Quantum electrodynamics of two-body systems with arbitrary masses

Jacek Zatorski,1 Vojtěch Patkůš,2 and Krzysztof Pachucki1

1Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland
2Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague 2, Czech Republic

(Dated: July 29, 2022)

We perform a calculation of quantum electrodynamics effects in excited states with \( l > 1 \) of arbitrary two-body systems up to \( \alpha^6 \mu \) order. The obtained results are valid for hadronic atoms, as long as the strong interaction effects are negligible. We demonstrate that for circular states with \( l \sim n \), the effective expansion parameter is \( Z \alpha/n \), which extends the applicability of the derived formulas to heavy ions. Moreover, inclusion of higher-order terms is feasible, which indicates that accurate measurements of excited states of, for example, muonic or antiprotonic hydrogenic ions can be used to determine the fundamental constants and to search for the existence of yet unknown long-range interactions.

I. INTRODUCTION

Finite nuclear mass corrections to atomic energy levels are often the main limiting factor of theoretical predictions, for example in the isotope shift of regular atoms, or transition frequencies in exotic atoms such as muonium \( e^- \mu^+ \). It is because there is no fundamental equation for a two-body system with arbitrary masses which accounts for relativity. This is in contrast with the Dirac equation, which holds when one of the particles is infinitely heavy. Although there is an exact formula \( \alpha \), which gives the leading \( m/M \) correction valid for an arbitrary nuclear charge, the more general result for an arbitrary mass ratio \( m/M \) is not known. In the alternative approach one employs QED and expansion in the fine structure constant \( \alpha \) to derive an analytic formula for nuclear recoil corrections in consequence orders in \( \alpha \). Here we demonstrate that one can derive exact formulas for \( \alpha \) expansion coefficients for excited rotational \( l > 1 \) states, which are valid for arbitrary masses of its constituents. We perform calculations up to the order \( \alpha^6 \mu \) and indicate the possibility of further improvements. This would allow for extremely accurate theoretical predictions for excited hydrogenic states as long as the contact interactions, e.g. from strong forces, are negligible. A good example are excited states of antiprotonic atoms, like \( \bar{p}p \) or \( \bar{p} \). If corresponding measurements are available, this would allow for more accurate determination of fundamental constants or tests of the existence of unknown long-range interactions, similarly to precision tests performed with antiprotonic helium \( \bar{p}p \), but much more accurate.

Several accurate results have been obtained for excited states of hydrogenic systems including two-loop QED in the infinite nuclear mass limit, and leading \( m/M \) corrections. This, in combination with \( \mu \)H Lamb shift measurement, allowed for the determination of the Rydberg constant and the proton charge radius. The measurement of magnetic interactions in hydrogen-like carbon is currently the best determination of the electron mass in atomic mass units. The measurement of muonium \( 1S - 2S \) will in the future provide the \( \mu \) mass. If accurate measurements are available for hydrogenic rotational states \( 6 \), this would allow not only for more accurate determination of fundamental constants, but also will allow for the search of long-range interactions. For all these examples, accurate theoretical predictions of energy levels are necessary, and in this work we demonstrate the availability of highly accurate results for rotational levels.

The rest of this paper is organized as follows. In Section II we outline the method of calculation. Section III contains details of the calculation of the leading relativistic correction to energy. In Section IV we present the leading QED correction to energy levels, and Section V is devoted to higher-order QED corrections to the energy levels, followed by a summary in Section VI.

II. EXPANSION OF ENERGY IN POWERS OF THE FINE STRUCTURE CONSTANT \( \alpha \)

In this work we consider two-body systems consisting of a negatively charged particle of mass \( m_1 \) and a positively charged nucleus of mass \( m_2 \). From the theoretical perspective the relevant atomic transitions are those between states of the angular momentum number \( l \approx n \). For that reason, during calculations we will omit contributions coming from operators containing short-range interactions, namely those of the nuclear size. We will neglect also (electronic) vacuum polarization, which, however, can be included separately, and its significance depends on \( n, l \), and constituent masses.

As a consequence, the energy of a two-body system with masses \( m_1, m_2 \), charges \( e_1, e_2 \), spins \( s_1, s_2 \), and g-factors \( g_1, g_2 \) can be expressed as a series in powers of the fine structure constant \( \alpha \),

\[
E(\alpha) = E^{(0)} + E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + o(\alpha^7),
\]

where each individual term \( E^{(j)} \) is of the order \( \alpha^j \). In particular,

\[
E^{(0)} = m_1 + m_2,
\]
and $E^{(2)}$ is the eigenvalue of the nonrelativistic two-body Hamiltonian $H_0 = H^{(2)}$ in the center of mass frame,

$$H_0 = \frac{p^2}{2\mu} + \frac{e_1 e_2}{4\pi} \frac{1}{r}. \tag{3}$$

When we set $e_1 = -e, e_2 = Z e$, it is equal to

$$E^{(2)} = E_0 = -\frac{(Z \alpha)^2 \mu}{2 n^2}, \tag{4}$$

with $\mu = m_1 m_2 / (m_1 + m_2)$ being the reduced mass.

### III. LEADING RELATIVISTIC CORRECTION $E^{(4)}$

$E^{(4)}$ is the leading relativistic correction, namely the expectation value of the Breit Hamiltonian $H^{(4)}$ with the nonrelativistic wave function,

$$H^{(4)} = -\frac{\tilde{p}^4}{8 m_1^2} - \frac{\tilde{p}^4}{8 m_2^2} + \frac{e_1 e_2}{4 \pi} \left\{ \frac{1}{2 m_1 m_2} \tilde{p}^2 \left( \frac{\delta^{ij}}{r} + \frac{r_i r_j}{r^3} \right) \tilde{p}^2 + \frac{g_1 g_2}{4 m_1 m_2} \left[ \tilde{s}_1^i \tilde{s}_2^j \left( \delta^{ij} - \frac{r_i r_j}{r^3} \right) - \frac{8 \pi}{3} \tilde{s}_1 \tilde{s}_2 \delta^{(3)}(\vec{r}) \right] \right\} - \frac{e_1 e_2}{6} \left( \langle \tilde{r}_E^2 \rangle \tilde{I}_1 + \langle \tilde{r}_E^2 \rangle \tilde{I}_2 \right) \delta^{(3)}(\vec{r}), \tag{5}$$

where $\vec{r} = \vec{r}_{12}, \vec{p} = \vec{p}_1 = -\vec{p}_2$, and we neglect the quadrupole moment of any of particles. The $g$-factor is related to the magnetic moment anomaly by $g = 2(1 + \kappa)$. For the proton it amounts to $g_p = 5.5856946893(16)$, and for the antiproton it is the same. For the case of a spin 1/2 point-like particle the charge radius is

$$\langle \tilde{r}_E^2 \rangle = \frac{3}{4 m^2}. \tag{6}$$

For a spinless particle it is $\langle \tilde{r}_E^2 \rangle = g = 0$. Let us note that Hamiltonian (5) does not account for any potential annihilation effects, which would be present, for example, in positronium. It also does not account for strong interaction effects, which are present for hadronic particles.

From the Hamiltonian in Eq. (5) one obtains $E^{(4)}$ by taking the expectation value with the nonrelativistic eigenfunction of $H_0$. The result for a state with the principal quantum number $n$ and the angular momentum $l$ is

$$E^{(4)} = \mu^3 (Z \alpha)^4 \left\{ \frac{1}{8 n^4} \left( \frac{3}{\mu^2} - \frac{1}{m_1 m_2} \right) - \frac{1}{\mu^2 (2l + 1) n^3} + \frac{2 \delta_{l0}}{3 n^3} \left( \langle \tilde{r}_E^2 \rangle \tilde{I}_1 + \langle \tilde{r}_E^2 \rangle \tilde{I}_2 \right) + \frac{\delta_{l0}}{m_1 m_2 n^3} \right\} + \frac{2 \delta_{l0}}{3 m_1 m_2 n^3} \left( \tilde{L} \cdot \tilde{s}_1 \left( \frac{1 + 2 \kappa_1}{2m_1^2} + \frac{1 + \kappa_1}{m_1 m_2} \right) + \tilde{L} \cdot \tilde{s}_2 \left( \frac{1 + 2 \kappa_2}{2m_2^2} + \frac{1 + \kappa_2}{m_1 m_2} \right) \right) + \frac{8 \delta_{l0}}{3 m_1 m_2 n^3} (1 + \kappa_1)(1 + \kappa_2) \tilde{s}_1 \cdot \tilde{s}_2 \right\}. \tag{7}$$

In the last equation we have introduced a symmetric traceless tensor $(L^i L^j)^{(2)}$, which is defined as

$$(L^i L^j)^{(2)} = \frac{1}{4} (L^i L^j + L^j L^i) - \frac{\delta^{ij}}{3} \tilde{L}^2. \tag{8}$$

Expression (7) is valid for arbitrary spin of both particles, point-like or hadronic. We will now explore particular cases of the general result in Eq. (7).

**A. Dirac limit of an infinitely heavy and point-like nucleus**

For an infinitely heavy $M = m_2$ and point-like nucleus we set $m = m_1, \tilde{s} = \tilde{s}_1, \kappa = \kappa_1$ to obtain

$$E^{(4,0)} = m (Z \alpha)^4 \left\{ \frac{3}{8 n^4} - \frac{1}{(2l + 1) n^3} + \frac{1 + 2 \kappa}{l(l + 1)(2l + 1) n^3} \tilde{L} \cdot \tilde{s} + \frac{2 \delta_{l0}}{3 n^3} m^2 \langle \tilde{r}_E^2 \rangle \right\}. \tag{9}$$

If the first particle is also point-like, then

$$E^{(4,0)} = m (Z \alpha)^4 \left\{ \frac{3}{8 n^4} - \frac{1}{(2l + 1) n^3} \right\}.$$
Using the total angular momentum $\vec{J} = \vec{L} + \vec{s}$, it can be rewritten in the form

$$E^{(4,0)} = m (Z\alpha)^4 \left\{ \frac{3}{8n^4} - \frac{1}{(2j + 1)n^3} \right\}. \quad (11)$$

This can be compared to the result obtained from the Dirac equation, which is

$$E_D = m f(n,j), \quad (12)$$

$$f(n,j) = \left[ 1 + \frac{(Z\alpha)^2}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - (Z\alpha)^2}} \right]^{-\frac{1}{2}}. \quad (13)$$

Expanding this up to the order $(Z\alpha)^4$ we get

$$E_D = m \left[ 1 - \frac{(Z\alpha)^2}{2n^2} + (Z\alpha)^4 \left\{ \frac{3}{8n^4} - \frac{1}{(2j + 1)n^3} \right\} \right]. \quad (14)$$

The second term is nonrelativistic energy, and the third term is the relativistic correction, in agreement with Eq. (11).

**B. Atom with a spinless, point nucleus and point, spin-1/2 particle**

For the case of a spinless point nucleus of finite mass $M = m_2$ and spin 1/2 point particle of mass $m = m_1$ with $\vec{s} = \vec{s}_1$ we get

$$E^{(4)} = \frac{\mu (Z\alpha)^4}{n^3} \left\{ \frac{1}{8n^3} \left( 3 - \frac{\mu^2}{mM} \right) - \frac{1}{(2l + 1)} \right\}$$

$$+ \left( \frac{\mu^2}{m^2} + \frac{2\mu^2}{mM} \right) \left\{ \frac{\delta_{l0}}{2} + \frac{1}{l(l + 1)(2l + 1)} \vec{L} \cdot \vec{s} \right\}. \quad (15)$$

If the spinless nucleus is much heavier than the point spin-1/2 particle, then the leading recoil correction from Eq. (15) equals

$$E^{(4,1)} = \frac{m^2}{M} (Z\alpha)^4 \left\{ - \frac{1}{2n^4} + \frac{1}{(2j + 1)n^3} \right\}. \quad (16)$$

This is in agreement with the known recoil correction to the Dirac energy $[2]$,

$$E_{\text{rec}}(n,j) = \frac{m}{2M} (1 - f(n,j)^2) \quad (17)$$

Expanding this to the fourth order in $Z\alpha$ we obtain a result in agreement with Eq. (10).

**C. Two point spin-1/2 particles with equal mass**

For two point particles with equal mass $m_1 = m_2 = m$ and spin 1/2 we can define the total spin $\vec{S} = \vec{s}_1 + \vec{s}_2$ and get

$$E^{(4)} = \frac{m \alpha^4}{8n^3} \left\{ \frac{11}{8n} - \frac{4}{(2l + 1)} + \frac{4}{3} \delta_{l0} \vec{S}^2 \right\}$$

$$+ \frac{3}{l(l + 1)(2l + 1)} \left\{ \vec{L} \cdot \vec{S} - 2S^i S^j (L^i L^j)^{(2)} \right\} \quad (18)$$

where

$$\vec{L} \cdot \vec{S} = \frac{1}{2} [j(j + 1) - l(l + 1) - s(s + 1)], \quad (19)$$

$S^i S^j (L^i L^j)^{(2)} = (\vec{L} \cdot \vec{S})^2 + \frac{1}{2} \vec{L} \cdot \vec{S} - \frac{1}{3} l(l + 1) s(s + 1). \quad (20)$

This relativistic energy does not account for annihilation terms.

**D. Both particles spinless and point-like**

Finally, the case of both particles being spinless and point-like is

$$E^{(4)} = \frac{\mu(Z\alpha)^4}{n^3} \left\{ \frac{1}{8n} \left( 3 - \frac{\mu^2}{m_1 m_2} \right) - \frac{1}{(2l + 1)} + \delta_{l0} \frac{\mu^2}{m_1 m_2} \right\}. \quad (21)$$

In the infinite nuclear mass $M = m_2$ limit

$$E^{(4,0)} = m(Z\alpha)^4 \left\{ \frac{3}{8n^4} - \frac{1}{(2l + 1)n^3} \right\}. \quad (22)$$

It has the same form as result (11) from the Dirac equation with $j$ replaced by $l$, while the leading recoil correction is

$$E^{(4,1)} = \frac{m^2}{M} (Z\alpha)^4 \left\{ - \frac{1}{2n^4} + \frac{1}{(2l + 1)n^3} \right\}, \quad (23)$$

which is different from the case of the Dirac particle in Eq. (10).

**IV. LEADING QED CORRECTION $E^{(5)}$**

QED effects for $l > 0$ are partially accounted for in the $g$-factor, which is present in the Breit-Pauli Hamiltonian $H^{(4)}$. Additional QED corrections are represented as $E^{(5)}$, and for $l > 0$ they have the form

$$E^{(5)} = - \frac{14 (Z\alpha)^2}{3m_1 m_2} \left\{ \frac{1}{4 \pi} \frac{1}{r^7} - \frac{2\alpha}{3 \pi} \left( \frac{1}{m_1} + \frac{Z}{m_2} \right)^2 \right\} \quad (24)$$
\[
\times \left\langle \vec{p} (H_0 - E_0) \ln \left[ \frac{2(H_0 - E_0)}{\mu(Z\alpha)^2} \right] \vec{p} \right\rangle \quad (24)
\]

The second term is related to the so-called Bethe logarithm \(\ln[k_0(n,l)]\) by

\[
\ln[k_0(n,l)] = \frac{n^3}{2\mu^3(Z\alpha)^4}
\]

\[
\times \left\langle \phi \left( \vec{p} (H_0 - E_0) \ln \left[ \frac{2(H_0 - E_0)}{\mu(Z\alpha)^2} \right] \vec{p} \right) \phi \right\rangle \quad (25)
\]

and has been tabulated for many hydrogenic states. Let us also write \(E^{(5)}\) as a function of quantum numbers \(n\) and \(l\). Making use of definition (26) and Eq. (23) we obtain

\[
E^{(5)} = -\frac{7}{3\pi} \frac{(Z\alpha)^5 \mu^3}{m_1 m_2} \frac{1}{l(l+1)(2l+1)n^3}
\]

\[
-\frac{4}{3\pi} \left( \frac{1}{m_1} + \frac{Z}{m_2} \right) \frac{\alpha(Z\alpha)^4 \mu^3}{n^3} \ln k_0(n,l) \quad (26)
\]

in agreement with Eq. (19) from Ref. [7].

V. HIGHER-ORDER QED CORRECTION \(E^{(6)}\)

The total contribution of the order \(m\alpha^6\) to energy can be split into two parts: i) the expectation value of the first-order operators with nonrelativistic wave function, and ii) the second-order contribution induced by the Breit Hamiltonian \(H^{(4)}\),

\[
E^{(6)} = \langle H^{(6)} \rangle + \langle H^{(4)} \rangle (E_0 - H_0) (H^{(4)})^{-1}. \quad (27)
\]

Here the prime in \((E_0 - H_0)^\prime\) means that we exclude the reference state from the resolvent. The effective operator \(H^{(6)}\) can be derived within the framework of NRQED. In general, both the first-order and the second-order contributions separately contain singular operators that cancel each other when combined together. However, because we are interested in states with \(l > 1\) then all singularities vanish. Omitting contact interactions, the NRQED Hamiltonian for a spin \(s = 0, 1/2\) and finite size particle, from Ref. [8] is

\[
H_{\text{NRQED}} = e A_0 + \frac{1}{2m} \left[ \vec{r} \cdot B - 2(1 + \kappa) \vec{s} \cdot \vec{B} \right]
\]

\[
-\frac{1}{8m^3} [\vec{s}^2 - 2e (p^2, \vec{s} \cdot \vec{B}) - 2e\kappa (\vec{s} \cdot \vec{B}, \vec{r} \cdot \vec{s})] + \frac{p^6}{16m^5} - \frac{1 + 2\kappa}{4m^2} e \vec{s} \cdot (\vec{E} \times \vec{r} - \vec{E} \times \vec{s})
\]

\[
\delta H_0 = \frac{p^6}{16m^4} + \frac{p^6}{16m^2}, \quad (30)
\]

\[
\delta H_1 = \sum_a \frac{3Z\alpha}{16m_a^4} \left( 1 + \frac{4\kappa_a}{3} \right) \vec{L} \cdot \vec{s}_a \{p^2, \frac{1}{r^3}\}
\]

\[
+ \frac{1}{32m_a^4} \left( 1 + \frac{s_a(s_a + 1)}{3} \right) [p^2, \{p^2, \vec{r} \cdot \vec{V}\}], \quad (31)
\]

\[
\delta H_2 = \frac{Z\alpha}{4m_a^2} \frac{(1 + 2\kappa_1)(1 + 2\kappa_2)}{m_2^2} \left( \vec{s}_2 \times \vec{p} \right) \left( \frac{\delta^{ij}}{r^3} - \frac{\vec{r} \cdot \vec{r}^j}{r^5} \right) (\vec{s}_1 \times \vec{p})^j, \quad (32)
\]

\[
\delta H_3 = \sum_a \frac{1}{4m_a^3} \left( \{p^2, \vec{p}_a \cdot e_a \vec{A}_a\} + \{p^2, \vec{s}_a \cdot \vec{V}_a \times e_a \vec{A}_a\} \right), \quad (33)
\]

\[
\delta H_4 = \sum_a e^2 \vec{s}_a \times \vec{A}_a, \quad (34)
\]

\[
\delta H_5 = \sum_a e^2 \left( 1 + \frac{2\kappa_a}{m_a^3} \right) \vec{s}_a \cdot \vec{E}_a \times \vec{A}_a, \quad (35)
\]

\[
\delta H_6 = \delta H_6^A + \delta H_6^B + \delta H_6^C, \quad (36)
\]

where
\[
\delta H_7 = \sum_a e_a^2 \frac{(1 + 2\kappa_a)}{2m_a^2} \vec{s}_a \cdot \vec{E}_a \times \vec{A}_a 
+ \frac{ie_a(1 + 2\kappa_a)}{8m_a^2} \left[ \vec{A}_a \cdot (\vec{p}_a \times \vec{s}_a) + (\vec{p}_a \times \vec{s}_a) \cdot \vec{A}_a, \vec{p}_a \right]
\]

\[
\delta H_8 = -\frac{1}{2} \sum_a \left( \alpha E_a - \frac{s_a(s_a + 1)}{3m_a^3} \right) \vec{Z}^2\alpha^2 \vec{r}^4,
\]

\[
\delta H_9 = \sum_a e_a \kappa_a \frac{1}{4m_a^3} \left[ \vec{p}_a \cdot \vec{\nabla}_a + \vec{A}_a, \vec{p}_a \right].
\]

The static fields \(A_i\) and \(E_i\) are defined as

\[
e_1A_1 = -\frac{Z\alpha}{2r} \left( \delta^i + \frac{r^i}{r^2} \right) \frac{p_i^2}{m_2} - \frac{Z\alpha (\vec{s}_2 \times \vec{r})^i}{r^3} (1 + \kappa_2),
\]

\[
e_2A_2 = -\frac{Z\alpha}{2r} \left( \delta^i + \frac{r^i}{r^2} \right) \frac{p_i^2}{m_1} + \frac{Z\alpha (\vec{s}_1 \times \vec{r})^i}{r^3} (1 + \kappa_1),
\]

\[
e_1E_1 = -Z\alpha \frac{\vec{r}}{r^2}, \quad e_2E_2 = Z\alpha \frac{\vec{r}}{r^2}.
\]

In the case when one of the particles is spinless and the other one has spin 1/2, the effective operators (30-42) are modified by setting \(s_1 = s_2 = 1\), \(s_1 = s_2 = 0\), and the same for static fields \(e_a\vec{A}_a\).

The evaluation of the expectation value of \(H^{(6)}\) with nonrelativistic wave function and the second-order contribution with the Breit Hamiltonian for individual cases of particles is then presented in Appendices B, C, and D. The results for energies are presented in the following subsections.

### A. Two particles with spins \(s_1 = s_2 = 0\)

We will begin with the case when both the positively charged nucleus and negatively charged particle are spinless. The final result for the energy \(E^{(6)}\) is the sum of the first-order and second-order contributions evaluated in Appendix B

\[
f^{(6)}(n, j) = -5 \frac{1}{16n^6} + \frac{2}{2(2j + 1)n^5} - \frac{3}{2(2j + 1)^2n^4} - \frac{1}{(2j + 1)^3n^3}
\]

we obtain the correction of the order \(m^2\alpha^6\)

\[
E^{(6)} = (Z\alpha)^6 \left[ f^{(6)}(n, l) + \frac{\mu^2}{m_1 m_2} \left( \frac{3}{16n^6} - \frac{8l(l + 1) - 3}{2(2l - 1)(2l + 1)(2l + 3)n^5} + \frac{6}{(2l - 1)(2l + 1)(2l + 3)n^5} \right) \right.
\]

\[
- \frac{\mu^4}{16 m_1^2 m_2^2 n^6} + \frac{2\mu^3(\alpha_{E1} + \alpha_{E2})}{(2l - 1)(2l + 1)(2l + 3)} \left( \frac{1}{n^5} - \frac{3}{l(l + 1)n^3} \right) \right].
\]

Similarly to \(E^{(4)}\), we can explore particular limiting cases of the general result in Eq. (47). Firstly we perform the limit where mass \(M = m_2\) of the nucleus is infinitely heavy, to obtain the result in agreement with the Klein-Gordon equation:

\[
E^{(6,0)} = m(Z\alpha)^6 f^{(6)}(n, l).
\]

We may also expand Eq. (17) up to the order \(m^2/M\) to obtain the first-order recoil correction

\[
E^{(6,1)} = (Z\alpha)^6 \frac{m^2}{M} f^{(6,1)}(n, l),
\]

where we introduce the function

\[
f^{(6,1)}(n, l) = \frac{1}{2n^6} + \frac{6 - 10l(l + 1)}{(2l - 1)(2l + 1)(2l + 3)n^5}.
\]
With the help of substitutions

\[ E_{s_1 = s_2 = 0} = \frac{\mu (Z \alpha) l^6}{l(l+1)(2l-1)(2l+1)(2l+3)} \left[ A + B \vec{L} \cdot \vec{s}_2 \right]. \tag{51} \]

With the help of substitutions

\[ \lambda_0 = \frac{(2l+1)(2l+3)}{2l+1} = 2l + 1 - \frac{4}{2l+1}, \tag{52} \]

\[ \lambda_1 = \frac{3}{2l(l+1)} + \frac{4}{(2l+1)^2}, \tag{53} \]

\[ \lambda_2 = -\frac{3}{4l^2} + \frac{13}{4l(l+1)} - \frac{3}{4(l+1)^2} + \frac{8}{(2l+1)^2}. \tag{54} \]

and the definition

\[ X = \frac{X_5}{n^6} + \frac{X_4}{n^4} + \frac{X_3}{n^2}. \tag{55} \]

For \( s_1 = 0, s_2 = 1/2 \)

For the case when one of the particles is spinless while the other one has spin 1/2, the derivation of the first-order and second-order contributions is presented in Appendix. In the resulting expression for energy \( E^{(6)} \) we can separate the part which is already contained in the final result for two spinless particles, Eq. (47). If we denote the spinless energy (47) as

\[ E^{(6)} = \frac{\mu (Z \alpha) l^6}{l(l+1)(2l-1)(2l+1)(2l+3)} \left[ A + B \vec{L} \cdot \vec{s}_2 \right]. \tag{51} \]

With the help of substitutions

\[ \lambda_0 = \frac{(2l+1)(2l+3)}{2l+1} = 2l + 1 - \frac{4}{2l+1}, \tag{52} \]

\[ \lambda_1 = \frac{3}{2l(l+1)} + \frac{4}{(2l+1)^2}, \tag{53} \]

\[ \lambda_2 = -\frac{3}{4l^2} + \frac{13}{4l(l+1)} - \frac{3}{4(l+1)^2} + \frac{8}{(2l+1)^2}. \tag{54} \]

and the definition

\[ X = \frac{X_5}{n^6} + \frac{X_4}{n^4} + \frac{X_3}{n^2}. \tag{55} \]

for \( X = A, B \) the coefficients \( A \) and \( B \) in Eq. (51) can be written as

\[ A_5 = \frac{l(l+1)}{2} \left[ g_2^2 \frac{\mu^2}{2m_2^2} + (\lambda_1 - 9) \frac{\mu^4}{4m_2^4} \right], \tag{56} \]

\[ A_4 = 3\lambda_0 \left[ -g_2^2 \frac{\mu^2}{2m_2^2} + g_2 \frac{\mu^3}{m_2^3} - \frac{\mu^4}{2m_2^4} \right], \tag{56} \]

\[ A_3 = g_2^2 \left( \lambda_1 - 9 \right) \frac{\mu^2}{2m_2^2} + \left( 3(2 + 5g_2 - g_2^2) - 2g_2 \lambda_1 \right) \frac{\mu^3}{4m_2^4} + (\lambda_1 - 9) \frac{\mu^4}{4m_2^4}. \tag{56} \]

In order to verify the correctness of our results we will compare them with known results for limiting cases. We restrict now to point-like particles by setting \( \alpha \text{recoil} = 0 \). Firstly, we perform the limit of \( m_1 \to \infty \) in Eq. (51), i.e., the limit of an infinitely heavy spinless particle. Defining

\[ k = (l - j)(2j + 1) \tag{58} \]

then Eq. (51) leads to the nonrecoil result

\[ \lim_{m_1 \to \infty} E^{(6)} = m_2 (Z \alpha) l^6 \left[ f^{(6)}(n,j) \right. \]

\[ + \kappa_2 \left( \frac{-9 + 19k + 16k^2}{2k(2k-1)(2k+1)(2k+3) n^6} - \frac{2k^2 + 2k + 1}{2k^2 + 2k + 1} \right) \]

\[ + \kappa_2^2 \left( \frac{-9 + 19k + 16k^2}{2k(2k-1)(2k+1)(2k+3) n^6} - \frac{2k^2 + 2k + 1}{2k^2 + 2k + 1} \right) \]. \tag{59} \]

For \( \kappa_2 = 0 \) and both \( k = j \pm 1/2 \) the expression (55) coincides with the Dirac result acquired by expanding the expression on the right-hand side of Eq. (51) up to the order \( (Z \alpha) l^6 \). The leading recoil correction of the order \( m_2^2/m_1 \) can be compared with the result from the literature. Defining the function

\[ j^{(6,1)}_{1/2}(n,k) = \frac{1}{2n^6} - \frac{3 - 2k + 14k^2 + 10k^3}{k(2k-1)(2k+1)(2k+3)n^6} + \frac{3}{8k^2 n^4} + \frac{3 - 2k + 12k^2 + 56k^3}{8k^2(2k-1)(2k+1)(2k+3)n^6}. \tag{60} \]
then by expanding Eq. \((51)\) for large \(m_1\) up to the order \(m_2^2/m_1\), we get the leading recoil correction
\[
E^{(6,1)} = (Z\alpha)^6 \frac{m_2^2}{m_1} f_0^{(6,1)}(n, k) \\
+ \kappa_2 \left( -\frac{12 + 27k + 2k^2}{|k|(2k-1)(2k+1)(2k+3)n^5} + \frac{3}{k^2(2k+1)n^4} + \frac{-3 - 5k + 9k^2 + 96k^3 + 36k^4}{|k|^2(k+1)(2k-1)(2k+1)(2k+3)^2n^3} \right) \\
+ \kappa_2 \left( -\frac{9 + 11k}{2|k|(2k-1)(2k+1)(2k+3)n^5} + \frac{9}{2k^2(2k+1)n^4} + \frac{3(3 - 5k + 5k^2 + 128k^3 + 68k^4)}{2|k|^2(k+1)(2k-1)(2k+1)^2(2k+3)^3n^3} \right) .
\]

This is in agreement with the known result from \([10]\) for \(l = 1\) and \(\kappa_2 = 0\). For the more general case of \(l > 0\) the energy correction can be obtained by means of combining the expansion of Eq. \((7)\) up to the order \((Z\alpha)^6\) with Eq. \((75)\) from Ref. \([11]\). The resulting sum can be written as follows
\[
E^{(6,1)}(n, j, l) = \frac{m_2^2}{m_1} (Z\alpha)^6 \left[ \frac{1}{2n^6} - \frac{2}{(2j+1)n^5} + \frac{3}{2(2j+1)^2n^4} + \frac{1}{(2j+1)^3n^3} \right] + \frac{m_2^2}{m_1} \frac{(Z\alpha)^2}{2\rho^4} \left\langle \vec{L}^2 + \frac{1}{r^4} \right\rangle,
\]
where \(\langle 1/r^4 \rangle\) is given in Eq. \((64)\). Comparing equation \((61)\) for \(\kappa_2 = 0\) with \((62)\) for \(l = j \pm 1/2\) confirms that they agree.

The next term in the mass ratio expansion, of the order \(m_2^3/m_1^2\) for \(\kappa_2 = 0\), is
\[
E^{(6,2)} = (Z\alpha)^6 \frac{m_2^3}{m_1^2} \left[ -\frac{15}{16n^6} - \frac{9 - 22k + 84k^2 + 72k^3}{4|k|(2k-1)(2k+1)(2k+3)n^5} - \frac{3(2k-1)}{8k^2(2k+1)n^4} \right. \\
- \frac{3 - k - 20k^2 + 184k^3 + 480k^4 + 304k^5}{8|k|^2(k+1)(2k-1)(2k+1)(2k+3)^3n^3} \left. \right],
\]
which can be considered as a new result.

Secondly, we can verify that in the limiting case of Eq. \((51)\), when the spin-1 particle becomes infinitely heavy, we obtain the result in agreement with that obtained from the Klein-Gordon equation, i.e.,
\[
\lim_{m_2 \to \infty} E^{(6)} = m_1 (Z\alpha)^6 f^{(6)}(n, l) .
\]
Similarly as in the leading relativistic correction \(E^{(4)}\) this coincides with the Dirac result in Eq. \((59)\) by replacing \(j\) by \(l\) and setting \(\kappa_2 = 0\). Lastly, we also present the next term in the expansion of Eq. \((51)\) in terms of the \(m_1^2/m_2^2\) ratio. Namely,
\[
E^{(6,1)} = (Z\alpha)^6 \frac{m_2^2}{m_1^2} f_0^{(6,1)}(n, l) + g_2 \vec{L} \cdot \vec{s}_2 \left( -\frac{2}{l(l+1)(2l+1)n^5} + \frac{3}{l(l+1)(2l+1)^2n^4} + \frac{1 + 6l(l+1)}{l^2(l+1)^2(2l+1)^3n^3} \right) .
\]

where \(f_0^{(6,1)}(n, l)\) is defined in Eq. \((50)\).

C. Two particles with spins \(s_1 = s_2 = 1/2\)

Finally, we present the result for the energy \(E^{(6)}\) for the case of two spin-1/2 particles. The corresponding derivation of the first-order and second-order contributions is presented in Appendix \([2]\) We express the result using a set of basic spin-dependent operators. To do that we use the identities presented in Appendix \([C]\). Moreover, to keep the formulas compact, we introduce the following symbols
\[
\lambda_3 = -\frac{3}{(2l-1)(2l+3)} + \frac{1}{2(2l+1)^2} ,
\]
\[
\lambda_4 = -\frac{3}{4l(l+1)} - \frac{3}{(2l-1)(2l+3)} - \frac{3}{2(2l+1)^2} ,
\]
\[
\lambda_5 = \frac{3}{2l^2} - \frac{1}{2l(l+1)} + \frac{3}{2(l+1)^2} ,
\]
\[
\lambda_6 = \frac{3}{4l^2} - \frac{9}{4l(l+1)} + \frac{3}{4(l+1)^2} + \frac{4}{(2l-1)(2l+3)} - \frac{6}{(2l+1)^2} ,
\]
\[
\lambda_7 = -\frac{3}{4l(l+1)} + \frac{2}{3(2l+1)^2} ,
\]
\[
\lambda_8 = -\frac{3}{l^2} + \frac{7}{l(l+1)} - \frac{2}{(l+1)^2} - \frac{72}{(2l-1)(2l+3)} .
\]
The coefficient for $B$ where the symbol $(1 \leftrightarrow E) = B = 3$ in addition to $\lambda_0$, $\lambda_1$, and $\lambda_2$ defined in the previous section. The final result for $E^{(6)}$ of two spin-1/2 particles is then

$$E^{(6)} = E^{(6)}_{s_1=s_2=0} + \frac{\mu(Z\alpha)^6}{l(l+1)(2l-1)(2l+1)(2l+3)} \left[ A + B \bar{L} \cdot \bar{s}_1 + C \bar{L} \cdot \bar{s}_2 + D \bar{s}_1 \cdot \bar{s}_2 + F (L^i L^j) s_i^1 s_2^j \right],$$

where we have again subtracted the spinless result $E^{(6)}_{s_1=s_2=0}$ given by Eq. (77). Using once more the definition (85) for $X = A, B, C, D, F$ we get the following coefficients

$$A_5 = \frac{l(l+1)(g_1-2)}{4} \left( \frac{g_1 + \frac{2 \mu^2}{m_1^2} + (g_1-1) \frac{\mu^3}{m_1^2}}{2} \right) + \frac{\mu^4}{m_1^2 m_2^2} \frac{l(l+1)}{2} + (1 \leftrightarrow 2),$$

$$A_4 = -3 \frac{\lambda_0}{16} - 3 \frac{\lambda_0}{4} (g_1-2) \left( \frac{g_1 + \frac{2 \mu^2}{m_1^2} - \frac{\mu^3}{m_1^2}}{2} \right) - \frac{\mu^4}{m_1^2 m_2^2} \frac{3}{8(2l+1)} \left( 4l(l+1) + \frac{3 g_1^2 g_2^2}{16} - 3 \right) + (1 \leftrightarrow 2),$$

$$A_3 = \frac{\lambda_3 - 3}{8} + \frac{(g_1-2)}{4} \left( \frac{g_1 + \frac{2 \mu^2}{m_1^2} - \frac{\mu^3}{m_1^2}}{2} \left( -9 + 2 \lambda_1 \right) \frac{\mu^2}{m_1^2} - (-9 + 3 g_1 + 2 \lambda_1) \frac{\mu^3}{m_1^2} \right)$$

$$+ \frac{1}{m_1^2 m_2^2} \left( - \frac{9}{2} + \lambda_3 + \frac{g_1^2 g_2^2}{16} - \lambda_4 \right) + (1 \leftrightarrow 2),$$

where the symbol $(1 \leftrightarrow 2)$ stands for the exchange of masses $m_1 \leftrightarrow m_2$ and g-factors $g_1 \leftrightarrow g_2$ of both particles. For the spin-orbit contribution coefficient $B$ we get the following result,

$$B_5 = \frac{\mu^2}{8 m_1^2} \left[ 24(g_1-1) - 6 g_1^2 - 3 g_1 g_2 (1-g_2) + 16 l(l+1)(2-g_1) \right] + \frac{\mu^2}{8 m_1^2} g_1 \left( 48 + 3 g_2 (1-g_2) - 64 l(l+1) \right)$$

$$- \frac{3 \mu^3}{8 m_1^2} \left( 12(1-g_1) - g_1 g_2 (1-g_2) - 16 l(l+1)(1-g_1) \right) + \frac{\mu^4}{m_1^2 m_2^2} \left( - \frac{9}{2} - \frac{3}{2} g_1^2 + \frac{3}{32} g_1^2 g_2^2 + 6 l(l+1) \right),$$

$$B_4 = \frac{3}{8(2l+1)} \left[ \frac{\mu^2}{m_1^2} \left( 2(g_1^2 - 1) + g_1 g_2 (1-g_2) + 8 l(l+1)(1-g_1) \right) + \frac{\mu^2}{m_1^2} g_1 \left( g_2 (g_2 - 1) + 8 l(l+1) \right) \right.$$

$$+ \frac{\mu^3}{m_1^2} \left( 4(1-g_1) - g_1 g_2 (1-g_2) \right) + \frac{\mu^4}{m_1^2 m_2^2} \left( 9 g_1^2 g_2^2 + g_1 g_2 + 2 \right) \frac{32 l(l+1) - 24}{8(2l+1)} \right],$$

$$B_3 = \frac{\mu^2}{2 m_1^2} \left( -6 + (2 g_1 (g_1-1) + g_1 g_2 (1-g_2)) \lambda_2 + (1-g_1) \lambda_5 \right) + \frac{\mu^3}{2 m_1^2 m_2^2} \left( 12 - 2 + g_2 (1-g_2) \right) \lambda_2 - \lambda_3$$

$$+ \frac{\mu^3}{2 m_1^2} \left( 12 g_1 (1-g_1) + (4(1-g_1) - g_1 g_2 (1-g_2)) \lambda_2 \right) + \frac{\mu^4}{2 m_1^2 m_2^2} \left( -6 + (2 + g_2) \lambda_2 + \frac{3}{8} g_1^2 g_2^2 \lambda_6 \right).$$

The coefficient $C$ is obtained from $B$ simply by the exchange $(1 \leftrightarrow 2)$. The spin-spin coefficient $D$ reads

$$D_5 = \frac{\mu^2}{m_1 m_2} \frac{l(l+1) g_1 g_2}{6} + \frac{\mu^4}{m_1^2 m_2^2} \frac{4 l(l+1)}{3},$$

$$D_4 = - \frac{\mu^3}{2 m_1^2 m_2 (g_1-2) \lambda_0} - \frac{\mu^2}{2 m_1 m_2} \frac{3}{32(2l+1)} \left( 3 g_1^2 g_2^2 - 16 \right) + \frac{\mu^4}{m_1^2 m_2^2} \frac{3 (g_1^2 g_2^2 - 16) + 64 l(l+1)}{32(2l+1)} + (1 \leftrightarrow 2),$$

$$D_3 = \frac{\mu^3}{2 m_1^2 m_2} \left( 2(g_1-2)(\lambda_1 - 3) \right) + \frac{\mu^4}{12 m_1 m_2} \left( 24 g_1 (1-g_1) - 15 g_1 g_2 + 4(2 - g_1) + g_1 g_2 \right) \lambda_1$$

$$+ \frac{\mu^4}{2 m_1^2 m_2^2} \left( \frac{1}{12} (g_1^2 g_2^2 - 16) \lambda_4 + 6 + \lambda_7 \right) + (1 \leftrightarrow 2).$$
Finally, the coefficient $F$ of the tensor spin-spin interaction is the most complicated and equals

\[ F_5 = \frac{1}{(2l-1)(2l+3)} \left[ \frac{\mu^3}{m_1 m_2} \frac{9}{4} (g_1 - 2)(4 - 6g_2 + 3g_1g_2 + 16l(l + 1)) \right. \\
+ \frac{\mu^2}{2m_1 m_2} \left( 18(l - g_1) - \frac{45}{4} g_1g_2 + l(l + 1)(47g_1g_2 + 72(1 - g_1)) \right) \\
+ \frac{\mu^4}{m_1^2 m_2^2} \left( \lambda_0(5 - 3g_1g_2)(2l + 1) + 6 + \frac{9}{2} g_1g_2 - \frac{9}{8} g_1^2 g_2^2 \right) \left(1 \leftrightarrow 2\right), \]

\[ F_4 = -\frac{\mu^3}{m_1^2 m_2^2} \frac{3(g_1 - 2)}{4l(l + 1)(2l + 1)} (24 - 18g_2 + 9g_1g_2 + 16l(l + 1)) \]

\[ + \frac{3\mu^4}{2m_1^2 m_2} \left( \frac{48 - 72g_1g_2 + 15g_1^2 g_2^2 + l(l + 1)(12g_1^2 g_2^2 - 64) - 3g_1^2 g_2^2}{16(l + 1)(2l + 1)} \right) \left(1 \leftrightarrow 2\right), \]

\[ F_3 = \frac{\mu^3}{4m_1^2 m_2} (g_1 - 2)(8\lambda_8 + 9(g_1 - 2)g_2\lambda_9) + \frac{\mu^2}{8m_1 m_2} \frac{300g_1g_2}{\lambda_0(2l + 1)} - \frac{g_1(7g_2 - 4)\lambda_{10} - 8(g_1 - 2)\lambda_8 + 36(g_1 - 1)g_2\lambda_9}{\lambda_0(2l + 1)} \]

\[ + \frac{\mu^4}{2m_1^2 m_2^2} \left( -\lambda_{10} - \frac{12}{\lambda_0(2l + 1)} + \frac{9}{2} g_1g_2 \left( \lambda_9 + \frac{4}{\lambda_0(2l + 1)} \right) \right) \left(1 \leftrightarrow 2\right). \]

The above coefficients can be verified against the positronium limit of (75) by setting $m_1 = m_2$, $Z = 1$, $\kappa_1 = \kappa_2 = 0$ and both particles being point-like. The obtained result is in agreement with the former one from Ref. 12. It is worth mentioning that although we derived the result for the case of $l > 1$ the final formula gives a correct result also for $l = 1$. Moreover, we would like to point out that in Ref. 13 during the evaluation of Eq. (125) for $\delta E_5$ an error was made for the case of $l > 1$. Namely, in the final result for $\delta E^{(6)}(n, j, l, s)$ instead of the value $l$, the number 1 was inserted in the part coming from $\delta E_5$ affecting results in Eqs. (205), (209), (213), and (217). After correcting this error, the results of Ref. 13 are in accordance with those of Ref. 14 as well as with this work.

Exploring now the limiting case of Eq. (75) for two point-like particles when the particle of mass $m_1$ is infinitely heavy, we set $\kappa_2 = 0$ and obtain the Dirac result

\[ E^{(6,0)} = m_2 (Z\alpha)^6 f^{(6)}(n, j), \]

where we used the total angular momentum $\vec{J} = \vec{L} + \vec{s}_2$. The first-order recoil correction given by expanding Eq. (75) for large $m_1$ up to the order $m_2^2/m_1$, using Eq. (60), reads

\[ E^{(6,1)} = (Z\alpha)^6 \frac{m_2^2}{m_1} \left[ f^{(6,1)}_{1/2}(n, k) \right. \\
+ \frac{g_1}{2} \left( \frac{2}{3(2l - 1)(2l + 1)(2l + 3)n^5} - \frac{2}{l(l + 1)(2l + 1)^2 n^4} \right) \\
+ \frac{\lambda_1}{2} \left( \frac{-21 + 32l + 32l^2}{2(l + 1)(2l - 1)(2l + 1)(2l + 3)n^5} + \frac{3}{2l^2(l + 1)^2 n^4} \right) + \frac{-3 - 5l + 19l^2 + 48l^3 + 24l^4}{2l^3(l + 1)^3(2l - 1)(2l + 1)(2l + 3)n^3} \right) \\
+ \left( \frac{L \cdot L}{2} \right)^2 \frac{1}{2l^3}(l + 1)^3(2l + 1)^2(2l + 3)^2 n^5 - \frac{9}{l^3(l + 1)^3(2l - 1)^2(2l + 1)^2(2l + 3)^2 n^4} \right) \]

\[ \left. - \frac{63 + 116l + 116l^2}{l^3(l + 1)^3(2l - 1)^2(2l + 1)^3(2l + 3)^2 n^4} \right) \right] \]

and can be considered as a new result.

\[ \left. - \frac{63 + 116l + 116l^2}{l^3(l + 1)^3(2l - 1)^2(2l + 1)^3(2l + 3)^2 n^4} \right) \right] \]

The expansion of energy levels up to $\alpha^6 \mu$ has been
obtained in an analytic form and verified against special cases where one of the particles is much heavier. The first two expansion terms in the mass ratio have a universal character. The leading term coincides with the solution of the Klein-Gordon or Dirac equation, while the term proportional to the mass ratio does not depend on the spin of the heavier particle. The next expansion terms are not universal and depend on both particle spins. In addition, the special case of positronium \( m_1 = m_2 \), and \( \kappa_1 = \kappa_2 = 0 \) was used to verify the correctness of our results. Although in our calculations we assumed \( l > 1 \), our results were in agreement also for the case of \( l = 1 \). It is not proof, but it may indicate that the presented results are valid in the more general case of \( l > 0 \) for point particles.

The obtained general formulas are valid for many two-body systems, including muonic and antiprotonic atoms. This demonstrates that precise measurements of energy levels can serve not only for the determination of fundamental constants, but also for the search of unknown interactions in the range not accessible in normal atoms, namely from 1 MeV up to 100 MeV. Although there are no definite plans to study rotational states of, for example, proton or \( \bar{p} \alpha \), the availability of a high-precision result is crucial for planning the corresponding measurements.

One such measurement is considered at NIST [6], which involves rotational states of heavy hydrogen-like ions, with the purpose of an independent determination of the Rydberg constant. The vacuum polarization is completely negligible, and formulas obtained in this paper will be valid also for circular states of heavy ions because the effective expansion parameter for these states is \((Z\alpha/\hbar)^6\). If necessary, inclusion of the \( \alpha^7 \) contribution for an arbitrary mass ratio is feasible along the lines of Ref. [13]. This means that one may explore the potential of high accuracy results for an arbitrary two-body system in search for physics beyond the Standard Model.

ACKNOWLEDGMENTS

This work was supported by the National Science Center (Poland) Grant No. 2017/27/B/ST2/02459. JZ would like to thank Gregory Adkins for spotting the problem with \( \delta E_5 \).

Appendix A: Derivation of the effective operator \( H^{(6)} \)

Using the NRQED Hamiltonian in Eq. (28) we derive individual first-order effective operators of the order \( \alpha^6 \) for the case of two spin-1/2 particles with omitting all the local terms. The derivation proceeds along the same lines as in Ref. [9]. For spinless particles the effective operators are obtained by omitting the corresponding spin terms.

The first effective operator comes from the fourth term in the NRQED Hamiltonian \( H_{\text{NRQED}} \) in Eq. (28) and represents the higher-order relativistic correction to the kinetic energy,

\[
\delta H_0 = \frac{p_1^2}{16m_1^2} + \frac{p_2^2}{16m_2^2}.
\]  

\( \delta H_1 \) comes from the interaction between particles when one vertex is given by the sixth and seventh terms in \( H_{\text{NRQED}} \), and the other one is \( eA_0 \). It leads to

\[
\delta H_1 = \sum_a \frac{3}{16m_a^2} \left( 1 + 4\kappa_a \right) \hat{s}_a \cdot \{ p_a^2, e_a \hat{s}_a \times \vec{p}_a \} + \frac{1}{32m_a^2} \left( 1 + \frac{s_a(s_a+1)}{3} \right) [p_a^2, [p_a^2, V]],
\]

where the potential \( V \) is

\[
V = \frac{e_1e_2}{r} = \frac{Z\alpha}{r}
\]

and the electrostatic fields \( \hat{s}_a \) are defined in Eq. (45).

\( \delta H_2 \) arises when both particles interact via the fifth term in \( H_{\text{NRQED}} \). It leads to the effective operator

\[
\delta H_2 = \frac{e_1e_2}{4m_1^2m_2^2} \left( 1 + 2\kappa_1 \right) \left( 1 + 2\kappa_2 \right) \left( \hat{s}_1 \times \vec{p}_2 \right) \hat{j}^1 \left( \delta^{ij} - 3\rho^i\rho^j \right) \left( \hat{s}_1 \times \vec{p}_1 \right) \hat{j}^2.
\]

\( \delta H_3 \) arises when one of the particles interacts through part of the second term in \( H_{\text{NRQED}} \),

\[-\frac{e}{m} \vec{p} \cdot \vec{A} - \frac{e}{m} (1 + \kappa) \hat{s} \cdot \vec{B},
\]

while the other particle through part of the third term in \( H_{\text{NRQED}} \),

\[-\frac{1}{8m^3} \left( \pi^4 - 2e\hat{s} \cdot \vec{B} \pi^2 - 2e^2\hat{s} \cdot \vec{B} \right).
\]

If we define static vector potentials by Eqs. (43) and (44), then we can write the effective operator \( \delta H_3 \) as

\[
\delta H_3 = \frac{1}{4} \sum_{a=1,2} \frac{1}{m_a^3} \{ p_a^2, e_a \vec{A}_a \cdot \hat{s}_a \cdot \left( \nabla_a \times e_a \hat{\vec{s}}_a \right) \}.
\]

\( \delta H_4 \) comes from the exchange of two transverse photons between particles. One of the particles interacts twice by the term \( \frac{e^2}{\pi^2} \), and the other one by \( \frac{e^2}{2m} \vec{A}^2 \). The resulting effective operator can then be obtained simply by replacing the vector potential \( \vec{A} \) by the static field \( \vec{A} \),

\[
\delta H_4 = \sum_{a=1,2} \frac{e^2}{2m_a} \vec{A}_a^2.
\]
\( \delta H_5 \) corresponds to the case where one of the particles interacts through the fifth term in \( H_{NRQED} \), and the other one through (A5) and \( eA_0 \),

\[
\delta H_5 = \sum_{a=1,2} \frac{e^2}{4m_a^2} (1 + 2\kappa a) \hat{s}_a \cdot (\vec{\xi}_a \times \hat{A}_a - \vec{\xi}_a \times \hat{A}_a). \tag{A9}
\]

\( \delta H_6 \) represents the retardation correction to the single transverse photon exchange between particles when both particles interact through (A5). The corresponding \( \alpha^6 \) contribution is

\[
\langle \delta H_6 \rangle = \sum_{a \neq b} \sum_{\vec{k}} \frac{e_a e_b}{m_a m_b} \int \frac{d^3 k}{(2\pi)^3} \frac{k_i k_j}{k^2} \left\langle \hat{s}_a \cdot \vec{\xi}_a \times \hat{A}_a - \vec{\xi}_a \times \hat{A}_a \right\rangle e^{i \vec{k} \cdot \vec{r}_a}.
\]

(A10)

Commuting out the expression \( (H_0 - E_0)^2 \) and performing the integration we obtain the effective operator \( \delta H_6 \) in Eq. (36).

\( \delta H_7 \) is a retardation correction in a single transverse photon exchange where one vertex is (A3), and the other one comes from the fifth term in \( H_{NRQED} \),

\[
- \frac{e(1 + 2\kappa)}{4m^2} \hat{s} \cdot (\vec{E} \times \vec{p} - \vec{p} \times \vec{E}). \tag{A11}
\]

The resulting effective operator is then

\[
\delta H_7 = \sum_{a=1,2} \frac{e^2}{4m_a^2} (1 + 2\kappa a) \hat{s}_a \cdot (\vec{\xi}_a \times \hat{A}_a - \vec{\xi}_a \times \hat{A}_a) + \frac{i e_a (1 + 2\kappa a)}{8m_a^2} \left[ \hat{A}_a \cdot (\vec{p}_a \times \hat{s}_a) + (\vec{p}_a \times \hat{s}_a) \cdot \hat{A}_a \cdot \vec{p}_a \right]. \tag{A12}
\]

\( \delta H_8 \) comes as a correction to the Coulomb interaction between particles. One particle interacts through the eighth term in \( H_{NRQED} \), and the other one by \( eA_0 \). Then

\[
\delta H_8 = - \frac{1}{2} \sum_a \left( \alpha E_a - \frac{\hat{s}_a (s_a + 1)}{3m_a^2} \right) \frac{Z^2 \alpha^2}{r^4}. \tag{A13}
\]

Finally, the effective operator \( \delta H_9 \) arises when one of the particles interacts through part of the third term in \( H_{NRQED} \),

\[
\frac{e \kappa}{4m^2} \{ \vec{\pi} \cdot \vec{B}, \vec{\pi} \cdot \vec{s} \}, \tag{A14}
\]

and the second particle through (A5), giving rise to the single transverse photon exchange without retardation. The resulting effective operator can be obtained simply by replacing \( \vec{B} \) in the last equation by its static form. Namely, we can write

\[
\delta H_9 = \sum_a \frac{e_a \kappa a}{4m_a^3} \{ \vec{p}_a \cdot \vec{\xi}_a \times \hat{A}_a, \vec{p}_a \cdot \vec{s}_a \}. \tag{A15}
\]

This concludes the derivation of effective operators of the order \( \alpha^6 \) for two spin-1/2 particles for states with \( l > 0 \).

**Appendix B: Expectation values for particles with \( s_1 = s_2 = 0 \)**

To simplify the expectation values we set \( Z\alpha = 1 \). The final result then needs to be multiplied by a factor \( (Z\alpha)^6 \). Let us denote the individual contributions in Eq. (27) as

\[
E^{(6)} = \delta_1 E^{(6)} + \delta_2 E^{(6)}. \tag{B1}
\]

We start by evaluating the first-order part \( \delta E_1^{(6)} \) and again stress that we omitted all the local Dirac delta-like contributions because we are focusing on states with \( l > 1 \).

**First-order contribution \( \delta_1 E^{(6)} \)**. The first-order correction to the energy is the expectation value of operator \( H^{(6)} \), and for two spinless particles we use the effective operators (42) omitting all spins. We separate \( \delta_1 E^{(6)} \) into expectation values of individual operators appearing in \( H^{(6)} \); thus, in general we have

\[
\delta_1 E^{(6)} = \sum_{i=0}^9 \delta E_i, \tag{B2}
\]

where

\[
\delta E_i = \langle \delta H_i \rangle. \tag{B3}
\]

However, for spinless particles the effective operators \( \delta H_2, \delta H_5, \delta H_7, \) and \( \delta H_9 \) vanish, so the corresponding contributions to energy are zero,

\[
\delta E_2 = \delta E_5 = \delta E_7 = \delta E_9 = 0. \tag{B4}
\]

The first nonzero contribution is the higher-order relativistic correction to kinetic energy, which can be evaluated to

\[
\delta E_0 = \frac{\mu^2}{2} \left( \frac{1}{m^2_1} + \frac{1}{m^2_2} \right) \left( \mu E^2_0 + 3 \mu E^2_0 \left\langle \frac{1}{r} \right\rangle \right) + 3 \mu E_0 \left\langle \frac{1}{r^2} \right\rangle \mu \left( \frac{1}{r^3} \right) + \frac{1}{2} \left\langle \frac{1}{r^4} \right\rangle, \tag{B5}
\]

where \( E_0 = -\frac{\mu}{2m^2} \). The expectation value of operators \( 1/r^k \) will be resolved with the help of the formulas in Appendix E. The next corrections are

\[
\delta E_1 = - \frac{\mu}{8} \left( \frac{1}{m^4_1} + \frac{1}{m^4_2} \right) \left\langle \frac{1}{r^4} \right\rangle, \tag{B6}
\]

\[
\delta E_3 = \frac{\mu}{m_1 m_2} \left( \frac{1}{m^3_1} + \frac{1}{m^3_2} \right) \left( 2\mu E_0 \left\langle \frac{1}{r^3} \right\rangle + 4\mu E_0 \left\langle \frac{1}{r^2} \right\rangle \right) + (2\mu - E_0(l + 1)) \left\langle \frac{1}{r^3} \right\rangle + \frac{1}{2} \left( 1 - l(l + 1) \right) \left\langle \frac{1}{r^4} \right\rangle, \tag{B7}
\]

\[
\delta E_4 = \frac{E_0}{m_1 m_2} \left\langle \frac{1}{r^4} \right\rangle + \frac{1}{m_1 m_2} \left\langle \frac{1}{r^3} \right\rangle + \frac{1}{m_1 m_2} \left[ 1 - \frac{3l(l + 1)}{4} \right] \left\langle \frac{1}{r^4} \right\rangle. \tag{B8}
\]

The retardation correction due to single transverse photon exchange is
Finally, correction $\delta E_8$ is

$$\delta E_8 = -\frac{1}{2} (\alpha_{E1} + \alpha_{E2}) \left\langle \frac{1}{r^4} \right\rangle,$$

which concludes the evaluation of the first-order expectation values for two spinless particles.

Second-order contribution $\delta_2 E^{(6)}$. The second-order contribution of the order $(Z\alpha)^6$ is induced by the Breit Hamiltonian $H^{(4)}$,

$$\delta_2 E^{(6)} = \left\langle H^{(4)} \frac{1}{(E_0 - H_0)} \right\rangle H^{(4)}.$$

In general, such a contribution contains singularities that must be isolated by means of regularization and then cancelled when combined with the corresponding first-order contribution. All such singularities are, however, proportional to the Dirac delta function and thus vanish for $l > 0$. Therefore, we can ignore these singularities and write the Breit Hamiltonian for spinless particles in the form (omitting local terms)

$$H^{(4)} = -A \left\langle \frac{1}{r} H_0 + H_0 \frac{1}{r} \right\rangle - B \frac{1}{r^2} + C \frac{1}{r^3},$$

where

$$A = \frac{\mu^2}{m_1 m_2} \left( \frac{1}{m_1^2} + \frac{1}{m_2^2} \right),$$

$$B = \frac{2 \mu}{m_1 m_2} \left( \frac{1}{m_1^2} + \frac{1}{m_2^2} \right),$$

$$C = \frac{l(l + 1)}{2m_1 m_2}.$$

After elementary calculations we can express the second-order contribution in terms of the first-order operators $(1/r^l)$ listed in Appendix B and $E_{ij}$ listed in Appendix C. Then,

$$\delta_2 E^{(6)} = 4 A^2 E_0 \left\langle \frac{1}{r^2} \right\rangle - 4 A^2 E_0 \left\langle \frac{1}{r^2} \right\rangle + 2 A B \left\langle \frac{1}{r} \right\rangle \left\langle \frac{1}{r^2} \right\rangle - 2 A B \left\langle \frac{1}{r^2} \right\rangle - 2 A C \left\langle \frac{1}{r} \right\rangle \left\langle \frac{1}{r^2} \right\rangle + 2 A C \left\langle \frac{1}{r^2} \right\rangle \left\langle \frac{1}{r^2} \right\rangle + 4 A^2 E_0^2 E_{11} + 4 A B E_0 E_{12} + 2 B^2 E_{22} + 4 A C E_0 E_{13} - 2 B C E_{23} + C^2 E_{33}.$$

Combining the first-order contribution $\delta_1 E^{(6)}$ with the second-order term $\delta_2 E^{(6)}$, and using the expectation values from Appendices B and C we obtain the total correction to the energy $E^{(6)}$ for two spinless particles, presented in Eq. (17).

Appendix C: Expectation values for particles with $s_1 = 0$, $s_2 = 1/2$

The next case is when one particle is spinless and the other one has spin $s_2 = 1/2$. In contrast to the previous section the effective operators $\delta H_5$ and $\delta H_7$ do not vanish, and operators $\delta H_1$, $\delta H_3$, $\delta H_4$, and $\delta H_6$, and also the Breit Hamiltonian $H^{(4)}$ now have spin-dependent parts.

First-order contribution $\delta_1 E^{(6)}$. The first-order contribution is given by the sum (B2) with the individual contributions resolved as follows. Contribution $\delta E_0 = \langle \delta H_0 \rangle$ is the same as in the spinless case, given by Eq. (B5). The next term differs from the spinless case and is

$$\delta E_1 = \delta E_{s_1 = s_2 = 0} = -\mu \left[ \frac{1}{32m_2} \left( \frac{1}{m_1^2} + \frac{1}{m_2^2} \right) \left( 3 + \kappa_2 \right) \right] \left\langle \frac{1}{r^4} \right\rangle.$$

Here $\delta E_{s_1 = s_2 = 0}$ stands for the spinless result (B6). We will use this notation throughout the following sections.

The next term $\delta E_2 = 0$ again vanishes. The remaining nonvanishing contributions are

$$\delta E_3 = \delta E_{s_1 = s_2 = 0} = \mu \left[ \frac{1}{4m_1 m_2} \left( \frac{1}{m_1^2} + \frac{1}{m_2^2} \right) \left( 3 + \kappa_2 \right) \right] \left\langle \frac{1}{r^4} \right\rangle.$$

Combining the first-order contribution $\delta_1 E^{(6)}$ with the second-order term $\delta_2 E^{(6)}$, and using the expectation values from Appendices B and C we obtain the total correction to the energy $E^{(6)}$ for two spinless particles, presented in Eq. (17).
spinless case with one difference. The Breit Hamiltonian is again expressed in the form (112) with the coefficients $A$ and $B$ being the same as in the spinless case. However, coefficient $C$ now contains a spin-dependent part. The derivation proceeds along the same line leading to the result (110) where for the coefficient $C$ we obtain

\[ C = \frac{\vec{L} \cdot \vec{s}_2}{2m_1m_2} + \left( \frac{1 + 2\kappa_2}{m_2^2} + \frac{1 + \kappa_2}{m_1m_2} \right) \vec{L} \cdot \vec{s}_2 \]  \quad \text{(C7)}

instead of (110). To evaluate the term $(\vec{L} \cdot \vec{s}_2)^2$ we use Eq. (C2).

**Appendix D: Expectation values for particles with $s_1 = s_2 = 1/2$**

Finally we evaluate the most complicated case, i.e., two spin-1/2 particles, such as in antiprotonic hydrogen or positronium. For the first-order contribution we will use the effective operators (12) with both spins nonzero.

**First-order contribution $\delta_1 E^{(6)}$**. The contribution to the energy of the order $(Za)^6$ for states with $l > 1$ coming from the first-order operators is again expressed in the form of series (12). The effective operators $\delta H_1$ may contain spin-dependent terms from both particles. The first contribution $\delta E_0$ is the same as in the spinless case, given by Eq. (156). The next contribution is

\[ \delta E_1 = \delta E_1^{s_1 = s_2 = 0} = -\mu \left[ \frac{1}{32m_1^2} + \frac{1}{32m_2^2} \right] \]

The next terms are

\[ \delta E_3 = \delta E_3^{s_1 = s_2 = 0} + \frac{\mu}{m_1m_2} \left[ \left( -E_0 \left\langle \frac{1}{r^3} \right\rangle - \left\langle \frac{1}{r^3} \right\rangle \right) \left( \frac{1}{2m_1^2} + \frac{1}{m_2^2} \right) \vec{L} \cdot \vec{s}_2 + \left( \frac{1 + \kappa_2}{m_2^2} + \frac{1 + \kappa_1}{m_1m_2} \right) \vec{L} \cdot \vec{s}_1 \right] \]

\[ + \frac{6}{m_1m_2} \left( \frac{1 + \kappa_2}{m_2^2} + \frac{1 + \kappa_1}{m_1m_2} \right) \left( \frac{1}{r^3} \right) \left( \left\langle \frac{1 + \kappa_1}{m_1} \right\rangle \vec{L} \cdot \vec{s}_1 + \left\langle \frac{1}{m_2} \right\rangle \vec{L} \cdot \vec{s}_2 \right) \]

\[ \delta E_4 = \delta E_4^{s_1 = s_2 = 0} + \frac{1}{m_1m_2} \left( \frac{1}{4m_1} (1 + \kappa_1)^2 + \frac{1}{4m_2} (1 + \kappa_2)^2 - \frac{1}{2m_1} \vec{L} \cdot \vec{s}_1 - \frac{1 + \kappa_2}{2m_2} \vec{L} \cdot \vec{s}_2 \right) \left\langle \frac{1}{r^3} \right\rangle \]

\[ \delta E_5 = \frac{1}{4m_1m_2} \left( \vec{L} \cdot \vec{s}_1 - 4(1 + \kappa_2) \left( \frac{1}{2l - 1} \frac{3}{2l + 3} \right) \left\langle \vec{s}_1 \cdot \vec{s}_2 \right\rangle \right) \left\langle \frac{1}{r^3} \right\rangle + (1 \leftrightarrow 2), \]

\[ \delta E_6 = \delta E_6^{s_1 = s_2 = 0} + \frac{\mu}{m_1m_2} \left( \frac{1}{2m_1^2} (1 + \kappa_1) \vec{L} \cdot \vec{s}_1 + \frac{1 + \kappa_2}{2m_2^2} \vec{L} \cdot \vec{s}_2 \right) \left\langle \frac{1}{r^3} \right\rangle \]

\[ - \frac{\mu}{m_1m_2} \left( \frac{1}{2m_1^2} (1 + \kappa_1)(1 + \kappa_2) \left( \frac{2}{3} \vec{s}_1 \cdot \vec{s}_2 - \frac{(1 + \kappa_1)(1 + \kappa_2)}{(2l - 1)(2l + 3)} \right) \right) \left\langle \frac{1}{r^3} \right\rangle \]

\[ \delta E_7 = - \frac{\mu}{m_1m_2} \left( \frac{1 + \kappa_1}{4m_1m_2} \vec{L} \cdot \vec{s}_1 + 4(1 + \kappa_2) \left( \frac{1}{2l - 1} \frac{3}{2l + 3} \right) \left\langle \vec{s}_1 \cdot \vec{s}_2 \right\rangle \right) \left\langle \frac{1}{r^3} \right\rangle + (1 \leftrightarrow 2) + \delta E_5. \]

Contribution $\delta E_8$ is obtained from the spinless case (110) by transition $\alpha_{E_j} \rightarrow \alpha_{E_j} - (4m_1^3)^{-1}$. Finally,

\[ \delta E_9 = \frac{\kappa_1(1 + \kappa_2)}{2m_1m_2} \left( \left\langle 8\mu E_0 \frac{1}{r^3} \right\rangle + 8\mu \left\langle \frac{1}{r^3} \right\rangle - 6(l - 1)(l + 2) \left\langle \frac{1}{r^3} \right\rangle \right) \left( \frac{1}{2l - 1} \frac{3}{2l + 3} \right) \]

\[ + \left( -\frac{4}{3} \mu E_0 \left\langle \frac{1}{r^3} \right\rangle - \frac{4}{3} \mu \left\langle \frac{1}{r^3} \right\rangle + (l - 1)(l + 2) \left\langle \frac{1}{r^3} \right\rangle \right) \left\langle \frac{1}{r^3} \right\rangle. \]
The total first-order correction $\delta_1 E^{(6)}$ is a sum $\sum_{i=0}^9 \delta E_i$.

**Second-order contribution $\delta_2 E^{(6)}$.** The second-order contribution in the case of two particles with spin 1/2 is more complicated than in the previous cases due to the presence of a tensor-like term in the Breit Hamiltonian. We write the Hamiltonian $H^{(4)}$ in the form

$$H^{(4)} = -\frac{\mu^2}{2} \left[ \frac{1}{m_1^3} + \frac{1}{m_2^3} \right] H_0^2 - \frac{\mu^2}{r^2} \left[ \frac{1}{m_1^3} + \frac{1}{m_2^3} \right] \frac{1}{m_1 m_2} - \mu \left[ \frac{1}{m_1^3} + \frac{1}{m_2^3} \right] \frac{1}{m_1 m_2} \left( -\frac{1}{r} H_0 + \frac{1}{r} \right)$$

$$+ \frac{1}{r^3} \left( \frac{1 + \kappa_1}{m_1 m_2} + \frac{1 + 2 \kappa_1}{m_2^3} \right) \vec{L} \cdot \vec{s}_1 + \left( \frac{1 + \kappa_2}{m_1 m_2} + \frac{1 + 2 \kappa_2}{m_2^3} \right) \vec{L} \cdot \vec{s}_2 + \frac{\vec{L}^2}{2m_1 m_2} + \frac{3}{m_1 m_2} (1 + \kappa_1)(1 + \kappa_2) \frac{(n^s n^j)^2 s_1^i s_2^j}{r^3},$$

(D10)

with $(n^s n^j)^2 = n^s n^j - \delta^{ij}/3$ being a symmetric, traceless tensor. The evaluation of the second-order contribution with the Breit Hamiltonian in the form (D10) proceeds along the same line as in the previous cases using identities in Appendices [F] and [G] with the exception of the term

$$\left\langle \frac{(n^s n^j)^2 s_1^i s_2^j r^3}{(E_0 - H_0)^2} \right\rangle.$$ (D11)

There are three possible contributions that correspond to three possible values of the angular momentum of the intermediate state $l' = l, l \pm 2$. Let us denote by $Q = (n^s n^j)^2 s_1^i s_2^j$ and by $\hat{P}_l$ the projection operator into the subspace with angular momentum $l$. Assuming that the outer states have the angular momentum $l$, we get for the diagonal term

$$Q \hat{P}_l Q = \frac{l(l+1)}{24(2l-1)(2l+3)} \left( 1 + \frac{4}{3} \vec{s}_1 \cdot \vec{s}_2 \right)$$

$$- \frac{1}{8(2l-1)(2l+3)} \vec{L} \cdot (\vec{s}_1 + \vec{s}_2)$$

$$- \frac{(2l-3)(2l+5)}{6(2l-1)^2(2l+3)^2} (L^i L^j)^{(2)} s_1^i s_2^j.$$ (D12)

For off-diagonal terms we get

$$Q \hat{P}_{l+2} Q = \frac{l(l+1)(l+2)}{16(2l+1)(2l+3)} \left( 1 + \frac{4}{3} \vec{s}_1 \cdot \vec{s}_2 \right)$$

$$+ \frac{(l+2)}{8(2l+1)(2l+3)} \vec{L} \cdot (\vec{s}_1 + \vec{s}_2)$$

$$+ \frac{(l+2)}{2(2l+1)(2l+3)^2} (L^i L^j)^{(2)} s_1^i s_2^j,$$ (D13)

and

$$Q \hat{P}_{l-2} Q = \frac{l(l-1)}{16(2l-1)(2l+1)} \left( 1 + \frac{4}{3} \vec{s}_1 \cdot \vec{s}_2 \right)$$

$$- \frac{(l-1)}{8(2l-1)(2l+1)} \vec{L} \cdot (\vec{s}_1 + \vec{s}_2)$$

$$+ \frac{(l-1)}{2(2l-1)(2l+1)^2} (L^i L^j)^{(2)} s_1^i s_2^j.$$ (D14)

**Appendix E: Expectation values of the basic first-order operators**

Here we list the expectation values used in this work. Derivation of the expectation values for operators $1/r^k$ can be found in the third section of the first chapter of book [16], and setting $Z_a = 1$ they are

$$\left\langle \frac{1}{r} \right\rangle = \frac{\mu}{n^2},$$ (E1)

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2\mu^2}{(2l+1)n^3},$$ (E2)

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2\mu^3}{l(l+1)(2l+1)n^3},$$ (E3)

$$\left\langle \frac{1}{r^4} \right\rangle = \frac{4\mu^4}{(l+1)(2l+1)(2l+3)n^5},$$ (E4)

$$\left\langle \frac{1}{r^5} \right\rangle = \frac{4\mu^5}{(l-1)(l+1)(l+2)(2l-1)(2l+1)(3+2l)n^6}.$$ (E5)

These equations are valid for $l > 1$.

**Appendix F: The second-order matrix elements**

In this section we present the expectation values of the second-order operators of the form

$$\mathcal{E}_{nm} = \left\langle \frac{1}{r^m} \frac{1}{(E_0 - H_0)^2} \frac{1}{r^m} \right\rangle.$$ (F1)

We again set $Z_a = 1$ for simplification of the results. When the angular momentum of the intermediate states is the same as for the reference state then we obtain the following results:

$$\mathcal{E}_{11} = -\frac{\mu}{2n^2},$$ (F2)

$$\mathcal{E}_{12} = -\frac{2\mu^2}{(2l+1)n^3},$$ (F3)

$$\mathcal{E}_{22} = -\mu^3 (\frac{6}{(2l+1)^2 n^4} + \frac{4}{(2l+1)^3 n^5}),$$ (F4)
\[ E_{13} = \frac{\mu}{2l(l+1)} \left( 2E_{12} - \frac{1}{r^2} \right), \quad (F5) \]
\[ E_{23} = \frac{\mu}{l(l+1)} \left( E_{22} - \frac{1}{r^2} \right), \quad (F6) \]
\[ E_{33} = \frac{\mu^2}{l^2(l+1)^2} E_{22} - \frac{\mu^2}{l^2(l+1)^2} \left( \frac{1}{r^3} \right) - \frac{3\mu}{2l(l+1)} \left( \frac{1}{r^2} \right). \quad (F7) \]

The second-order expectation values involving the \(1/r^3\) operator were derived with the help of the identity
\[ \frac{1}{r^3} = \frac{\mu}{l(l+1)} \left( \frac{1}{r^2} - [D_r, H_0] \right), \quad (F8) \]
where \(D_r = \partial_r + \frac{\hat{s}}{2r}\). For off-diagonal terms with \(1/r^3\) the evaluation is more complicated. In the case of \(l' = l + 2\) we need to calculate the expression
\[ \left< \frac{1}{r^3} (E_0 - H_{l+2})' \frac{1}{r^3} \right> \quad (F9) \]
in which we defined the radial part of the Hamiltonian as
\[ H_l = -\frac{1}{2\mu} \left( \partial_r^2 + \frac{2}{r} \partial_r - \frac{l(l+1)}{r^2} \right) - \frac{1}{r}. \quad (F10) \]

Using the identities
\[ \frac{1}{r^3} = H_l \hat{\alpha} - \alpha H_{l+2}, \quad (F11) \]
\[ \frac{1}{r^3} = \hat{\beta} H_l - H_{l+2} \hat{\beta}, \quad (F12) \]
where operators \(\hat{\alpha}\) and \(\hat{\beta}\) are defined by
\[ \hat{\alpha} = -\frac{\mu}{3l(l+1)(l+2)} D_r - \frac{\mu(2l+3)}{3(l+1)(l+2)} \frac{1}{r}, \quad (F13) \]
\[ \hat{\beta} = \frac{\mu}{3l(l+1)(l+2)} D_r - \frac{\mu(2l+3)}{3l+1(l+2)} \frac{1}{r}, \quad (F14) \]
we can simplify the radial part to
\[ \left< \frac{1}{r^3} (E_0 - H_{l+2})' \frac{1}{r^3} \right> = \left< \hat{\alpha} (E_0 - H_{l+2}) \hat{\beta} \right> \]
\[ = -\frac{2\mu^2(2l+3)}{9(l+1)^2(l+2)^2} E_0 \left< \frac{1}{r^2} \right> - \frac{\mu^2(7 + 9l + 3l^2)}{3(l+1)^2(l+2)^2(2l+3)} \left< \frac{1}{r^3} \right> - \frac{\mu(27 + 45l + 25l^2 + 4l^3)}{18(l+1)^2(l+2)^2} \left< \frac{1}{r^4} \right> \quad (F15) \]
For the radial part with the angular momentum of the intermediate states equal to \(l' = l - 2\) we repeat the calculation using
\[ \frac{1}{r^3} = H_{l} \hat{\delta} - \delta H_{l-2}, \quad (F16) \]
\[ \frac{1}{r^3} = \hat{\gamma} H_{l} - H_{l-2} \hat{\gamma}, \quad (F17) \]
with
\[ \hat{\delta} = -\frac{\mu}{3l(l-1)} D_r - \frac{\mu(2l-1)}{3l(l-1)} \frac{1}{r} - \frac{\mu^2}{3l(l-1)(2l-1)}, \quad (F18) \]
\[ \hat{\gamma} = \frac{\mu}{3l(l-1)} D_r - \frac{\mu(2l-1)}{3l(l-1)} \frac{1}{r} - \frac{\mu^2}{3l(l-1)(2l-1)}. \quad (F19) \]
Then the radial part is
\[ \left< \frac{1}{r^3} (E_0 - H_{l-2})' \frac{1}{r^3} \right> = \hat{\delta} (E_0 - H_{l-2}) \hat{\gamma} \]
\[ = \frac{2\mu^2(2l-1)}{9(l-1)^2l^2} E_0 \left< \frac{1}{r^2} \right> + \frac{\mu^2(1 - 3l + 3l^2)}{3(l-1)^2l^2(2l-1)} \left< \frac{1}{r^3} \right> + \frac{\mu(-3 + 7l - 13l^2 + 4l^3)}{18(l-1)^2l^2} \left< \frac{1}{r^4} \right>. \quad (F20) \]

Eqs. (F15) and (F20) are used for evaluation of the second-order contribution for two spin-1/2 particles.

Appendix G: Reduction of spin-angular operators

To calculate the second-order contribution in \(E^{(6)}\) we use the following identities to evaluate products of spin-angular operators:
\[ (\vec{L} \cdot \vec{s}_1)^2 = \frac{l(l+1)}{4} - \frac{1}{2} \vec{L} \cdot \vec{s}_1, \quad (G1) \]
\[ (\vec{L} \cdot \vec{s}_2)^2 = \frac{l(l+1)}{4} - \frac{1}{2} \vec{L} \cdot \vec{s}_2, \quad (G2) \]
\[ \frac{1}{2} \{ \vec{L} \cdot \vec{s}_1, \vec{L} \cdot \vec{s}_2 \} = (L^L L^j)^{(2)} s_1^j s_2^j + \frac{l(l+1)}{3} \vec{s}_1 \cdot \vec{s}_2, \quad (G3) \]
\[ \frac{1}{2} \{ (L^L L^j)^{(2)} s_1^j s_2^j, \vec{L} \cdot \vec{s}_1 \} = \frac{(2l-1)(2l+3)}{24} \vec{L} \cdot \vec{s}_2 - \frac{3}{4} (L^L L^j)^{(2)} s_1^j s_2^j, \quad (G4) \]
\[ \frac{1}{2} \{ (L^L L^j)^{(2)} s_1^j s_2^j, \vec{s}_1 \cdot \vec{s}_2 \} = \frac{3}{4} (L^L L^j)^{(2)} s_1^j s_2^j \quad (G5) \]
\[ (\vec{s}_1 \cdot \vec{s}_2)^2 = \frac{3}{16} - \frac{1}{2} \vec{s}_1 \cdot \vec{s}_2. \quad (G6) \]

The second-order contribution is then expressed as a linear combination of the basic spin-angular operators in the same way as the first-order contribution.
[1] B. Ohayon, G. Janka, I. Cortinovis, Z. Burkley, L. d. S. Borges, E. Depero, A. Golovizin, X. Ni, Z. Salman, A. Suter, C. Vigo, T. Prokscha, and P. Crivelli (Mu-MASS Collaboration), Phys. Rev. Lett. 128, 011802 (2022).

[2] H. Grotch and D. R. Yennie, Z. Phys 202, 425 (1967); Rev. Mod. Phys. 41, 350 (1969).

[3] Eberhard Widmann, Few-Body Systems 45, 165 (2009).

[4] R. S. Hayano, M. Hori, D. Horvath and E. Widmann, Rep. Prog. Phys. 70, 1995 (2007).

[5] M. Hori et al., Phys. Rev. Lett. 94, 063401 (2005).

[6] J. N. Tan, S. M. Brewer, and N. D. Guise, Phys. Scr. 2011, 014009 (2011).

[7] A. Veitia and K. Pachucki, Phys. Rev. A 69, 042501 (2004).

[8] J. Zatorski and K. Pachucki, Phys. Rev. A 82, 052520 (2010).

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

[10] E. A. Golosov, I. B. Khriplovich, A. I. Milstein and A. S. Yelkhovsky, Zh. Eksp. Teor. Fiz. 107, 393 (1995) [Sov. Phys. JETP 80, 208 (1995)].

[11] U. Jentschura and K. Pachucki, Phys. Rev. A 54, 1853 (1996).

[12] G. S. Adkins, B. Akers, M. F. Alam, L. M. Tram, X. Zhang, ”Calculation of higher order corrections to positronium energy levels, Proc. Sci. 353 (2019).

[13] J. Zatorski, Phys. Rev. A 78, 032103 (2008).

[14] G. S. Adkins, D. B. Cassidy, and J. Pérez-Ríos, ”Precision spectroscopy of positronium: Testing bound-state QED theory and the search for physics beyond the Standard Model.” Physics Reports 975 (2022): 1-61.

[15] U.D. Jentschura, A. Czarnecki, and K. Pachucki, Phys. Rev. A 72, 062102 (2005).

[16] H.A. Bethe and E.E. Salpeter, Quantum Mechanics Of One- And Two-Electron Atoms (Plenum Publishing Corporation, New York, 1977).