{10} + 4Z^2\,T_{11} + 4Z^2\,T_{12} - 4Z\,T_{13} - 8Z\,T_{14} + 4\,T_{15} - 3\,T_{16} + 2\,T_{17} + 2Z\,T_{18} + 4\,T_{19} - 2\,T_{20} + 2Z\,T_{21}\\ &-3\,(T_{22}+T_{23}+T_{24}) - \frac{Z}{2}T_{25} - \frac{3}{2}T_{26} + \frac{3}{2}T_{27}\biggr\rangle\,.\end{aligned} \tag{62}$$

V. CONCLUSION

In this work we derived the complete expressions for the $\alpha^6\,m$ QED corrections to the Lamb shift, the fine and hyperfine structure of light N-electron atoms. The obtained formulas generalize previous expressions derived for the specific cases of the helium atom [8, 9] and the fine and hyperfine structure of lithium [13, 14]. The obtained formulas pave the way for improving of theory of light few-electron atoms, first of all, lithium and beryllium atoms.

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Appendix A: Derivation of operators H_i

In this section we describe the derivation of the $m\alpha^6$ operators H_i for the energy centroids. The starting point is the Foldy-Wouthuysen (FW) Hamiltonian derived in Refs. [4,20]:

$$H_{FW} = e\,A^0 + \frac{\pi^2}{2\,m} - \frac{e}{4\,m}\,\sigma^{ij}\,B^{ij} - \frac{\pi^4}{8\,m^3} + \frac{e}{16\,m^3}\bigl\{\sigma^{ij}\,B^{ij},\,p^2\bigr\} - \frac{e}{8\,m^2}\Bigl(\vec\nabla\cdot\vec E_\parallel + \sigma^{ij}\,\bigl\{E^i_\parallel,\,p^j\bigr\}\Bigr) + \frac{e^2}{2\,m^2}\,\sigma^{ij}\,E^i_\parallel\,A^j$$

TABLE III. Definitions of the hyperfine-structure $\alpha^6\, m$ operators T_i.

T_1	$\sum_a \vec{J}\cdot\vec{\sigma}_a\, 4\pi\delta^3(r_a)$
T_2	$\sum_{b<c}\sum_c\sum_a \vec{J}\cdot\vec{\sigma}_a\, 4\pi\delta^3(r_{bc})/r_a$
T_3	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 4\pi\delta^3(r_a)/r_b$
T_4	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 4\pi\delta^3(r_a)p_b^2$
T_5	$\sum_{b<c}\sum_c\sum_a \vec{J}\cdot\vec{\sigma}_a\, 4\pi\delta^3(r_a)/r_{bc}$
T_6	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 4\pi\delta^3(r_b)/r_a$
T_7	$\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/r_a$
T_8	$\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/r_a^2$
T_9	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a r_b)$
T_{10}	$\sum_{b<c}\sum_c\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a r_{bc})$
T_{11}	$\sum_{b\neq a}\sum_{c\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a r_b r_c)$
T_{12}	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a^2 r_b)$
T_{13}	$\sum_{b<c}\sum_c\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a^2 r_{bc})$
T_{14}	$\sum_{b<c}\sum_c\sum_{d\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a r_{bc} r_d)$
T_{15}	$\sum_{b<c}\sum_c\sum_{d<e}\sum_e\sum_a \vec{J}\cdot\vec{\sigma}_a\, 1/(r_a r_{bc} r_{de})$
T_{16}	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, \frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\frac{\vec{r}_a}{r_a^3}$
T_{17}	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, \frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\frac{\vec{r}_b}{r_b^3}$
T_{18}	$\sum_{b\neq a}\sum_a \vec{J}\cdot\vec{\sigma}_a\, p_b^2/r_a^2$
T_{19}	$\sum_{b<c}\sum_c\sum_a \vec{J}\cdot\vec{\sigma}_a\, p_b^i\,(\delta^{ij}/r_{bc}+r_{bc}^i r_{bc}^j/r_{bc}^3)/r_a\, p_c^j$
T_{20}	$\sum_{b<c}\sum_c\sum_a \vec{J}\cdot\vec{\sigma}_a\, p_b^2/r_a\, p_c^2$
T_{21}	$\sum_a \vec{J}\cdot\vec{\sigma}_a\, \vec{p}_a/r_a^2\, \vec{p}_a$
T_{22}	$\sum_a \vec{J}\cdot p_a^2\, \frac{\vec{r}_a}{r_a^3}\times\vec{p}_a$
T_{23}	$\sum_{b\neq a}\sum_a \vec{J}\cdot\frac{\vec{r}_b}{r_{ab} r_b^3}\times\vec{p}_a$
T_{24}	$\sum_{b\neq a}\sum_a \vec{J}\cdot\frac{\vec{r}_b}{r_b^3}\times\frac{\vec{r}_{ab}}{r_{ab}^3}\,(\vec{r}_{ab}\cdot\vec{p}_a)$
T_{25}	$\sum_a J^i\sigma_a^j(3r_a^i r_a^j/r_a^2-\delta^{ij})/r_a^4$
T_{26}	$\sum_a J^i\sigma_a^j p_a^2\,(3r_a^i r_a^j/r_a^2-\delta^{ij})/r_a^3$
T_{27}	$\sum_{b\neq a}\sum_a J^i\sigma_a^j\,(3r_{ab}^j r_a^i-\delta^{ij}\vec{r}_{ab}\cdot\vec{r}_a)/(r_a^3 r_{ab}^3)$

$$
\begin{aligned}
&+\frac{i\,e}{16\,m^3}\,[\sigma^{ij}\,\{A^i,\,p^j\}\,,\,p^2]+\frac{e^2}{8\,m^3}\,\vec{E}_\parallel^2+\frac{3\,e}{32\,m^4}\,\{p^2\,,\,\sigma^{ij}\,E_\parallel^i\,p^j\}+\frac{5}{128\,m^4}\,[p^2,[p^2,e\,A^0]]\\
&-\frac{3}{64\,m^4}\,\Big\{p^2\,,\,\nabla^2(e\,A^0)\Big\}+\frac{1}{16\,m^5}\,p^6\,,
\end{aligned}
\tag{A1}
$$

where $\vec{E}_\parallel = -\vec{\nabla}A^0$ and

$$
\sigma^{ij}=\frac{1}{2i}\big[\sigma^i,\sigma^j\big]\,,\qquad B^{ij}=\partial^i A^j-\partial^j A^i\,. \tag{A2}
$$

Following the approach of Ref. [20] we derive the effective operators H_i as follows.

1. H_1

Term H_1 is the relativistic correction to the kinetic energy. We evaluate it as

$$
H_1=\frac{1}{16}\sum_a p_a^6=\frac{1}{16}\bigg\{\Big(\sum_a p_a^2\Big)^3-3\Big(\sum_a p_a^2\Big)\Big(\sum_{b<c}\sum_c p_b^2p_c^2\Big)+3\sum_{a<b<c}p_a^2p_b^2p_c^2\bigg\}=H_1^A+H_1^B+H_1^C\,. \tag{A3}
$$

The individual parts are calculated as

$$
H_1^A=\frac{1}{16}\,\Big(\sum_a p_a^2\Big)^3=\frac{1}{4}\,(E_0-V)\sum_a p_a^2\,(E_0-V)=\frac{1}{2}\,(E_0-V)^3+\frac{1}{4}\sum_a(\nabla_a V)^2\,, \tag{A4}
$$

$$H_1^B = -\frac{3}{16}\Big(\sum_a p_a^2\Big)\Big(\sum_{b<c}\sum_c p_b^2 p_c^2\Big) = -\frac{3}{8}\,(E_0 - V)\Big(\sum_{b<c}\sum_c p_b^2 p_c^2\Big)$$
$$= \sum_{b<c}\sum_c \bigg\{ -\frac{3}{8}\,p_b^2\,(E_0 - V)\,p_c^2 + \frac{3}{16}\left[p_b^2, \left[p_c^2, \left[\frac{1}{r_{bc}}\right]_\epsilon\right]\right]\bigg\},$$

and

$$H_1^C = \frac{3}{16}\sum_{a<b<c} p_a^2 p_b^2 p_c^2\,. \tag{A5}$$

2. H_2

H_2 is a correction due to the static electric interaction,

$$H_2 = \sum_a\bigg(\frac{(\nabla_a V)^2}{8} + \frac{5}{128}\,[p_a^2,[p_a^2,V]] - \frac{3}{64}\left\{p_a^2\,,\,\nabla_a^2 V\right\}\bigg)$$
$$= H_2^A + H_2^B + H_2^C\,. \tag{A6}$$

The first term is just

$$H_2^A = \sum_a \frac{(\nabla_a V)^2}{8}\,. \tag{A7}$$

The second term is transformed as

$$H_2^B = \sum_a \frac{5}{128}\,[p_a^2,[p_a^2,V]]$$
$$= \frac{5}{128}\bigg(\sum_a\sum_b [p_a^2,[p_b^2,V]] - \sum_{a\neq b}\sum_b [p_a^2,[p_b^2,V]]\bigg)$$
$$= -\frac{5}{64}\bigg(2\sum_a (\nabla_a V)^2 + \sum_{a<b}\sum_b [p_a^2,[p_b^2,V]]\bigg)\,. \tag{A8}$$

The third term is

$$H_2^C = -\frac{3}{32}\sum_a p_a^2\nabla_a^2 V = -\frac{3}{32}\bigg(\sum_a\sum_b p_a^2\nabla_b^2 V$$
$$- \sum_{a\neq b}\sum_b p_a^2\nabla_b^2 V\bigg)$$
$$= -\frac{3}{32}\bigg(\sum_b 2(E_0 - V)\nabla_b^2 V - \sum_{a\neq b}\sum_b p_a^2\nabla_b^2 V\bigg)\,. \tag{A9}$$

Using the identity

$$\nabla_b^2 V = 4\pi\Big[Z\delta^d(r_b) - \sum_{c\neq b}\delta^d(r_{bc})\Big]\,, \tag{A10}$$

we express it as

$$H_2^C = -\frac{3}{32}\bigg[\sum_b\bigg(2(E_0 - V) - \sum_{a\neq b} p_a^2\bigg)4\pi Z\delta^3(r_b)$$
$$- \sum_{c\neq b}\sum_b\bigg(2(E_0 - V) - \sum_{a\neq b} p_a^2\bigg)4\pi\delta^3(r_{bc})\bigg]\,. \tag{A11}$$

Taking into account that

$$\sum_{a\neq b}\sum_{c\neq b}\sum_b p_a^2\delta^3(r_{bc})$$
$$= \sum_a\sum_{b<c}\sum_c p_a^2\delta^3(r_{bc}) + \sum_{\substack{a\neq b\\ a\neq c}}\sum_{b<c}\sum_c p_a^2\delta^3(r_{bc})$$
$$= \sum_{b<c}\sum_c 2(E_0 - V)\delta^3(r_{bc}) + \sum_{\substack{a\neq b\\ a\neq c}}\sum_{b<c}\sum_c p_a^2\delta^3(r_{bc})\,, \tag{A12}$$

we finally get

$$H_2^C = -\frac{3}{32}\bigg[\sum_b\bigg(2(E_0 - V) - \sum_{a\neq b} p_a^2\bigg)4\pi Z\delta^3(r_b)$$
$$- \sum_{b<c}\sum_c\bigg(2(E_0 - V) - \sum_{\substack{a\neq b\\ a\neq c}} p_a^2\bigg)4\pi\delta^3(r_{bc})\bigg]\,. \tag{A13}$$

3. H_3

Term H_3 represents another correction to the Coulomb interaction between electrons, coming from higher-order terms in the FW Hamiltonian. Corresponding operator is

$$H_3 = \sum_{a<b}\sum_b \frac{1}{64}\bigg[-4\pi\nabla^2\delta^d(r_{ab}) + \frac{4}{d(d-1)}\sigma_a^{ij}\sigma_b^{ij}$$
$$\times\bigg(\frac{(d-1)}{d}\,\vec p_a\,4\pi\delta^d(r_{ab})\,\vec p_b - p_a^i\left[\frac{1}{r_{ab}^3}\bigg(\delta^{ij} - 3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\bigg)\right]_\epsilon p_b^j\bigg)\bigg]\,. \tag{A14}$$

This term will be simplified using various identities later on.

4. H_4

H_4 corresponds to the relativistic correction due to the transverse photon exchange and is given by

$$H_4 = \frac{1}{8}\sum_a \left[\sum_{b\neq a}\left\{p_a^2\,,\, p_a^i\left[\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right]_\epsilon p_b^j\right\} + \frac{\sigma_a^{ij}\,\sigma_b^{ij}}{2d}\left\{p_a^2\,,\, 4\,\pi\,\delta^d(r_{ab})\right\}\right] = H_4^A + H_4^B. \tag{A15}$$

The first term is transformed as

$$\begin{aligned}
H_4^A &= \frac{1}{4}\sum_{b\neq a}\sum_a p_a^2\, p_a^i\left[\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right]_\epsilon p_b^j \\
&= \frac{1}{4}\left[\sum_c\sum_{a<b}\sum_b p_c^2\, p_a^i\left[\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right]_\epsilon p_b^j - \sum_{\substack{c\neq a\\ c\neq b}}\sum_{a<b}\sum_b p_c^2\, p_a^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right)p_b^j\right] \\
&= \frac{1}{2}\left(\sum_{a<b}\sum_b p_a^i\,(E_0-V)\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right)p_b^j - \frac{1}{2}\left[p_a^i,\left[p_b^j,\left[\frac{1}{r_{ab}}\right]_\epsilon\right]\right]\left[\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right]_\epsilon\right. \\
&\quad \left. -\frac{1}{2}\sum_{\substack{c\neq a\\ c\neq b}}\sum_{a<b}\sum_b p_c^2\, p_a^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right)p_b^j\right).
\end{aligned} \tag{A16}$$

The second term is finite and is evaluated as

$$\begin{aligned}
H_4^B &= \frac{1}{8d}\sum_a\sum_{b\neq a}\sigma_a^{ij}\,\sigma_b^{ij}\,p_a^2\,4\,\pi\,\delta^3(r_{ab}) = \frac{1}{8d}\left(\sum_{a<b}\sum_b\Big(\sum_c p_c^2 - \sum_{\substack{c\neq a\\ c\neq b}} p_c^2\Big)\sigma_a^{ij}\,\sigma_b^{ij}\,4\,\pi\,\delta^3(r_{ab})\right) \\
&= \frac{1}{8d}\left(\sum_{a<b}\sum_b\Big(2(E_0-V) - \sum_{\substack{c\neq a\\ c\neq b}} p_c^2\Big)\sigma_a^{ij}\,\sigma_b^{ij}\,4\,\pi\,\delta^3(r_{ab})\right).
\end{aligned} \tag{A17}$$

5. H_5

Term H_5 is another correction to the transverse photon exchange,

$$\begin{aligned}
H_5 = \sum_{b\neq a}\sum_a\frac{\sigma_a^{ij}\,\sigma_b^{ij}}{2d}\left(-\frac{1}{2}\left[\frac{\vec r_{ab}}{r_{ab}^3}\right]_\epsilon\cdot\vec\nabla_a V \right. \\
\left. +\frac{1}{16}\left[\left[\frac{1}{r_{ab}}\,,\,p_a^2\right],\,p_a^2\right]\right) = H_5^A + H_5^B.
\end{aligned} \tag{A18}$$

The first term is calculated as

$$\begin{aligned}
H_5^A &= -\sum_{b\neq a}\sum_a\frac{\sigma_a^{ij}\,\sigma_b^{ij}}{4d}\left[\frac{\vec r_{ab}}{r_{ab}^3}\right]_\epsilon\cdot\vec\nabla_a V \\
&= -\sum_{a<b}\sum_b\frac{\sigma_a^{ij}\,\sigma_b^{ij}}{4d}\left\{\left(\frac{Z\vec r_a}{r_a^3}-\frac{Z\vec r_b}{r_b^3}\right)\cdot\frac{\vec r_{ab}}{r_{ab}^3} - 2\left[\frac{1}{r_{ab}^4}\right]_\epsilon\right. \\
&\quad\left. -\sum_{\substack{c\neq a\\ c\neq b}}\left(\frac{\vec r_{ac}}{r_{ac}^3}+\frac{\vec r_{cb}}{r_{cb}^3}\right)\cdot\frac{\vec r_{ab}}{r_{ab}^3}\right\},
\end{aligned} \tag{A19}$$

whereas the second term is

$$\begin{aligned}
H_5^B &= \sum_{b\neq a}\sum_a\frac{\sigma_a^{ij}\,\sigma_b^{ij}}{32d}\left[\left[\left[\frac{1}{r_{ab}}\right]_\epsilon,\,p_a^2\right],\,p_a^2\right] \\
&= \sum_{b\neq a}\sum_a\frac{\sigma_a^{ij}\,\sigma_b^{ij}}{32d}\left\{\sum_c\left[\left[\left[\frac{1}{r_{ab}}\right]_\epsilon,\,p_a^2\right],\,p_c^2\right] - \left[\left[\left[\frac{1}{r_{ab}}\right]_\epsilon,\,p_a^2\right],\,p_b^2\right]\right\} \\
&= -\sum_{a<b}\sum_b\frac{\sigma_a^{ij}\,\sigma_b^{ij}}{16d}\left\{-2\left(\frac{Z\vec r_a}{r_a^3}-\frac{Z\vec r_b}{r_b^3}\right)\cdot\frac{\vec r_{ab}}{r_{ab}^3} + 4\left[\frac{1}{r_{ab}^4}\right]_\epsilon + 2\sum_{\substack{c\neq a\\ c\neq b}}\left(\frac{\vec r_{ac}}{r_{ac}^3}+\frac{\vec r_{cb}}{r_{cb}^3}\right)\cdot\frac{\vec r_{ab}}{r_{ab}^3} + \left[p_a^2,\left[p_b^2,\left[\frac{1}{r_{ab}}\right]_\epsilon\right]\right]\right\}.
\end{aligned} \tag{A20}$$

6. H_6 (A23)

H_6 comes from the double transverse photon exchange,

$$H_6 = \sum_{b\neq a}\sum_{c\neq a}\sum_{a}\Big[\frac{1}{8}\, p_b^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r^i_{ab}\, r^j_{ab}}{r^3_{ab}}\right)\left(\frac{\delta^{jk}}{r_{ac}} + \frac{r^j_{ac}\, r^k_{ac}}{r^3_{ac}}\right) p_c^k + \frac{\sigma_b^{ij}\sigma_c^{ij}}{8d}\left[\frac{\vec r_{ab}}{r^3_{ab}}\cdot\frac{\vec r_{ac}}{r^3_{ac}}\right]_\epsilon\Big] = H_6^A + H_6^B\,, \tag{A21}$$

where

$$H_6^A = \frac{1}{8}\Big[\sum_{b\neq a}\sum_{a} p_a^i\left(\frac{\delta^{ij}}{r^2_{ab}} + 3\frac{r^i_{ab}\, r^j_{ab}}{r^4_{ab}}\right) p_a^i + 2\sum_{\substack{c\neq a\\ c\neq b}}\sum_{a<b}\sum_{b} p_a^i\left(\frac{\delta^{ij}}{r_{ac}} + \frac{r^i_{ac}\, r^j_{ac}}{r^3_{ac}}\right)\left(\frac{\delta^{jk}}{r_{bc}} + \frac{r^j_{bc}\, r^k_{bc}}{r^3_{bc}}\right) p_b^k\Big] \tag{A22}$$

and

$$H_6^B = \frac{1}{8d}\sum_{a<b}\sum_{b}\Big[(\sigma_a^2+\sigma_b^2)\left[\frac{1}{r^4_{ab}}\right]_\epsilon + 2\sum_{c\neq a,b}\sigma_b^{ij}\sigma_c^{ij}\frac{\vec r_{ab}\cdot\vec r_{ac}}{r^3_{ab} r^3_{ac}}\Big] = = \frac{1}{4d}\sum_{a<b}\sum_{b}\Big[d(d-1)\left[\frac{1}{r^4_{ab}}\right]_\epsilon + \sum_{c\neq a,b}\sigma_b^{ij}\sigma_c^{ij}\frac{\vec r_{ab}\cdot\vec r_{ac}}{r^3_{ab} r^3_{ac}}\Big]\,, \tag{A24}$$

where we have used the identity $(\sigma_a^{ij})^2 \equiv \sigma_a^2 = d(d-1)$.

7. H_7

Finally, the term $H_7 = H_{7a} + H_{7c}$ is the double retardation correction to the nonrelativistic single transverse photon exchange, We evaluate the first part as

$$H_{7a} = \sum_{a<b}\sum_{b} -\frac{1}{8}\Big\{\nabla_a^i V\left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon \nabla_b^j V - i\,\nabla_a^i V\left[\frac{p_b^2}{2}, \left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon\right] p_b^j + i\, p_a^i\left[\left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon, \frac{p_a^2}{2}\right]\nabla_b^j V + p_a^i\left[\frac{p_b^2}{2}, \left[\left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon, \frac{p_a^2}{2}\right]\right] p_b^j\Big\} = H_{7a}^A + H_{7a}^B + H_{7a}^C\,. \tag{A25}$$

Here,

$$\begin{aligned} H_{7a}^A &= -\frac{1}{8}\sum_{a<b}\sum_{b}\nabla_a^i V\left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon \nabla_b^j V \\ &= -\frac{1}{8}\sum_{a<b}\sum_{b}\left(\frac{Z r_a^i}{r_a^3} - \left[\frac{r^i_{ab}}{r^3_{ab}}\right]_\epsilon - \sum_{\substack{c\neq a,\\ c\neq b}}\frac{r^i_{ac}}{r^3_{ac}}\right)\left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon\left(\frac{Z r_b^j}{r_b^3} + \left[\frac{r^j_{ab}}{r^3_{ab}}\right]_\epsilon + \sum_{\substack{d\neq a,\\ d\neq b}}\frac{r^j_{db}}{r^3_{db}}\right) \\ &= -\frac{1}{8}\sum_{a<b}\sum_{b}\Big\{\left(\frac{Z r_a^i}{r_a^3} - \sum_{\substack{c\neq a,\\ c\neq b}}\frac{r^i_{ac}}{r^3_{ac}}\right)\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\left(\frac{Z r_b^j}{r_b^3} + \sum_{\substack{d\neq a,\\ d\neq b}}\frac{r^j_{db}}{r^3_{db}}\right) - 2\left(\frac{Z\vec r_a}{r_a^3} - \frac{Z\vec r_b}{r_b^3}\right)\cdot\frac{\vec r_{ab}}{r^2_{ab}} \\ &\quad + 2\left[\frac{1}{r^3_{ab}}\right]_\epsilon - 14\,\pi\delta^3(r_{ab}) + 2\sum_{\substack{c\neq a\\ c\neq b}}\left(\frac{\vec r_{ac}}{r^3_{ac}} + \frac{\vec r_{cb}}{r^3_{cb}}\right)\cdot\frac{\vec r_{ab}}{r^2_{ab}}\Big\}\,. \end{aligned} \tag{A26}$$

Furthermore,

$$\begin{aligned} H_{7a}^B &= -\frac{1}{8}\sum_{a<b}\sum_{b}(-i)\nabla_a^i V\left[\frac{p_b^2}{2}, \left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon\right] p_b^j + i\, p_a^i\left[\left[\frac{r^i_{ab}\, r^j_{ab} - 3\,\delta^{ij}\, r^2_{ab}}{r_{ab}}\right]_\epsilon, \frac{p_a^2}{2}\right]\nabla_b^j V \\ &= -\frac{1}{8}\sum_{a<b}\sum_{b}\Big[\Big\{\left(\frac{Z r_a^i}{r_a^3} - \sum_{\substack{c\neq a,\\ c\neq b}}\frac{r^i_{ac}}{r^3_{ac}}\right) p_b^k\left(\delta^{jk}\frac{r^i_{ab}}{r_{ab}} - \delta^{ik}\frac{r^j_{ab}}{r_{ab}} - \delta^{ij}\frac{r^k_{ab}}{r_{ab}} - \frac{r^i_{ab} r^j_{ab} r^k_{ab}}{r^3_{ab}}\right) p_b^k \\ &\quad - p_b^j\,\frac{1}{r^4_{ab}}(\delta^{jk}\, r^2_{ab} - 3 r^j_{ab} r^k_{ab})\, p_b^k + (a\leftrightarrow b)\Big\} - 2\left[\frac{1}{r^4_{ab}}\right]_\epsilon + 6\,\pi\delta^3(r_{ab})\Big]\,. \end{aligned} \tag{A27}$$

Finally,

$$H_{7a}^C = -\frac{1}{8}\sum_{a<b}\sum_b p_a^i\left[\frac{p_b^2}{2},\left[\left[\frac{r_{ab}^i\,r_{ab}^j - 3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\right]_\epsilon,\frac{p_a^2}{2}\right]\right]p_b^j$$

$$= \frac{1}{8}\sum_{a<b}\sum_b p_a^k p_b^l\left[\left(-\frac{\delta^{il}\delta^{jk}}{r_{ab}} + \frac{\delta^{ik}\delta^{jl}}{r_{ab}} - \frac{\delta^{ij}\delta^{kl}}{r_{ab}} - \frac{\delta^{jl}r_{ab}^i r_{ab}^k}{r_{ab}^3} - \frac{\delta^{ik}r_{ab}^j r_{ab}^l}{r_{ab}^3} + 3\frac{r_{ab}^i r_{ab}^j r_{ab}^k r_{ab}^l}{r_{ab}^5}\right)\right]_\epsilon p_a^i p_b^j\,. \tag{A28}$$

The term H_{7c} is simply

$$H_{7c} = \sum_{a<b}\sum_b \frac{\sigma_a^{ij}\sigma_b^{ij}}{16d}\left[p_a^2,\left[p_b^2,\left[\frac{1}{r_{ab}}\right]_\epsilon\right]\right]. \tag{A29}$$

Appendix B: Separation of singularities from second-order correction

In this section we examine the second-order perturbation correction induced by the Breit Hamiltonian

$$\left\langle H^{(4)}\,\frac{1}{(E_0-H_0)'}\,H^{(4)}\right\rangle, \tag{B1}$$

with $H^{(4)} = H_A + H_B + H_C$. The second-order correction induced by the spin-independent part of the Breit Hamiltonian H_A contains divergent $\sim 1/(d-3)$ contributions which need to be separated out in terms of expectation values of some (singular) first-order operators, as explained below.

Following the approach of Ref. [8], we represent the spin-independent part of the Breit Hamiltonian as

$$H_A = H_{AR} + \{H_0 - E_0, Q\}\,, \tag{B2}$$

where

$$Q = -\frac{1}{4}\sum_a\left[\frac{Z}{r_a}\right]_\epsilon + \frac{(d-1)}{4}\sum_{a<b}\sum_b\left[\frac{1}{r_{ab}}\right]_\epsilon. \tag{B3}$$

The regularized operator H_{AR} acts on the ket vector of a trial function $|\phi\rangle$ as

$$H_{AR}|\phi\rangle = \left[-\frac{1}{2}(E_0-V)^2 + \frac{1}{4}\sum_{a<b}\sum_b \vec\nabla_a^2\vec\nabla_b^2 \right. \tag{B4}$$
$$\left. -\frac{Z}{4}\sum_a\frac{\vec r_a\cdot\vec\nabla_a}{r_a^3} - \sum_{a<b}\sum_b\frac{1}{2}\,p_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right)p_b^j\right]|\phi\rangle\,.$$

Using Eq. (B2), the second-order correction induced by H_A can be rewritten as

$$\left\langle H_A\,\frac{1}{(E_0-H_0)'}\,H_A\right\rangle = \left\langle H_{AR}\,\frac{1}{(E_0-H_0)'}\,H_{AR}\right\rangle + X_1 + X_2 + X_3\,, \tag{B5}$$

where

$$X_1 = \Big\langle Q(H_0-E_0)Q\Big\rangle,\quad X_2 = 2\,\langle H_A\rangle\,\langle Q\rangle,\quad X_3 = -2\,\langle H_A Q\rangle\,. \tag{B6}$$

The second-order correction induced by H_{AR} in Eq. (B5) is finite for $d=3$ and can be calculated numerically in its present form. The other terms are transformed as

$$X_1 = \frac{1}{2}\Big\langle[\,Q,[\,H_0-E_0,Q]]\Big\rangle = \frac{1}{2}\sum_a\Big\langle(\nabla_a Q)^2\Big\rangle \tag{B7}$$

$$X_2 = 2E^{(4)}\left\langle\frac{E_0}{2} + \frac{1}{4}\sum_{a<b}\sum_b\frac{1}{r_{ab}}\right\rangle. \tag{B8}$$

The evaluation of the third term is more complicated. We transform it as follows

$$X_3 = -2\left\langle\left[-\frac{1}{8}\left(\sum_a p_a^2\right)^2 + \frac{1}{4}\sum_{a<b}\sum_b p_a^2\,p_b^2 + \frac{Z\pi}{2}\sum_a\delta^d(r_a) + (d-2)\pi\sum_{a<b}\sum_b\delta^d(r_{ab})\right.\right.$$
$$\left.\left. -\frac{1}{2}\sum_{a<b}\sum_b p_a^i\left[\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right]_\epsilon p_b^j\right]Q\right\rangle = \left\langle X_3^A + X_3^B + X_3^C + X_3^D + X_3^E\right\rangle. \tag{B9}$$

The individual terms are evaluated as

$$X_3^A = \frac{1}{4}\left(\sum_a p_a^2\right)^2 Q = \frac{1}{2}(E_0-V)\left(\sum_a p_a^2\right)Q = -\frac{1}{2}\sum_a(\vec\nabla_a V)\cdot(\vec\nabla_a Q) + (E_0-V)^2 Q\,, \tag{B10}$$

$$X_3^B = -\frac{1}{2}\sum_{a<b}\sum_b p_a^2\,p_b^2\,Q = -\frac{1}{2}\sum_{a<b}\sum_b p_a^2\,Q\,p_b^2 - \frac{d-1}{16}\bigg[p_a^2,\bigg[p_b^2,\bigg[\frac{1}{r_{ab}}\bigg]_\epsilon\bigg]\bigg]\,, \tag{B11}$$

$$X_3^C = -Z\pi\sum_a \delta^3(r_a)\,Q = \frac{Z\pi}{4}\sum_a\bigg(\sum_{b\neq a}\frac{Z-2}{r_b} - \sum_{\substack{b<c\\ b\neq a}}\sum_{c\neq a}\frac{2}{r_{bc}}\bigg)\,\delta^3(r_a)\,, \tag{B12}$$

$$X_3^D = -2\pi\sum_{a<b}\sum_b \delta^3(r_{ab})\,Q = \frac{\pi}{2}\sum_{a<b}\sum_b\bigg(\sum_c\frac{Z}{r_c} - \sum_{\substack{c<d\\ cd\neq ab}}\sum_d\frac{2}{r_{cd}}\bigg)\,\delta^3(r_{ab})\,, \tag{B13}$$

$$X_3^E = \sum_{a<b}\sum_b p_a^i\bigg[\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\bigg]_\epsilon p_b^j\,Q = \sum_{a<b}\sum_b p_a^i\,Q\bigg(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\bigg)\,p_b^j + \frac{(d-1)}{8}\bigg[p_a^i,\bigg[p_b^j,\bigg[\frac{1}{r_{ab}}\bigg]_\epsilon\bigg]\bigg]\,\bigg[\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\bigg]_\epsilon\,. \tag{B14}$$

Appendix C: Elimination of singularities

In this section we list the identities in $d = 3 - 2\epsilon$ dimensions that were used in order to algebraically cancel the singularities and to get the simplified expression for the final formula for E_Q. The following notations are used: $\vec{P}_{ab} = \vec{p}_a + \vec{p}_b$ and $\vec{p}_{ab} = (\vec{p}_a - \vec{p}_b)/2$, and $\langle 1/r_{ab}^3\rangle$ is defined in Eq. (22). The identities are:

$$\begin{aligned}\bigg[p_a^2,\bigg[p_b^2,\bigg[\frac{1}{r_{ab}}\bigg]_\epsilon\bigg]\bigg] &= -(\vec\nabla_a V)\bigg(\vec\nabla_a\frac{1}{r_{ab}}\bigg) - (\vec\nabla_b V)\bigg(\vec\nabla_b\frac{1}{r_{ab}}\bigg) - \frac{P_{ab}^2}{3}\,4\pi\,\delta^3(r_{ab}) + P_{ab}^i P_{ab}^j\,\frac{3r_{ab}^i r_{ab}^j - \delta^{ij}\,r_{ab}^2}{r_{ab}^5}\\ &= -\bigg[\frac{2}{r_{ab}^4}\bigg]_\epsilon + \bigg(\frac{Z\vec r_a}{r_a^3}-\frac{Z\vec r_b}{r_b^3}\bigg)\cdot\frac{\vec r_{ab}}{r_{ab}^3} - \sum_{\substack{c\neq a\\ c\neq b}}\bigg(\frac{\vec r_{ac}}{r_{ac}^3}+\frac{\vec r_{cb}}{r_{cb}^3}\bigg)\cdot\frac{\vec r_{ab}}{r_{ab}^3} - \frac{P_{ab}^2}{3}\,4\pi\,\delta^3(r_{ab}) + P_{ab}^i P_{ab}^j\,\frac{3r_{ab}^i r_{ab}^j - \delta^{ij}\,r_{ab}^2}{r_{ab}^5}\,,\end{aligned} \tag{C1}$$

$$\begin{aligned}p_a^2\,\bigg[\frac{1}{r_{ab}}\bigg]_\epsilon p_b^2 &= (E_0 - V)^2\bigg[\frac{1}{r_{ab}}\bigg]_\epsilon - \frac{1}{4}\sum_{\substack{c\neq a\\ c\neq b}}\sum_{\substack{d\neq a\\ d\neq b}} p_c^2\,\frac{1}{r_{ab}}\,p_d^2 + 2\pi\sum_{\substack{c\neq a\\ c\neq b}}\bigg(\sum_{d\neq c}\delta^3(r_{cd}) - Z\delta^3(r_c)\bigg)\frac{1}{r_{ab}}\\ &\quad - \sum_{\substack{c\neq a\\ c\neq b}}\vec p_c\,(E_0 - V)\,\frac{1}{r_{ab}}\,\vec p_c - \vec p_{ab}\cdot\vec P_{ab}\,\frac{1}{r_{ab}}\,\vec p_{ab}\cdot\vec P_{ab}\,,\end{aligned} \tag{C2}$$

$$\bigg[\frac{1}{r_{ab}^4}\bigg]_\epsilon = \frac{1}{2}\,\vec p_a\,\frac{1}{r_{ab}^2}\,\vec p_a + \frac{1}{2}\,\vec p_b\,\frac{1}{r_{ab}^2}\,\vec p_b - \bigg(E + \sum_c\frac{Z}{r_c} - \sum_{d<c}\sum_c\bigg[\frac{1}{r_{cd}}\bigg]_\epsilon - \sum_{\substack{c\neq a\\ c\neq b}}\frac{p_c^2}{2}\bigg)\bigg[\frac{1}{r_{ab}^2}\bigg]_\epsilon\,, \tag{C3}$$

$$\bigg[\frac{Z^2}{r_a^4}\bigg]_\epsilon = \vec p_a\,\frac{Z^2}{r_a^2}\,\vec p_a + \sum_{b\neq a}p_b^2\,\frac{Z^2}{r_a^2} - 2\bigg(E + \sum_b\bigg[\frac{Z}{r_b}\bigg]_\epsilon - \sum_{b<c}\sum_c\frac{1}{r_{bc}}\bigg)\bigg[\frac{Z^2}{r_a^2}\bigg]\,, \tag{C4}$$

$$\begin{aligned}p_a^i\,\bigg[\frac{1}{r_{ab}^3}\bigg(\delta^{ij} - 3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\bigg)\bigg]_\epsilon p_b^j &= -\pi\nabla^2\delta^d(r_{ab}) + \frac{1}{3}\,\vec p_{ab}\,4\pi\delta^3(r_{ab})\,\vec p_{ab} + \frac{1}{2}\bigg[\frac{1}{r_{ab}^4}\bigg]_\epsilon - \frac{1}{4}\bigg(\frac{Z\vec r_a}{r_a^3}-\frac{Z\vec r_b}{r_b^3}\bigg)\cdot\frac{\vec r_{ab}}{r_{ab}^3}\\ &\quad + \frac{1}{4}\sum_{\substack{c\neq a\\ c\neq b}}\bigg(\frac{\vec r_{ac}}{r_{ac}^3}+\frac{\vec r_{cb}}{r_{cb}^3}\bigg)\cdot\frac{\vec r_{ab}}{r_{ab}^3} - \frac{1}{4}\,P_{ab}^i P_{ab}^j\,\frac{3r_{ab}^i r_{ab}^j - \delta^{ij}\,r_{ab}^2}{r_{ab}^5}\,,\end{aligned} \tag{C5}$$

$$\sum_a(\nabla_a V)^2 = \sum_a\bigg[\frac{Z^2}{r_a^4}\bigg]_\epsilon + 2\sum_{a<b}\sum_b\bigg[\frac{1}{r_{ab}^4}\bigg]_\epsilon - 2\sum_{a<b}\sum_b\bigg(\frac{Z\vec r_a}{r_a^3}-\frac{Z\vec r_b}{r_b^3}\bigg)\cdot\frac{\vec r_{ab}}{r_{ab}^3} + \sum_{\substack{c\neq a\\ c\neq b}}\sum_{a<b}\sum_b\bigg(\frac{\vec r_{ac}}{r_{ac}^3}+\frac{\vec r_{cb}}{r_{cb}^3}\bigg)\cdot\frac{\vec r_{ab}}{r_{ab}^3}\,, \tag{C6}$$

$$\sum_a (\nabla_a Q)^2 = \frac{1}{16}\sum_a \left[\frac{Z^2}{r_a^4}\right]_\epsilon + \frac{(d-1)^2}{8}\sum_{a<b}\sum_b \left[\frac{1}{r_{ab}^4}\right]_\epsilon - \frac{1}{4}\sum_{a<b}\sum_b \left(\frac{Z\vec{r}_a}{r_a^3} - \frac{Z\vec{r}_b}{r_b^3}\right)\cdot\frac{\vec{r}_{ab}}{r_{ab}^3}$$
$$+\frac{1}{4}\sum_{\substack{c\neq a\\ c\neq b}}\sum_{a<b}\sum_b \left(\frac{\vec{r}_{ac}}{r_{ac}^3} + \frac{\vec{r}_{cb}}{r_{cb}^3}\right)\cdot\frac{\vec{r}_{ab}}{r_{ab}^3}\,, \tag{C7}$$

$$\sum_{a<b}\sum_b p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right) p_b^j = -2\,E^{(4)} - (E_0 - V)^2 + \frac{1}{2}\sum_{a<b}\sum_b p_a^2\, p_b^2 + \sum_a Z\pi\delta^3(r_a) + 2\sum_{a<b}\sum_b \pi\delta^3(r_{ab})\,, \tag{C8}$$

$$p_a^i\, 4\pi\delta^3(r_{ab})\, p_b^j = -p_{ab}^i\, 4\pi\delta^3(r_{ab})\, p_{ab}^j + \pi\delta^3(r_{ab})\, P_{ab}^i P_{ab}^j\,, \tag{C9}$$

$$\vec{p}_a\cdot\vec{p}_b \left[\frac{1}{r_{ab}}\right]_\epsilon \vec{p}_a\cdot\vec{p}_b = p_a^2 \left[\frac{1}{r_{ab}}\right]_\epsilon p_b^2 - \vec{p}_a\times\vec{p}_b\,\frac{1}{r_{ab}}\,\vec{p}_a\times\vec{p}_b - 2\pi\delta^3(r_{ab})\,P_{ab}^2\,, \tag{C10}$$

$$\left[\frac{1}{2r_{ab}}\left(\delta^{ij} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right)\right]_\epsilon \nabla^i\nabla^j \left[\frac{1}{r_{ab}}\right]_\epsilon = \left[\frac{1}{r_{ab}^4}\right]_\epsilon - \pi\delta^3(r_{ab})\,, \tag{C11}$$

$$\left\langle\left[\frac{1}{r_{ab}^3}\right]_\epsilon\right\rangle = \left\langle\frac{1}{r_{ab}^3}\right\rangle + \langle\pi\delta^d(r_{ab})\rangle\left(\frac{1}{\epsilon} + 2\right), \tag{C12}$$

$$\nabla^2\delta^d(r_{ab}) = 2\,\vec{p}_{ab}\,\delta^d(r_{ab})\,\vec{p}_{ab} - 2\left[E_0 - \frac{P_{ab}^2}{4} - \sum_{\substack{c\neq a\\ c\neq b}}\frac{p_c^2}{2} - V\right]\delta^d(r_{ab})\,. \tag{C13}$$

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