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Higher-order effective Hamiltonian for light atomic systems

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Abstract

We present the derivation of the effective higher-order Hamiltonian, which gives $m\,\alpha^6$ contribution to energy levels of an arbitrary light atom. The derivation is based on the Foldy-Wouthuysen transformation of the one-particle Dirac Hamiltonian followed by perturbative expansion of the many particle Green function. The obtained results can be used for the high precision calculation of relativistic effects in atomic systems.

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I. INTRODUCTION

The calculation of relativistic corrections to energy levels of atomic systems is usually accomplished by using the many-electron Dirac-Coulomb (DC) Hamiltonian with possible inclusion of the Breit interaction between electrons. However, such a Hamiltonian can not be rigorously derived from Quantum Electrodynamic (QED) theory, and thus gives an incomplete treatment of relativistic and QED effects. The electron self-energy and vacuum polarization can be included in the DC Hamiltonian [1, 2], though only in an approximate way. A different approach, which is justified by quantum field theory, is to start from a well adapted one-electron local potential and build many body perturbation theory. This approach allows for the consistent inclusion of QED effects as well as a correct treatment of the so called "negative energy states". It is being pursued by Sapirstein and collaborators [3], but so far no high accuracy results have been achieved for neutral few electron atoms. An alternative approach, which is suited for light atoms, relies on expansion of energy levels in powers of the fine structure constant

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

where $E^{(n)}$ is the contribution of order $m\,\alpha^n$, so $E^{(2)}$ is the nonrelativistic energy as given by the Schrödinger Hamiltonian $H^{(2)} \equiv H_0$,

$$H_0 = \sum_a \biggl(\frac{\vec p_a^{\,2}}{2\,m} - \frac{Z\,\alpha}{r_a}\biggr) + \sum_{a>b}\sum_b \frac{\alpha}{r_{ab}}\,. \tag{2}$$

$E^{(4)}$ is the leading relativistic correction given by the Breit-Pauli Hamiltonian $H^{(4)}$ [4],

$$E^{(4)} = \langle\phi|H^{(4)}|\phi\rangle. \tag{3}$$

where

$$\begin{aligned}
H^{(4)} \;=\; & \sum_a \biggl\{-\frac{\vec p_a^{\,4}}{8\,m^3} + \frac{\pi\,Z\,\alpha}{2\,m^2}\,\delta^3(r_a) + \frac{Z\,\alpha}{4\,m^2}\,\vec\sigma_a\cdot\frac{\vec r_a}{r_a^3}\times\vec p_a\biggr\} \\
& + \sum_{a>b}\sum_b \biggl\{-\frac{\pi\,\alpha}{m^2}\,\delta^3(r_{ab}) - \frac{\alpha}{2\,m^2}\,p_a^i\,\biggl(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\biggr)\,p_b^j \\
& - \frac{2\,\pi\,\alpha}{3\,m^2}\,\vec\sigma_a\cdot\vec\sigma_b\,\delta^3(r_{ab}) + \frac{\alpha}{4\,m^2}\frac{\sigma_a^i\,\sigma_b^j}{r_{ab}^3}\,\biggl(\delta^{ij} - 3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\biggr) + \frac{\alpha}{4\,m^2\,r_{ab}^3} \\
& \times\,\Bigl[2\,(\vec\sigma_a\cdot\vec r_{ab}\times\vec p_b - \vec\sigma_b\cdot\vec r_{ab}\times\vec p_a) + (\vec\sigma_b\cdot\vec r_{ab}\times\vec p_b - \vec\sigma_a\cdot\vec r_{ab}\times\vec p_a)\Bigr]\biggr\}\,.
\end{aligned} \tag{4}$$

$E^{(5)}$ is the leading QED correction, which includes Bethe logarithms. It has been first obtained for hydrogen, for a review see Refs. [5, 6]. A few years later $E^{(5)}$ was obtained for the helium atom [7], see Ref. [8] for a recent simple rederivation. This result can be easily extended to arbitrary light atoms, and recently calculations of $E^{(5)}$ have been performed for lithium [9, 10] and beryllium atoms [11]. $E^{(6)}$ is a higher order relativistic correction and is the subject of the present work. It can be expressed as a sum of three terms,

$$E^{(6)} = \langle\phi|H^{(4)}\,\frac{1}{(E-H_0)'}\,H^{(4)}|\phi\rangle + \langle\phi|H^{(6)}|\phi\rangle + \alpha^3\lambda\langle\phi|\sum_{a>b}\sum_b \delta^{(3)}(r_{ab})|\phi\rangle, \tag{5}$$

where $H^{(6)}$ is an effective Hamiltonian of order $m\,\alpha^6$. It is well known that the second order correction from the Breit-Pauli Hamiltonian is divergent since it contains, for example, the Dirac δ functions. It is less well known that $H^{(6)}$ also leads to divergent matrix elements, and yet less well known that in the sum of both terms these divergences almost cancel out. The additional term containing λ is the contribution coming from the forward scattering three-photon exchange amplitude which cancels the last divergence in electron-electron interactions, which leads to a finite result. The cancellation of divergences requires at first the inclusion of a regulator, a cut-off in the maximum photon momenta, which is allowed to go to infinity when all terms are combined together.

The first derivation of $H^{(6)}$ was performed for helium fine-structure by Douglas and Kroll in [12]. In this case all matrix elements were finite because they considered only the splitting of nP_J levels. The numerical evaluation of this splitting has been performed to a high degree of precision by Yan and Drake in [13]. Since calculations of higher order relativistic corrections when singular matrix elements are present are rather complicated, they were first studied in detail for positronium, the electron-positron system. The $m\,\alpha^6$ contribution to positronium hyperfine splitting was first obtained (without annihilation terms) by Caswell and Lepage in [14], where they introduced a new approach to bound state QED namely, nonrelativistic quantum electrodynamics (NRQED). Although their original calculations happened to contain some mistakes the idea of NRQED was very fruitful, because it simplified enormously the treatment of bound states. Its use has led to significant progress in bound state QED, with the calculation of the complete three photon-exchange contribution of order $m\,\alpha^6$ to positronium energy levels in [15, 16], and [17]. It was shown there, that by introducing a regulator, either a photon momentum cut-off or dimensional regularization, one can derive and calculate all matrix elements in a consistent way. The agreement between these calculations and the other purely numerical calculation based on Bethe-Salpeter equation [18, 19] justify the correctness of the effective Hamiltonian or NRQED approaches. It was quickly found, after the positronium exercise, that a similar effective Hamiltonian $H^{(6)}$ can be derived for the Helium atom. Although the derivation of $H^{(6)}$ for S- and P-states of helium is rather straightforward [20], the elimination of electron-electron singularities and the calculation of matrix elements is quite involved. For this reason the first results have been obtained for triplet states 2^3S_1 in [21] and 2^3P [22], where electron-electron singularities are not present, because the wave function vanishes at $\vec{r}_1 = \vec{r}_2$. Within the dimensional regularization scheme Korobov and Yelkhovsky [23] were able to derive a complete set of finite operators and calculate their matrix elements for the 1^1S_0 ground state of helium. None of these results have been confirmed yet. In this work we present a simple derivation of effective operators contributing to $H^{(6)}$ for an arbitrary state of arbitrary light atoms. The results obtained agree for the special cases of the ${}^1S$, ${}^3S_1$ and ${}^3P_J$ levels of helium with the former result in [12, 20]. Since we do not explicitly eliminate here electron-electron singularities we were not able to verify the result [23] for the ground state of helium.

Our derivation consists of three steps. The first step is the Foldy-Wouthuysen (FW) transformation of a single electron Dirac equation in an electromagnetic field [24], performed to the appropriate level of accuracy. The second step is formal. It is the quantization of the electromagnetic field interacting with the atom, using the Feynman integration by paths method [24]. The third step is the derivation of an effective interaction through the perturbative expansion of the equal-time Green function of the total atomic system.

II. FOLDY-WOUTHUYSEN TRANSFORMATION

The Foldy-Wouthuysen (FW) transformation [24] is the nonrelativistic expansion of the Dirac Hamiltonian in an external electromagnetic field,

$$H = \vec{\alpha} \cdot \vec{\pi} + \beta\, m + e\, A^0\,, \tag{6}$$

where $\vec{\pi} = \vec{p} - e\,\vec{A}$. The FW transformation S [24] leads to a new Hamiltonian

$$H_{FW} = e^{i\,S}\,(H - i\,\partial_t)\,e^{-i\,S}\,, \tag{7}$$

which decouples the upper and lower components of the Dirac wave function up to a specified order in the $1/m$ expansion. Here we calculate FW Hamiltonian up to terms which contribute to $m\,\alpha^6$ to the energy. While it is not clear here which term contributes at which order, we postpone this to the next section where this issue become more obvious. Contrary to standard textbooks, we use a more convenient single Foldy-Wouthuysen operator S, which can be written as

$$S \;=\; -\frac{i}{2\,m}\left\{\beta\,\vec{\alpha}\cdot\vec{\pi}-\frac{1}{3\,m^2}\,\beta\,(\vec{\alpha}\cdot\vec{\pi})^3+\frac{1}{2\,m}\,[\vec{\alpha}\cdot\vec{\pi}\,,\,e\,A^0-i\,\partial_t]+Y\right\}. \tag{8}$$

where Y is an as yet unspecified odd operator $\{\beta, Y\} = 0$, such that $[Y, e\,A^0 - i\,\partial_t] \approx [Y, (\vec{\alpha}\cdot\vec{\pi})^3] \approx 0$. It will be fixed at the end to cancel all higher order odd terms. The F.W. Hamiltonian is expanded in a power series in S

$$H_{FW} = \sum_{j=0}^{6} \mathcal{H}^{(j)} + \ldots \tag{9}$$

where

$$\begin{aligned}
\mathcal{H}^{(0)} &= H,\\
\mathcal{H}^{(1)} &= [i\,S\,,\mathcal{H}^{(0)}-i\,\partial_t],\\
\mathcal{H}^{(j)} &= \frac{1}{j}\,[i\,S\,,\mathcal{H}^{(j-1)}]\ \text{for}\ j>1,
\end{aligned} \tag{10}$$

and higher order terms in this expansion, denoted by dots, are neglected. The calculations of subsequent commutators is rather tedious. For the reader's convenience we present a separate result for each $H^{(j)}$,

$$\begin{aligned}
\mathcal{H}^{(1)} \;=\;& \frac{\beta}{m}\,(\vec{\alpha}\cdot\vec{\pi})^2-\frac{\beta}{3\,m^3}\,(\vec{\alpha}\cdot\vec{\pi})^4-\frac{i\,e}{4\,m^2}[\vec{\alpha}\cdot\vec{\pi},\vec{\alpha}\cdot\vec{E}]+\frac{1}{2\,m}[Y,\vec{\alpha}\cdot\vec{\pi}]\\
&-\vec{\alpha}\cdot\vec{\pi}+\frac{1}{3\,m^2}\,(\vec{\alpha}\cdot\vec{\pi})^3-\beta\,Y-\frac{\beta}{6\,m^3}[(\vec{\alpha}\cdot\vec{\pi})^3,e\,A^0-i\,\partial_t]-\frac{e}{4\,m^2}\,\vec{\alpha}\cdot\dot{\vec{E}} \qquad (11)\\
\mathcal{H}^{(2)} \;=\;& -\frac{\beta}{2\,m}\,(\vec{\alpha}\cdot\vec{\pi})^2+\frac{\beta}{3\,m^3}\,(\vec{\alpha}\cdot\vec{\pi})^4-\frac{\beta}{18\,m^5}\,(\vec{\alpha}\cdot\vec{\pi})^6+\frac{i\,e}{8\,m^2}\,[\vec{\alpha}\cdot\vec{\pi},\vec{\alpha}\cdot\vec{E}]\\
&-\frac{1}{2\,m}\,[Y,\vec{\alpha}\cdot\vec{\pi}]-\frac{i\,e}{24\,m^4}\,[(\vec{\alpha}\cdot\vec{\pi})^3,\vec{\alpha}\cdot\vec{E}]\\
&+\frac{1}{24\,m^4}[\vec{\alpha}\cdot\vec{\pi},[(\vec{\alpha}\cdot\vec{\pi})^3,e\,A^0-i\,\partial_t]]-\frac{\beta\,e}{16\,m^3}\,(\vec{\alpha}\cdot\vec{\pi}\,\vec{\alpha}\cdot\dot{\vec{E}}+\vec{\alpha}\cdot\dot{\vec{E}}\,\vec{\alpha}\cdot\vec{\pi})\\
&-\frac{1}{2\,m^2}\,(\vec{\alpha}\cdot\vec{\pi})^3+\frac{1}{3\,m^4}\,(\vec{\alpha}\cdot\vec{\pi})^5-\frac{i\,\beta\,e}{16\,m^3}\,[\vec{\alpha}\cdot\vec{\pi},[\vec{\alpha}\cdot\vec{\pi},\vec{\alpha}\cdot\vec{E}]]\\
&-\frac{i\,\beta\,e}{8\,m^3}\,((\vec{\alpha}\cdot\vec{\pi})^2\,\vec{\alpha}\cdot\vec{E}+\vec{\alpha}\cdot\vec{E}\,(\vec{\alpha}\cdot\vec{\pi})^2) \qquad (12)\\
\mathcal{H}^{(3)} \;=\;& -\frac{\beta}{6\,m^3}\,(\vec{\alpha}\cdot\vec{\pi})^4+\frac{\beta}{6\,m^5}\,(\vec{\alpha}\cdot\vec{\pi})^6+\frac{i\,e}{96\,m^4}\,[\vec{\alpha}\cdot\vec{\pi},[\vec{\alpha}\cdot\vec{\pi},[\vec{\alpha}\cdot\vec{\pi},\vec{\alpha}\cdot\vec{E}]]]\\
&+\frac{i\,e}{48\,m^4}\,[\vec{\alpha}\cdot\vec{\pi},(\vec{\alpha}\cdot\vec{\pi})^2\,\vec{\alpha}\cdot\vec{E}+\vec{\alpha}\cdot\vec{E}\,(\vec{\alpha}\cdot\vec{\pi})^2]+\frac{i\,e}{24\,m^4}\,[(\vec{\alpha}\cdot\vec{\pi})^3,\vec{\alpha}\cdot\vec{E}]
\end{aligned}$$

$$
\begin{aligned}
& +\frac{1}{6\,m^2}\,(\vec\alpha\cdot\vec\pi)^3-\frac{1}{6\,m^4}\,(\vec\alpha\cdot\vec\pi)^5+\frac{i\,\beta\,e}{48\,m^3}\,[\vec\alpha\cdot\vec\pi,[\vec\alpha\cdot\vec\pi,\vec\alpha\cdot\vec E]] \\
& +\frac{i\,\beta\,e}{24\,m^3}\,((\vec\alpha\cdot\vec\pi)^3\,\vec\alpha\cdot\vec E+\vec\alpha\cdot\vec E\,(\vec\alpha\cdot\vec\pi)^3) \qquad (13)
\end{aligned}
$$

$$
\begin{aligned}
\mathcal{H}^{(4)} &= \frac{\beta}{24\,m^3}\,(\vec\alpha\cdot\vec\pi)^4-\frac{\beta}{18\,m^5}\,(\vec\alpha\cdot\vec\pi)^6-\frac{i\,e}{384}\,[\vec\alpha\cdot\vec\pi,[\vec\alpha\cdot\vec\pi,[\vec\alpha\cdot\vec\pi,\vec\alpha\cdot\vec E]]] \\
&\quad -\frac{i\,e}{192\,m^4}\,[\vec\alpha\cdot\vec\pi,(\vec\alpha\cdot\vec\pi)^2\,\vec\alpha\cdot\vec E+\vec\alpha\cdot\vec E\,(\vec\alpha\cdot\vec\pi)^2]-\frac{i\,e}{96\,m^4}\,[(\vec\alpha\cdot\vec\pi)^3,\vec\alpha\cdot\vec E] \\
&\quad +\frac{1}{24\,m^4}\,(\vec\alpha\cdot\vec\pi)^5 \qquad (14)
\end{aligned}
$$

$$
\mathcal{H}^{(5)} = -\frac{1}{120\,m^4}\,(\vec\alpha\cdot\vec\pi)^5+\frac{\beta}{120\,m^5}\,(\vec\alpha\cdot\vec\pi)^6 \qquad (15)
$$

$$
\mathcal{H}^{(6)} = -\frac{\beta}{720\,m^5}\,(\vec\alpha\cdot\vec\pi)^6 \qquad (16)
$$

The sum of $\mathcal{H}^{(i)}$, Eq. (9) gives a Hamiltonian, which still depends on Y. Following FW principle, this operator is now chosen to cancel all the higher order odd terms from this sum, namely:

$$
\begin{aligned}
Y &= \frac{\beta}{5\,m^4}\,(\vec\alpha\cdot\vec\pi)^5-\frac{\beta\,e}{4\,m^2}\,\vec\alpha\cdot\dot{\vec E}+\frac{i\,e}{24\,m^3}\,[\vec\alpha\cdot\vec\pi,[\vec\alpha\cdot\vec\pi,\vec\alpha\cdot\vec E]] \\
&\quad -\frac{i\,e}{3\,m^3}\,((\vec\alpha\cdot\vec\pi)^2\,\vec\alpha\cdot\vec E+\vec\alpha\cdot\vec E\,(\vec\alpha\cdot\vec\pi)^2). \qquad (17)
\end{aligned}
$$

Y fulfills the initial ansatz, that commutators $[Y,e\,A^0-i\,\partial_t]$ and $[Y,(\vec\alpha\cdot\vec\pi)^3]$ are of higher order and thus can be neglected. The resulting FW Hamiltonian is

$$
\begin{aligned}
H_{FW} &= e\,A^0+\frac{(\vec\sigma\cdot\vec\pi)^2}{2\,m}-\frac{(\vec\sigma\cdot\vec\pi)^4}{8\,m^3}+\frac{(\vec\sigma\cdot\vec\pi)^6}{16\,m^5}-\frac{i\,e}{8\,m^2}\,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E] \\
&\quad -\frac{e}{16\,m^3}\left(\vec\sigma\cdot\vec\pi\,\vec\sigma\cdot\dot{\vec E}+\vec\sigma\cdot\dot{\vec E}\,\vec\sigma\cdot\vec\pi\right)-\frac{i\,e}{128\,m^4}\,[\vec\sigma\cdot\vec\pi,[\vec\sigma\cdot\vec\pi,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]]] \\
&\quad +\frac{i\,e}{16\,m^4}\left((\vec\sigma\cdot\vec\pi)^2\,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]+[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]\,(\vec\sigma\cdot\vec\pi)^2\right), \qquad (18)
\end{aligned}
$$

where we used the commutator identity

$$
\begin{aligned}
[(\vec\sigma\cdot\vec\pi)^3,\vec\sigma\cdot\vec E] &= -\frac{1}{2}\,[\vec\sigma\cdot\vec\pi,[\vec\sigma\cdot\vec\pi,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]]] \\
&\quad +\frac{3}{2}\left((\vec\sigma\cdot\vec\pi)^2\,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]+[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]\,(\vec\sigma\cdot\vec\pi)^2\right) \qquad (19)
\end{aligned}
$$

to simplify H_{FW}. Moreover, there is some arbitrariness in the operator S, what means that H_{FW} is not unique. The standard approach [24], which relies on subsequent use of FW-transformations differs from this one, by the transformation S with some additional even operator. However, all H_{FW} have to be equivalent at the level of matrix elements between the states which satisfy the Schrödinger equation.

Let us now study the simple case of an external static potential $V \equiv e\,A^0$. The FW Hamiltonian with the help of simple commutations takes the form

$$\begin{aligned} H_{DC} \;=\; & V+\frac{p^2}{2\,m}-\frac{p^4}{8\,m^3}+\frac{p^6}{16\,m^5}+\frac{1}{8\,m^2}\Big(\nabla^2\,V+2\,\vec{\nabla}V\times\vec{p}\cdot\vec{\sigma}\Big) \\ & -\frac{3}{32\,m^4}\Big(p^2\,\vec{\nabla}V\times\vec{p}\cdot\vec{\sigma}+\vec{\nabla}V\times\vec{p}\cdot\vec{\sigma}\,p^2\Big)+\frac{1}{128\,m^4}\,[p^2,[p^2,V]] \\ & -\frac{3}{64\,m^4}\,\Big(p^2\,\nabla^2 V+\nabla^2 V\,p^2\Big). \end{aligned} \tag{20}$$

This Hamiltonian is equivalent to the one derived previously in [15], after use of the identity

$$\langle\phi|[p^2,[p^2,V]]|\phi\rangle = 4\,\langle\phi|(\vec{\nabla}V)^2|\phi\rangle \tag{21}$$

which holds for expectation values on stationary Schrödinger states ϕ. For the exact Coulomb potential $V=-Z\,\alpha/r$, matrix elements of H_{DC} become singular. Nevertheless, as was shown in [15], one can obtain Dirac energy levels up to order $m\,(Z\,\alpha)^6$ by regularizing the Coulomb potential in an arbitrary way, and all singularities cancel out between the first and second order matrix elements.

Our aim here is to obtain the Hamiltonian for further calculations of $m\,\alpha^6$ contribution to energy levels of an arbitrary light atom. For this one can neglect the vector potential $\vec{A}$ in all the terms having m^4 and m^5 in the denominator. Moreover, less obviously, one can neglect the term with $\vec{\sigma}\cdot\vec{A}\,\vec{\sigma}\cdot\dot{\vec{E}}$ and the $\vec{B}^2$ term. It is because they are of second order in electromagnetic fields which additionally contain derivatives, and thus contribute only at higher orders. After these simplifications, H_{FW} takes the form

$$\begin{aligned} H_{FW} \;=\; & e\,A^0+\frac{1}{2\,m}\,(\pi^2-e\,\vec{\sigma}\cdot\vec{B})-\frac{1}{8\,m^3}\,(\pi^4-e\,\vec{\sigma}\cdot\vec{B}\,\pi^2-\pi^2\,e\,\vec{\sigma}\cdot\vec{B}) \\ & -\frac{1}{8\,m^2}\Big(e\vec{\nabla}\cdot\vec{E}+e\,\vec{\sigma}\cdot(\vec{E}\times\vec{\pi}-\vec{\pi}\times\vec{E})\Big)-\frac{e}{16\,m^3}\,\Big(\vec{\sigma}\cdot\vec{p}\,\vec{\sigma}\cdot\dot{\vec{E}}+\vec{\sigma}\cdot\dot{\vec{E}}\,\vec{\sigma}\cdot\vec{p}\Big) \\ & -\frac{3}{32\,m^4}\Big(p^2\,\vec{\nabla}(e\,A^0)\times\vec{p}\cdot\vec{\sigma}+\vec{\nabla}(e\,A^0)\times\vec{p}\cdot\vec{\sigma}\,p^2\Big)+\frac{1}{128\,m^4}\,[p^2,[p^2,e\,A^0]] \\ & -\frac{3}{64\,m^4}\,\Big(p^2\,\nabla^2(e\,A^0)+\nabla^2(e\,A^0)\,p^2\Big)+\frac{1}{16\,m^5}\,p^6 \end{aligned} \tag{22}$$

From this Hamiltonian one builds the many body Lagrangian density

$$\mathcal{L}=\sum_a \phi_a^\star(i\,\partial_t-H_{FW})\phi_a+\mathcal{L}_{EM}, \tag{23}$$

where $\mathcal{L}_{EM}$ is a Lagrangian of the electromagnetic field, and with the help of perturbation theory calculates Green functions.

III. THE HIGHER ORDER BREIT-PAULI HAMILTONIAN

We consider the equal time retarded Green function $G = G(\{\vec{r}_a'\}, t'; \{\vec{r}_a\}, t)$, where by $\{\vec{r}_a\}$ we denote the set of coordinates for all particles of the system. This Green function is similar to that used by Shabaev in [25]. In the stationary case considered here, $G = G(t'-t)$. The Fourier transform of G in the time variable $t'-t$ can be written as

$$G(E) \equiv \frac{1}{E - H_{\rm eff}(E)} \tag{24}$$

which is the definition of the effective Hamiltonian $H_{\rm eff}(E)$. In the nonrelativistic case $H_{\rm eff} = H_0$. All the relativistic and QED corrections resulting from the Lagrangian can be represented as

$$\begin{aligned} G(E) &= \frac{1}{E-H_0} + \frac{1}{E-H_0}\,\Sigma(E)\,\frac{1}{E-H_0} + \frac{1}{E-H_0}\,\Sigma(E)\,\frac{1}{E-H_0}\,\Sigma(E)\,\frac{1}{E-H_0} + \ldots \\ &= \frac{1}{E-H_0-\Sigma(E)} \equiv \frac{1}{E-H_{\rm eff}(E)} \end{aligned} \tag{25}$$

where $\Sigma(E)$ is the n-particle irreducible contribution. The energy level can be interpreted as a pole of $G(E)$ as a function of E. For this it is convenient to consider the matrix element of G between the the nonrelativistic wave function corresponding to this energy level. There is always such a correspondence, since relativistic and QED effects are small perturbations of the system. We follow here a relativistic approach for the electron self-energy presented in [5]. This matrix element is

$$\langle\phi|G(E)|\phi\rangle = \langle\phi|\frac{1}{E-H_0-\Sigma(E)}|\phi\rangle \equiv \frac{1}{E-E_0-\sigma(E)} \tag{26}$$

where

$$\sigma(E) = \langle\phi|\Sigma(E)|\phi\rangle + \sum_{n\neq 0}\langle\phi|\Sigma(E)|\phi_n\rangle\,\frac{1}{E-E_n}\,\langle\phi_n|\Sigma(E)|\phi\rangle + \ldots \tag{27}$$

Having $\sigma(E)$, the correction to the energy level can be expressed as

$$\begin{aligned} \delta E &= E - E_0 = \sigma(E_0) + \sigma'(E_0)\,\sigma(E_0) + \ldots \\ &= \langle\phi|\Sigma(E_0)|\phi\rangle + \langle\phi|\Sigma(E_0)\,\frac{1}{(E_0-H_0)'}\,\Sigma(E_0)|\phi\rangle + \langle\phi|\Sigma'(E_0)|\phi\rangle\,\langle\phi|\Sigma(E_0)|\phi\rangle + \ldots \end{aligned} \tag{28}$$

Since the last term in Eq. (28) can be neglected up to order $m\,\alpha^6$, one can consider only $\Sigma(E_0)$. In most cases, the explicit dependence of Σ on state, through E_0, can be eliminated by appropriate transformations, with the help of various commutations. The only exception is the so called Bethe logarithm, which contributes only to the order $m\,\alpha^5$. If we consider this term separately, the operator Σ gives an effective Hamiltonian

$$H_{\rm eff} = H_0 + \Sigma = H_0 + H^{(4)} + H^{(5)} + H^{(6)} + \ldots \tag{29}$$

from which one calculates corrections to energy levels as in Eq. (5). The calculation of Σ follows from Feynman rules for Lagrangian in Eq. (23). We will use the photon propagator in the Coulomb gauge:

$$G_{\mu\nu}(k) = \begin{cases} -\frac{1}{\vec{k}^2} & \mu=\nu=0\,, \\ \frac{-1}{k_0^2-\vec{k}^2+i\,\epsilon}\Big(\delta_{ij} - \frac{k_i k_j}{\vec{k}^2}\Big) & \mu=i,\nu=j \end{cases}\,. \tag{30}$$

and consider separately corrections due to exchange of the Coulomb G_{00} and the transverse G_{ij} photon. The typical one photon exchange contribution between electrons a and b is:

$$\begin{aligned}\langle\phi|\Sigma(E_0)|\phi\rangle \;=\; & e^2\int\frac{d^4k}{(2\,\pi)^4\,i}\,G_{\mu\nu}(k)\,\bigg\{\bigg\langle\phi\bigg|\jmath_a^\mu(k)\,e^{i\,\vec{k}\cdot\vec{r}_a}\,\frac{1}{E_0-H_0-k^0+i\,\epsilon}\,\jmath_b^\nu(-k)\,e^{-i\,\vec{k}\cdot\vec{r}_b}\bigg|\phi\bigg\rangle \\ & +\bigg\langle\phi\bigg|\jmath_b^\mu(k)\,e^{i\,\vec{k}\cdot\vec{r}_b}\,\frac{1}{E_0-H_0-k^0+i\,\epsilon}\,\jmath_a^\nu(-k)\,e^{-i\,\vec{k}\cdot\vec{r}_a}\bigg|\phi\bigg\rangle\bigg\}\,,\end{aligned} \tag{31}$$

where ϕ is an eigenstate of H_0 and $\jmath_a^\mu$ is an electromagnetic current operator for particle a. One obtains the exact form of $\jmath^\mu(k)$ from the Lagrangian in Eq.(23), and is defined as the coefficient which multiplies the polarization vector ϵ^μ in the annihilation part of the electromagnetic potential

$$A^\mu(\vec{r},t) \sim \epsilon_\lambda^\mu\,e^{i\,\vec{k}\cdot\vec{r}-i\,k^0\,t}\,\hat{a}_\lambda + \text{h.c.} \tag{32}$$

The first terms of the nonrelativistic expansion of $\jmath^0$ component are

$$\jmath^0(\vec{k}) = 1 + \frac{i}{4\,m}\,\vec{\sigma}\cdot\vec{k}\times\vec{p} - \frac{1}{8\,m^2}\vec{k}^{\,2} + \ldots \tag{33}$$

and of the $\vec{\jmath}$ component are

$$\vec{\jmath}(\vec{k}) = \frac{\vec{p}}{m} + \frac{i}{2\,m}\,\vec{\sigma}\times\vec{k}\,. \tag{34}$$

Most of the calculation is performed in the nonretardation approximation, namely one sets $k^0 = 0$ in the photon propagator $G_{\mu\nu}(k)$ and $\jmath(k)$. The retardation corrections are considered separately. Within this approximation and using the symmetrization $k^0 \leftrightarrow -k^0$, the k^0 integral is

$$\frac{1}{2}\int\frac{d\,k^0}{2\,\pi\,i}\bigg[\frac{1}{-\Delta E-k^0+i\,\epsilon}+\frac{1}{-\Delta E+k^0+i\,\epsilon}\bigg] = -\frac{1}{2} \tag{35}$$

where we have assumed that ΔE is positive, which is correct when ϕ is the ground state. For excited states, the integration contour is deformed in such a way that all the poles from the electron propagator lie on one side, so it is not strictly speaking the Feynman contour. However the result of the k^0 integration for excited states is the same as in the above, which leads to

$$\langle\phi|\Sigma(E_0)|\phi\rangle = -e^2 \int \frac{d^3k}{(2\,\pi)^3}\, G_{\mu\nu}(\vec{k}) \left\langle\phi\middle| j_a^\mu(\vec{k})\, e^{i\,\vec{k}\cdot(\vec{r}_a-\vec{r}_b)}\, j_b^\nu(-\vec{k}) \middle|\phi\right\rangle. \tag{36}$$

The $\vec{k}$ integral is the Fourier transform of the photon propagator in the nonretardation approximation

$$G_{\mu\nu}(\vec{r}) = \int \frac{d^3k}{(2\,\pi)^3} G_{\mu\nu}(\vec{k}) = \frac{1}{4\,\pi} \begin{cases} -\frac{1}{r} & \mu=\nu=0\,, \\ \frac{1}{2\,r}\Big(\delta_{ij} + \frac{r_i r_j}{\vec{r}^{\,2}}\Big) & \mu=i,\nu=j \end{cases}. \tag{37}$$

One easily recognizes that in the nonrelativistic limit G_{00} is the Coulomb interaction. However this term is already included in H_0, which means that this nonrelativistic Coulomb interaction has to be excluded from the perturbative expansion. Next order terms resulting from j^0 and $\vec{j}$ lead to the Breit Pauli Hamiltonian, Eq. (4). Below we derive the higher order term in the nonrelativistic expansion, namely the $m\,\alpha^6$ Hamiltonian, which we call here the higher order effective Hamiltonian $H^{(6)}$. It is expressed as a sum of various contributions

$$H^{(6)} = \sum_{i=0,9} \delta H_i \tag{38}$$

which are calculated in the following.

δH_0 is the kinetic energy correction

$$\delta H_0 = \sum_a \frac{p_a^6}{16\,m^5}\,. \tag{39}$$

δH_1 is a correction due to the last three terms in H_{FW} in Eq. (22). These terms involve only A^0, so the nonretardation approximation is strictly valid here. This correction δH_1 includes the Coulomb interaction between the electron and the nucleus, and between electrons. So, if we denote by V the nonrelativistic interaction potential

$$V \equiv \sum_a -\frac{Z\,\alpha}{r_a} + \sum_{a>b}\sum_b \frac{\alpha}{r_{ab}} \tag{40}$$

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

$$e\,\vec{\mathcal{E}}_a \equiv -\nabla_a V = -Z\,\alpha\,\frac{\vec{r}_a}{r_a^3} + \sum_{b\neq a} \alpha\,\frac{\vec{r}_{ab}}{r_{ab}^3} \tag{41}$$

then δH_1 can be written as

$$\begin{aligned}\delta H_1 \;=\; & \sum_a \frac{3}{32\,m^4}\,\vec\sigma_a\cdot\Big(p_a^2\,e\,\vec{\mathcal{E}}_a\times\vec p_a + e\,\vec{\mathcal{E}}_a\times\vec p_a\,p_a^2\Big)\\ & + \frac{1}{128\,m^4}\,[p_a^2,[p_a^2,V]] - \frac{3}{64\,m^4}\,\Big(p_a^2\,\nabla_a^2 V + \nabla_a^2 V\,p_a^2\Big)\end{aligned} \tag{42}$$

δH_2 is a correction to the Coulomb interaction between electrons which comes from the $4^{\rm th}$ term in H_{FW}, namely

$$-\frac{1}{8\,m^2}\Big(e\vec\nabla\cdot\vec E + e\,\vec\sigma\cdot(\vec E\times\vec p - \vec p\times\vec E)\Big) \tag{43}$$

If interaction of both electrons is modified by this term, it can be obtained in the nonretardation approximation Eq. (36), so one obtains

$$\begin{aligned}\delta H_2 \;=\; & \sum_{a>b}\sum_b \int d^3k\,\frac{4\,\pi}{k^2}\,\frac{1}{64\,m^4}\,\Big(k^2 + 2\,i\,\vec\sigma_a\cdot\vec p_a\times\vec k\Big)\,e^{i\,\vec k\cdot\vec r_{ab}}\,\Big(k^2 + 2\,i\,\vec\sigma_b\cdot\vec k\times\vec p_b\Big)\\ =\; & \sum_{a>b}\sum_b \frac{1}{64\,m^4}\,\Big\{-4\,\pi\,\nabla^2\,\delta^3(r_{ab}) - 8\,\pi\,i\,\vec\sigma_a\cdot\vec p_a\times\delta^3(r_{ab})\,\vec p_a - 8\,\pi\,i\,\vec\sigma_b\cdot\vec p_b\times\delta^3(r_{ab})\,\vec p_b\\ & + 4\,(\vec\sigma_a\times\vec p_a)^i\Big[\frac{\delta^{ij}}{3}\,4\,\pi\,\delta^3(r_{ab}) + \frac{1}{r_{ab}^3}\,\Big(\delta^{ij} - 3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\Big)\Big](\vec\sigma_b\times\vec p_b)^j\Big\}\end{aligned} \tag{44}$$

We have encountered here for the first time singular electron-electron operators. One can make them meaningful by appropriate regularization of the photon propagator, or by dimensional regularization. In general it is a difficult problem and, as we have written in the introduction, the explicit solution was demonstrated for the positronium and helium atom only.

δH_3 is an correction that comes from $5^{\rm th}$ term in Eq. (22),

$$-\frac{e}{16\,m^3}\,\Big(\vec\sigma\cdot\vec p\,\vec\sigma\cdot\dot{\vec E} + \vec\sigma\cdot\dot{\vec E}\,\vec\sigma\cdot\vec p\Big)\,. \tag{45}$$

To calculate it, we have to return to the original expression for one-photon exchange. We assume that particle a interacts by this term, while particle b by nonrelativistic coupling $e\,A^0$ and obtain

$$\begin{aligned}\delta E_3 \;=\; & \sum_{a\neq b}\sum_b -e^2\int\frac{d^4k}{(2\,\pi)^4\,i}\,\frac{1}{\vec k^2}\,\frac{1}{16\,m^3}\\ & \Big\{\langle\phi|\Big(\vec\sigma_a\cdot\vec p_a\,\vec\sigma_a\cdot\vec k\,e^{i\,\vec k\cdot\vec r_a} + e^{i\,\vec k\cdot\vec r_a}\,\vec\sigma_a\cdot\vec p_a\,\vec\sigma_a\cdot\vec k\Big)\,\frac{k^0}{E_0 - H_0 - k^0 + i\,\epsilon}\,e^{-i\,\vec k\cdot\vec r_b}|\phi\rangle\\ & + \langle\phi|e^{i\,\vec k\cdot\vec r_b}\,\frac{k^0}{E_0 - H_0 - k^0 + i\,\epsilon}\,\Big(\vec\sigma_a\cdot\vec p_a\,\vec\sigma_a\cdot\vec k\,e^{i\,\vec k\cdot\vec r_a} + e^{i\,\vec k\cdot\vec r_a}\,\vec\sigma_a\cdot\vec p_a\,\vec\sigma_a\cdot\vec k\Big)|\phi\rangle\Big\}\end{aligned} \tag{46}$$

We replace $\vec{k} \to -\vec{k}$ in the second term, then perform the k^0 integral, and obtain

$$\begin{aligned}\delta E_3 &= \sum_{a\neq b}\sum_b -\frac{e^2}{2}\int\frac{d^3k}{(2\,\pi)^3}\,\frac{1}{\vec{k}^2}\,\frac{1}{16\,m^3}\\ &\quad\Big\{\langle\phi|\Big(\vec{\sigma}_a\cdot\vec{p}_a\,\vec{\sigma}_a\cdot\vec{k}\,e^{i\,\vec{k}\cdot\vec{r}_a}+e^{i\,\vec{k}\cdot\vec{r}_a}\,\vec{\sigma}_a\cdot\vec{p}_a\,\vec{\sigma}_a\cdot\vec{k}\Big)\,(H_0-E_0)\,e^{-i\,\vec{k}\cdot\vec{r}_b}|\phi\rangle\\ &\quad+\langle\phi|e^{i\,\vec{k}\cdot\vec{r}_b}\,(H_0-E_0)\,\Big(\vec{\sigma}_a\cdot\vec{p}_a\,\vec{\sigma}_a\cdot\vec{k}\,e^{i\,\vec{k}\cdot\vec{r}_a}+e^{i\,\vec{k}\cdot\vec{r}_a}\,\vec{\sigma}_a\cdot\vec{p}_a\,\vec{\sigma}_a\cdot\vec{k}\Big)|\phi\rangle\Big\} \qquad (47)\end{aligned}$$

After commuting $(H_0 - E_0)$ with $e^{\pm i\,\vec{k}\cdot\vec{r}_b}$ one expresses this correction in terms of an effective operator

$$\delta H_3 = \sum_{a\neq b}\sum_b -\frac{1}{32\,m^4}\left[p_b^2,\left[p_a^2,\frac{\alpha}{r_{ab}}\right]\right] \qquad (48)$$

δH_4 is the relativistic correction to transverse photon exchange. The first electron is coupled to $\vec{A}$ by the nonrelativistic term

$$-\frac{e}{m}\,\vec{p}\cdot\vec{A}-\frac{e}{2\,m}\,\vec{\sigma}\cdot\vec{B} \qquad (49)$$

and the second one by the relativistic correction, the 3rd term in Eq. (22)

$$-\frac{1}{8\,m^3}\,(\pi^4 - e\,\vec{\sigma}\cdot\vec{B}\,\pi^2-\pi^2\,e\,\vec{\sigma}\cdot\vec{B}) \to \frac{e}{8\,m^3}\,(p^2\,2\,\vec{p}\cdot\vec{A}+2\,\vec{p}\cdot\vec{A}\,p^2+\vec{\sigma}\cdot\vec{B}\,p^2+p^2\,\vec{\sigma}\cdot\vec{B}) \qquad (50)$$

It is sufficient to calculate it in the nonretardation approximation

$$\begin{aligned}\delta H_4 &= \sum_{a\neq b}\sum_b\frac{\alpha}{8\,m^3}\left[2\,p_a^2\,p_a^i+p_a^2\,(\vec{\sigma}_a\times\nabla_a)^i\right]\\ &\quad\left[\frac{p_b^j}{m}+\frac{1}{2\,m}\,(\vec{\sigma}_b\times\,\nabla_b)^j\right]\frac{1}{2\,r_{ab}}\left(\delta^{ij}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)+\text{h.c.} \qquad (51)\end{aligned}$$

It is convenient at this point to introduce a notation for the vector potential at the position of particle a which is produced by other particles

$$e\,\mathcal{A}_a^i \equiv \sum_{b\neq a}\frac{\alpha}{2\,r_{ab}}\left(\delta^{ij}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)\frac{p_b^j}{m}+\frac{\alpha}{2\,m}\,\frac{(\vec{\sigma}_b\times\vec{r}_{ab})^i}{r_{ab}^3}\,, \qquad (52)$$

then this correction can be written as

$$\delta H_4 = \sum_a\frac{e}{8\,m^3}\left[2\,p_a^2\,\vec{p}_a\cdot\vec{\mathcal{A}}_a+2\,p_a\cdot\vec{\mathcal{A}}_a\,p_a^2+p_a^2\,\vec{\sigma}_a\cdot\nabla_a\times\vec{\mathcal{A}}_a+\vec{\sigma}_a\cdot\nabla_a\times\vec{\mathcal{A}}_a\,p_a^2\right] \qquad (53)$$

Let us notice that in the nonretardation approximation any correction can be simply obtained by replacing the magnetic field $\vec{A}$ by a static field $\vec{\mathcal{A}}_a$. We will use this fact in further calculations.

δH_5 comes from the coupling

$$\frac{e^2}{8\,m^2}\,\vec{\sigma}\cdot(\vec{E}\times\vec{A}-\vec{A}\times\vec{E}) \tag{54}$$

which is present in 4$^{\rm th}$ term in Eq. (22). The resulting correction is obtained by replacing the fields $\vec{E}$ and $\vec{A}$ by the static fields produced by other electrons

$$\delta H_5 = \sum_a \frac{e^2}{8\,m^2}\,\vec{\sigma}_a\cdot\left[\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a-\vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a\right] \tag{55}$$

δH_6 comes from the coupling

$$\frac{e^2}{2\,m}\,\vec{A}^2 \tag{56}$$

which is present in the second term of Eq. (22). Again, in the nonretardation approximation the $\vec{A}_a$ field is being replaced by the static fields produced by other electrons

$$\delta H_6 = \sum_a \frac{e^2}{2\,m^2}\,\vec{\mathcal{A}}_a^2 \tag{57}$$

δH_7 is a retardation correction in the nonrelativistic single transverse photon exchange. To calculate it, we have to return to the general one-photon exchange expression, Eq. (31), and take the transverse part of the photon propagator

$$\begin{aligned}\delta E \;=\; & -e^2\int\frac{d^4k}{(2\,\pi)^4\,i}\,\frac{1}{(k^0)^2-\vec{k}^2+i\,\epsilon}\left(\delta^{ij}-\frac{k^i\,k^j}{\vec{k}^2}\right)\\ & \left\langle\phi\middle|j^i_a(k)\,e^{i\,\vec{k}\cdot\vec{r}_a}\,\frac{1}{E_0-H_0-k^0+i\,\epsilon}\,j^j_b(-k)\,e^{-i\,\vec{k}\cdot\vec{r}_b}\middle|\phi\right\rangle+(a\leftrightarrow b)\,.\end{aligned} \tag{58}$$

We assume that the product $j^i_a(k)\;j^j_b(-k)$ contains at most a single power of k^0. This allows one to perform the k^0 integration by encircling the only pole $k^0=|\vec{k}|$ on $\Re(k^0)>0$ complex half plane and obtain

$$\begin{aligned}\delta E \;=\; & e^2\int\frac{d^3k}{(2\,\pi)^3\,2\,k}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)\\ & \left\langle\phi\middle|j^i_a(k)\,e^{i\,\vec{k}\cdot\vec{r}_a}\,\frac{1}{E_0-H_0-k}\,j^j_b(-k)\,e^{-i\,\vec{k}\cdot\vec{r}_b}\middle|\phi\right\rangle+(a\leftrightarrow b)\,.\end{aligned} \tag{59}$$

where $k=|\vec{k}|$. By using the nonrelativistic form of j^i and taking the third term in the retardation expansion,

$$\frac{1}{E_0-H_0-k}=-\frac{1}{k}+\frac{H_0-E_0}{k^2}-\frac{(H_0-E_0)^2}{k^3}+\ldots \tag{60}$$

where the first one contributes to the Breit-Pauli Hamiltonian, the second term to $E^{(5)}$, and the third term gives δE_7

$$\delta E_7 = \sum_{a\neq b}\sum_b -e^2 \int \frac{d^3k}{(2\,\pi)^3\,2\,k^4}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)\left\langle\phi\middle|\left(\frac{\vec p_a}{m}+\frac{1}{2\,m}\,\vec\sigma_a\times\nabla_a\right)^i e^{i\,\vec k\cdot\vec r_a}\right.$$
$$\left.(H_0-E_0)^2\left(\frac{\vec p_b}{m}+\frac{1}{2\,m}\,\vec\sigma_b\times\nabla_b\right)^j e^{-i\,\vec k\cdot\vec r_b}\middle|\phi\right\rangle. \tag{61}$$

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

$$\delta E_7 = \delta E_A + \delta E_B + \delta E_C \tag{62}$$

The part with double spin operators is

$$\delta E_C = \sum_a\sum_{a\neq b} -e^2 \int \frac{d^3k}{(2\,\pi)^3\,2\,k^4}\frac{(\vec\sigma_a\times\vec k)\cdot(\vec\sigma_b\times\vec k)}{4\,m^2}\left\langle\phi\middle|\,e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}\middle|\phi\right\rangle \tag{63}$$

One uses the commutation identity

$$\begin{aligned}\left\langle e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}\right\rangle + (a\leftrightarrow b) &= \left\langle\left[e^{i\,\vec k\cdot\vec r_a},\left[(H_0-E_0)^2,e^{-i\,\vec k\cdot\vec r_b}\right]\right]\right\rangle\\ &= -\frac{1}{2\,m^2}\left\langle[p_a^2,[p_b^2,e^{i\,\vec k\cdot\vec r_{ab}}]]\right\rangle\end{aligned} \tag{64}$$

to express this correction in terms of the effective operator δH_C.

$$\delta H_C = \sum_{a>b}\sum_b \frac{\alpha}{16\,m^4}\left[p_a^2,\left[p_b^2,\vec\sigma_a\cdot\vec\sigma_b\,\frac{2}{3\,r_{ab}}+\sigma_a^i\,\sigma_b^j\,\frac{1}{2\,r_{ab}}\left(\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}-\frac{\delta^{ij}}{3}\right)\right]\right] \tag{65}$$

The part with no spin operator is

$$\delta E_A = \sum_{a\neq b}\sum_b -e^2 \int \frac{d^3k}{(2\,\pi)^3\,2\,k^4}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)$$
$$\left\langle\phi\middle|\frac{p_a^i}{m}\left\{e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}-(H_0-E_0)^2\right\}\frac{p_b^j}{m}\middle|\phi\right\rangle. \tag{66}$$

We subtracted here the term with $k=0$. We ought to perform this in Eq. (61), where lower order terms were subtracted, but for simplicity of writing we have not done it until now. We use another commutator identity

$$\begin{aligned}&e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}-(H_0-E_0)^2 =\\ &(H_0-E_0)\,(e^{i\,\vec k\cdot\vec r_{ab}}-1)\,(H_0-E_0)+(H_0-E_0)\left[\frac{p_b^2}{2\,m},e^{i\,\vec k\cdot\vec r_{ab}}-1\right]\\ &+\left[e^{i\,\vec k\cdot\vec r_{ab}}-1,\frac{p_a^2}{2\,m}\right](H_0-E_0)+\left[\frac{p_b^2}{2\,m},\left[e^{i\,\vec k\cdot\vec r_{ab}}-1,\frac{p_a^2}{2\,m}\right]\right]\end{aligned} \tag{67}$$

and the integration formula

$$\int d^3k \frac{4\,\pi}{k^4}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)(e^{i\,\vec{k}\cdot\vec{r}}-1)=\frac{1}{8\,r}\,(r^i\,r^j-3\,\delta^{ij}\,r^2) \tag{68}$$

to obtain the effective operator δH_A

$$\begin{aligned}\delta H_A \;=\; & \sum_{a>b}\sum_b -\frac{\alpha}{8\,m^2}\biggl\{[p_a^i,V]\,\frac{r_{ab}^i\,r_{ab}^j-3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\,[V,p_b^j] \\ & +[p_a^i,V]\left[\frac{p_b^2}{2\,m},\frac{r_{ab}^i\,r_{ab}^j-3\,\delta^{ij}\,r_{ab}^2}{r_{ab}}\right]p_b^j+p_a^i\left[\frac{r_{ab}^i\,r_{ab}^j-3\,\delta^{ij}\,r_{ab}^2}{r_{ab}},\frac{p_a^2}{2\,m}\right][V,p_b^j] \\ & +p_a^i\left[\frac{p_b^2}{2\,m},\left[\frac{r_{ab}^i\,r_{ab}^j-3\,\delta^{ij}\,r_{ab}^2}{r_{ab}},\frac{p_a^2}{2\,m}\right]\right]p_b^j\biggr\}\end{aligned} \tag{69}$$

The part with the single spin operator is

$$\begin{aligned}\delta E_B \;=\; & \sum_{a\neq b}\sum_b -\frac{i\,e^2}{4\,m^2}\int\frac{d^3k}{(2\,\pi)^3\,k^4} \\ & \Bigl\{e^{i\,\vec{k}\cdot\vec{r}_a}\,(H_0-E_0)^2\,e^{-i\,\vec{k}\cdot\vec{r}_b}\,\vec{\sigma}_a\times\vec{k}\cdot\vec{p}_b-\vec{p}_a\cdot\vec{\sigma}_b\times\vec{k}\,e^{i\,\vec{k}\cdot\vec{r}_a}\,(H_0-E_0)^2\,e^{-i\,\vec{k}\cdot\vec{r}_b}\Bigr\}\end{aligned} \tag{70}$$

With the help of the commutator in Eq. (67) identity and the integral

$$\int d^3k\,\frac{4\,\pi\,\vec{k}}{k^4}\,e^{i\,\vec{k}\cdot\vec{r}}=\frac{i}{2}\,\frac{\vec{r}}{r} \tag{71}$$

one obtains

$$\begin{aligned}\delta H_B \;=\; & \sum_{a>b}\sum_b \frac{\alpha}{4\,m^2}\biggl\{\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2\,m}\right][V,\vec{p}_b]+\left[\frac{p_b^2}{2\,m},\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2\,m}\right]\right]\vec{p}_b \\ & -[\vec{p}_a,V]\left[p_b^2,\vec{\sigma}_b\times\frac{\vec{r}_{ab}}{r_{ab}}\right]-\vec{p}_a\left[\frac{p_a^2}{2\,m},\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_b^2}{2\,m}\right]\right]\biggr\}\end{aligned} \tag{72}$$

Finally, the operator δH_7 is a sum of already derived parts

$$\delta H_7=\delta H_A+\delta H_B+\delta H_C \tag{73}$$

δH_8 is a retardation correction in a single transverse photon exchange, where one vertex is nonrelativistic, Eq. (49) and the second comes from the 3rd term in Eq. (22)

$$-\frac{e}{8\,m^2}\,\vec{\sigma}\cdot(\vec{E}\times\vec{p}-\vec{p}\times\vec{E}) \tag{74}$$

With the help of Eq. (59) one obtains the following expression for δE_8

$$\begin{aligned}\delta E_8 \;=\; & \sum_{a\neq b}\sum_b e^2\int\frac{d^3k}{(2\,\pi)^3}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)\frac{i}{16\,m^3}\,\langle\phi|\Bigl(e^{i\,\vec{k}\cdot\vec{r}_a}\,\vec{p}_a\times\vec{\sigma}_a+\vec{p}_a\times\vec{\sigma}_a\,e^{i\,\vec{k}\cdot\vec{r}_a}\Bigr)^i \\ & \frac{1}{E_0-H_0-k}\left(\vec{p}_b-\frac{i}{2}\,\vec{\sigma}_b\times\vec{k}\right)^j\,e^{-i\,\vec{k}\cdot\vec{r}_b}\,|\phi\rangle+\text{h.c.}\end{aligned} \tag{75}$$

In the expansion of $1/(E_0 - H_0 - k)$ in Eq. (60) the first term vanishes because h.c. and the second term is a correction of order $m\,\alpha^6$. After commuting $(H_0 - E_0)$ on the left one obtains the effective operator δH_8

$$
\begin{aligned}
\delta H_8 \;=\; & \sum_{a\neq b}\sum_b e^2 \int \frac{d^3k}{(2\,\pi)^3}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)\frac{1}{k^2}\,\frac{i}{16\,m^3} \\
& \left[e^{i\,\vec k\cdot\vec r_{ab}}\,\vec p_a\times\vec\sigma_a+\vec p_a\times\vec\sigma_a\,e^{i\,\vec k\cdot\vec r_{ab}}, V+\frac{p_a^2}{2\,m}\right]^i\left(\vec p_b-\frac{i}{2}\,\vec\sigma_b\times\vec k\right)^j+\text{h.c.} \\
=\; & \sum_a \frac{e^2}{8\,m^2}\,\vec\sigma_a\cdot\left[\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a-\vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a\right] \\
& +\frac{i\,e}{16\,m^3}\left[\vec{\mathcal{A}}_a\cdot\vec p_a\times\vec\sigma_a+\vec p_a\times\vec\sigma_a\cdot\vec{\mathcal{A}}_a\,,p_a^2\right]
\end{aligned}
\tag{76}
$$

δH_9 is a one- and two-loop radiative correction

$$
\delta H_9 = H_{R1} + H_{R2} \tag{77}
$$

and its derivation requires a separate treatment. We base our treatment here on known results for helium, which in turn are based on hydrogen and positronium, and extend it to an arbitrary atom, as long as nonrelativistic expansion makes sense.

$$
\begin{aligned}
H_{R1} \;=\; & \sum_a \frac{\alpha\,(Z\,\alpha)^2}{m^2}\,9.61837\,\delta^3(r_a) \\
& +\sum_{a>b}\sum_b \frac{\alpha^3}{m^2}\,(14.33134-3.42651\,\vec\sigma_a\cdot\vec\sigma_b)\,\delta^3(r_{ab})
\end{aligned}
\tag{78}
$$

$$
\begin{aligned}
H_{R2} \;=\; & \sum_a \frac{\alpha^2\,(Z\,\alpha)}{m^2}\,0.17155\,\delta^3(r_a) \\
& +\sum_{a>b}\sum_b \frac{\alpha^3}{m^2}\,(-0.66526+0.08633\,\vec\sigma_a\cdot\vec\sigma_b)\,\delta^3(r_{ab}) \\
& +\left(\frac{\alpha}{\pi}\right)^2\left\{\sum_a \frac{Z\,\alpha}{4\,m^2}\,\vec\sigma_a\cdot\frac{\vec r_a}{r_a^3}\times\vec p_a\,2\,a_e^{(2)}\right. \\
& +\sum_{a>b}\sum_b \frac{\alpha}{4\,m^2}\,\frac{\sigma_a^i\,\sigma_b^j}{r_{ab}^3}\left(\delta^{ij}-3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)[2\,a_e^{(2)}+(a_e^{(1)})^2] \\
& \left.-\frac{\alpha}{4\,m^2\,r_{ab}^3}\,(\vec\sigma_a+\vec\sigma_b)\,\cdot\vec r_{ab}\times(\vec p_a-\vec p_b)\,2\,a_e^{(2)}\right\}.
\end{aligned}
\tag{79}
$$

where

$$
\kappa \;=\; \frac{\alpha}{\pi}\,a_e^{(1)}+\left(\frac{\alpha}{\pi}\right)^2 a_e^{(2)}+\ldots \tag{80}
$$

$$
a_e^{(1)} \;=\; 0.5\,, \tag{81}
$$

$$
a_e^{(2)} \;=\; -0.328\,478\,965\ldots \tag{82}
$$

and κ is the electron magnetic moment anomaly.

IV. SUMMARY

The obtained complete $m\,\alpha^6$ contribution $H^{(6)}$ Eq. (38) is in agreement with the former derivation for the particular case of helium S [20] and P levels [12], but is much more compact. Due to differing ways of representing various complicated operators, this comparison is rather nontrivial, and we had to refer in many case to momentum representation to find agreement. Since the present derivation differs from the former one, this agreement may be regarded as a justification of this, and as well as the former results. We have not derived here the term λ in Eq. (5). It is obtained by matching the forward scattering amplitude in full QED with the one obtained from the effective Hamiltonian or NRQED, and it accounts for the contribution with high electron momentum. λ depends however, on the regularization scheme, and once it is fixed it can be obtained in a similar way as in dimensional [23] or photon propagator regularizations [20].

$H^{(6)}$ can be used for high precision calculations of energy levels of few electron atoms, provided two difficulties are overcome. The first one is the algebraic elimination of electron-electron singularities. The elimination of electron-nucleus singularities was demonstrated on hydrogen and helium examples, and could easily be extended to an arbitrary atom. The elimination of electron-electron singularities using the dimensional regularization scheme was performed for the ground state of helium atom in [23], however this derivation was very complicated and so far this result has not been confirmed. The extension to more than two-electron atoms is even more complicated, therefore a new idea which will lead to elimination of electron-electron singularities is needed. The second difficulty is the lack of analytical values for integrals with basis sets, which fulfill the cusp conditions. For example, for the Hylleraas basis set only three-electron integrals are known analytically [26, 27]. This cusp condition is necessary, because effective operators present in $\delta H^{(6)}$ contain many derivatives. For these reasons the calculation of $m\,\alpha^6$ contribution to atomic energy levels has been accomplished only for a few states of helium atoms [13, 21–23] and hyperfine splitting [28], where a powerful random exponential basis set has been applied. For the three- [9, 10] and four-electron [11] systems the leading QED effects, namely the correction of order $m\,\alpha^5$ have only recently been calculated. Due to developments in the Hylleraas basis sets [27, 29] we think the calculation of $m\,\alpha^6$ contribution to lithium energy levels is now possible, particularly interesting is the $Q(\alpha^2)$ correction to hyperfine splitting, which may be regarded as a benchmark calculations for MCDF or MBPT methods. Another interesting example is the fine structure of P_J levels, where electron-electron singularities are not present, such as for helium fine structure.

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