Quantum electrodynamics of two-body systems with arbitrary masses up to α^6 order

Jacek Zatorski [1], Vojtěch Patkóš [2], and Krzysztof Pachucki[1]

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

We perform a calculation of quantum electrodynamics effects in excited states with $l > 1$ of arbitrary two-body systems up to α^6 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 $e^- \mu^+$ [1]. The reason is that there is no fundamental equation for a two-body system with arbitrary masses which accounts for relativity. This is in contrast to the Dirac equation, which holds when one of the particles is infinitely heavy. Although there is an exact formula [2,3], which gives the leading m/M correction valid for an arbitrary nuclear charge, the more general result for an arbitrary mass ratio is not known. In the alternative approach one employs QED and expansion in the fine-structure constant α to derive an analytic formula for nuclear recoil corrections in consequent orders of α. Here we demonstrate that one can derive exact formulas for α expansion coefficients for excited rotational $l > 1$ states, which are valid for arbitrary masses of their constituents. We perform calculations up to the order of α^6 for the case of two spinless particles (for example, pionic helium), one spinless particle and one spin-1/2 particle (for example, hydrogenlike helium), and two spin-1/2 particles (for example, a hydrogen atom), 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 is excited states of antiprotonic atoms, like $\bar{p}\alpha$. If corresponding measurements are available, this would allow for a more accurate determination of fundamental constants or tests for the existence of unknown long-range interactions, similar to precision tests performed with antiprotonic helium [4–6] 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 [7–9] and leading m/M corrections [10]. This, in combination with the μH Lamb-shift

measurement [11], allowed for the determination of the Rydberg constant and the proton charge radius [12]. The measurement of magnetic interactions in hydrogenlike carbon [13] 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 μ mass [14]. If accurate measurements were available for hydrogenic rotational states [15], they would allow not only for more accurate determination of fundamental constants but also for the search of long-range interactions [16]. 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 Sec. II we outline the method of calculation. Section III contains details of the calculation of the leading relativistic correction to energy. In Sec. IV we present the leading QED correction to energy levels, and Sec. V is devoted to higher-order QED corrections to the energy levels, followed by a summary in Sec. VI.

II. EXPANSION OF ENERGY IN POWERS OF THE FINE-STRUCTURE CONSTANT α

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 with the angular momentum number $l \approx n$. For that reason, during calculations we omit contributions from operators containing short-range interactions, namely, those of the nuclear size. We will neglect also the (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 and m_2, charges e_1 and e_2, spins s_1 and s_2, and g factors g_1 and g_2 can be expressed as a series in powers of the

fine-structure constant α,

$$E(\alpha) = E^{(0)} + E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + o(\alpha^7), \quad (1)$$

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

$$E^{(0)} = m_1 + m_2, \quad (2)$$

and $E^{(2)}$ is the eigenvalue of the nonrelativistic two-body Hamiltonian $H_0 = H^{(2)}$ in the center-of-mass frame,

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

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

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

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 $H^{(4)}$ [17] with the nonrelativistic wave function,

$$H^{(4)} = -\frac{\vec{p}^4}{8m_1^3} - \frac{\vec{p}^4}{8m_2^3} + \frac{e_1 e_2}{4\pi} \left\{ \frac{1}{2m_1 m_2} p^i \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p^j + \frac{g_1 g_2}{4m_1 m_2} \left[\frac{s_1^i s_2^j}{r^3} \left(\delta^{ij} - 3\frac{r^i r^j}{r^2} \right) - \frac{8\pi}{3} \vec{s}_1 \cdot \vec{s}_2 \delta^{(3)}(\vec{r}) \right] \right.$$

$$\left. - \frac{\vec{r} \times \vec{p}}{2r^3} \cdot \left[\frac{g_1}{m_1 m_2} \vec{s}_1 + \frac{g_2}{m_1 m_2} \vec{s}_2 + \frac{(g_2 - 1)}{m_2^2} \vec{s}_2 + \frac{(g_1 - 1)}{m_1^2} \vec{s}_1 \right] \right\} - \frac{e_1 e_2}{6} \left(\langle r_E^2 \rangle_1 + \langle r_E^2 \rangle_2 \right) \delta^{(3)}(\vec{r}), \quad (5)$$

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 $g_p = 5.585\,694\,689\,3(16)$, and for the antiproton it is the same. For the case of a spin-1/2 pointlike particle the charge radius is

$$\langle r_E^2 \rangle = \frac{3}{4m^2}. \quad (6)$$

For a spinless particle it is $\langle r_E^2 \rangle = g = 0$. 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 principal quantum number n and angular momentum l is

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

$$+ \frac{2\delta_{l0}}{3n^3} \left(\langle r_E^2 \rangle_1 + \langle r_E^2 \rangle_2 \right) + \frac{\delta_{l0}}{m_1 m_2 n^3}$$

$$+ \frac{2}{l(l+1)(2l+1)n^3} \left[\vec{L} \cdot \vec{s}_1 \left(\frac{1+2\kappa_1}{2m_1^2} + \frac{1+\kappa_1}{m_1 m_2} \right) \right.$$

$$+ \vec{L} \cdot \vec{s}_2 \left(\frac{1+2\kappa_2}{2m_2^2} + \frac{1+\kappa_2}{m_1 m_2} \right)$$

$$\left. - \frac{6(1+\kappa_1)(1+\kappa_2)}{m_1 m_2 (2l-1)(2l+3)} s_1^i s_2^j (L^i L^j)^{(2)} \right]$$

$$\left. + \frac{8\delta_{l0}}{3m_1 m_2 n^3} (1+\kappa_1)(1+\kappa_2) \vec{s}_1 \cdot \vec{s}_2 \right\}. \quad (7)$$

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

$$(L^i L^j)^{(2)} = \frac{1}{2} \left(L^i L^j + L^j L^i \right) - \frac{\delta^{ij}}{3} \vec{L}^2. \quad (8)$$

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

A. Dirac limit of an infinitely heavy and pointlike nucleus

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

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

$$\left. + \frac{1+2\kappa}{l(l+1)(2l+1)n^3} \vec{L} \cdot \vec{s} + \frac{2\delta_{l0}}{3n^3} m^2 \langle r_E^2 \rangle \right\}. \quad (9)$$

If the first particle is also pointlike, then

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

$$\left. + \frac{1}{l(l+1)(2l+1)n^3} \vec{L} \cdot \vec{s} + \frac{\delta_{l0}}{2n^3} \right\}. \quad (10)$$

Using the total angular momentum $\vec{J} = \vec{L} + \vec{s}$, it can be rewritten in the form

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

where j is the total angular momentum number. This can be compared to the result obtained with the Dirac equation, which is

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

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

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 spin-1/2 point 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

$$
E^{(4)} = \frac{\mu\,(Z\alpha)^4}{n^3}\left\{\frac{1}{8\,n}\left(3 - \frac{\mu^2}{m\,M}\right) - \frac{1}{(2l+1)}\right.
$$
$$
\left. + \left(\frac{\mu^2}{m^2} + \frac{2\,\mu^2}{mM}\right)\left[\frac{\delta_{l0}}{2} + \frac{1}{l(l+1)(2\,l+1)}\vec{L}\cdot\vec{s}\right]\right\}.
$$
(15)

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

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

This is in agreement with the known recoil correction to the Dirac energy [18],

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

Expanding this to the fourth order in $Z\alpha$, we obtain a result in agreement with Eq. (16).

C. Two spin-1/2 point 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

$$
E^{(4)} = \frac{m\,\alpha^4}{8\,n^3}\left\{\frac{11}{8\,n} - \frac{4}{(2l+1)} + \frac{4}{3}\delta_{l0}\,\vec{S}^2\right.
$$
$$
\left. + \frac{3}{l(l+1)(2\,l+1)}\left[\vec{L}\cdot\vec{S} - \frac{2\,S^iS^j(L^iL^j)^{(2)}}{(2\,l-1)(2\,l+3)}\right]\right\},
$$
(18)

where

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

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

This relativistic energy does not account for annihilation terms.

D. Both particles spinless and pointlike

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

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

In the infinite nuclear mass $M = m_2$ limit

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

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

$$
E^{(4,1)} = \frac{m^2}{M}(Z\alpha)^4\left\{-\frac{1}{2n^4} + \frac{1+\delta_{l0}}{(2l+1)\,n^3}\right\},
$$
(23)

which is different from the case of the Dirac particle in Eq. (16).

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 [19]

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

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

$$
\ln[k_0(n,l)] \equiv \frac{n^3}{2\mu^3(Z\alpha)^4}
$$
$$
\times\left\langle\phi\left|\vec{p}\,(H_0 - E_0)\,\ln\left[\frac{2(H_0 - E_0)}{\mu(Z\alpha)^2}\right]\vec{p}\right|\phi\right\rangle
$$
(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 (25) and Eq. (E3), we obtain

$$
E^{(5)} = -\frac{7}{3\pi}\frac{(Z\alpha)^5\mu^3}{m_1m_2}\frac{1}{l(l+1)(2l+1)\,n^3}
$$
$$
- \frac{4}{3\pi}\left(\frac{1}{m_1} + \frac{Z}{m_2}\right)^2\frac{\alpha(Z\alpha)^4\mu^3}{n^3}\,\ln k_0(n,l),
$$
(26)

in agreement with Eq. (19) from Ref. [20].

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 a nonrelativistic wave function and (ii) the second-order contribution induced by the Breit Hamiltonian $H^{(4)}$,

$$
E^{(6)} = \langle H^{(6)}\rangle + \left\langle H^{(4)}\,\frac{1}{(E_0 - H_0)'}\,H^{(4)}\right\rangle.
$$
(27)

Here the prime in $(E_0 - H_0)'$ means that we exclude the reference state from the resolvent. The effective operator $H^{(6)}$ can be derived within the framework of nonrelativistic QED (NRQED) [21]. In general, both the first-order and second-order contributions separately contain singular operators that

cancel each other when they are combined. However, because we are interested in states with $l > 1$, all singularities vanish. Omitting contact interactions, the NRQED Hamiltonian for a spin $s = 0, 1/2$ and finite-size particle, from Ref. [22], is

$$
\begin{aligned}
H_{\text{NRQED}} = & \, e A_0 + \frac{1}{2m}\left[\vec{\pi}^2 - 2e(1+\kappa)\vec{s}\cdot\vec{B}\right] \\
& - \frac{1}{8m^3}\left[\vec{\pi}^4 - 2e\{p^2, \vec{s}\cdot\vec{B}\} - 2e\kappa\{\vec{\pi}\cdot\vec{B}, \vec{\pi}\cdot\vec{s}\}\right] \\
& + \frac{p^6}{16m^5} - \frac{1+2\kappa}{4m^2}e\,\vec{s}\cdot(\vec{E}\times\vec{\pi} - \vec{\pi}\times\vec{E}) \\
& - \left(1+\frac{4\kappa}{3}\right)\frac{3e}{16m^4}\vec{s}\{p^2, \vec{\nabla}A_0\times\vec{p}\} \\
& + \frac{e}{32m^4}\left(1+\frac{s_a(s_a+1)}{3}\right)[p^2, [p^2, A_0]] \\
& - \frac{1}{2}\left(\alpha_E - \frac{s_a(s_a+1)}{3m^3}\right)e^2\vec{E}^2,
\end{aligned}
\tag{28}
$$

where $[X, Y] \equiv XY - YX$ is the commutator of two operators; $\{X, Y\} \equiv XY + YX$ is the anticommutator; $\vec{\pi} = \vec{p} - e\vec{A}$; e is the charge; κ is the magnetic-moment anomaly, which is related to the g factor by $g = 2(1+\kappa)$; and $e^2\alpha_E$ is the static electric dipole polarizability. For pointlike particles $\alpha_E = 0$ at the α^6 order. The radiative corrections to H_{NRQED} which go beyond electromagnetic form factors can be expressed at the α^7 order in terms of the electric dipole polarizability as calculated in Ref. [7].

Using the NRQED Hamiltonian in Eq. (28), we can derive the effective operator $H^{(6)}$ for the case of two spinless particles, for one spinless particle and one spin-1/2 particle, and for two spin-1/2 particles. The derivation of effective operators following Ref. [21] is presented in Appendix A. The general form of $H^{(6)}$ is

$$
H^{(6)} = \sum_{i=0,\dots,9} \delta H_i.
\tag{29}
$$

The individual effective operators are as follows:

$$
\delta H_0 = \frac{p^6}{16m_1^5} + \frac{p^6}{16m_2^5},
\tag{30}
$$

$$
\begin{aligned}
\delta H_1 = & \sum_a -\frac{3Z\alpha}{16m_a^4}\left(1+\frac{4\kappa_a}{3}\right)\vec{L}\cdot\vec{s}_a\left\{p^2, \frac{1}{r^3}\right\} \\
& + \frac{1}{32m_a^4}\left(1+\frac{s_a(s_a+1)}{3}\right)[p^2, [p^2, V]],
\end{aligned}
\tag{31}
$$

$$
\begin{aligned}
\delta H_2 = & \frac{Z\alpha}{4m_1^2 m_2^2}(1+2\kappa_1)(1+2\kappa_2) \\
& \times (\vec{s}_2\times\vec{p})^i\left(\frac{\delta^{ij}}{r^3} - 3\frac{r^i r^j}{r^5}\right)(\vec{s}_1\times\vec{p})^j,
\end{aligned}
\tag{32}
$$

$$
\delta H_3 = \sum_a \frac{1}{4m_a^3}(\{p^2, \vec{p}_a\cdot e_a\vec{\mathcal{A}}_a\} + \{p^2, \vec{s}_a\cdot\vec{\nabla}_a\times e_a\vec{\mathcal{A}}_a\}),
\tag{33}
$$

$$
\delta H_4 = \sum_a \frac{e_a^2}{2m_a}\vec{\mathcal{A}}_a^2,
\tag{34}
$$

$$
\delta H_5 = \sum_a \frac{e_a^2(1+2\kappa_a)}{2m_a^2}\vec{s}_a\cdot\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a,
\tag{35}
$$

$$
\delta H_6 = \delta H_6^A + \delta H_6^B + \delta H_6^C,
\tag{36}
$$

where

$$
\begin{aligned}
\delta H_6^A = & \frac{Z\alpha}{16m_1 m_2}\left\{\frac{2Z^2\alpha^2}{r^3} + \frac{iZ\alpha r^i}{r^3}\left[\frac{p^2}{2m_2}, \frac{r^i r^j - 3\delta^{ij} r^2}{r}\right]p^j \right. \\
& \left. - p^i\left[\frac{r^i r^j - 3\delta^{ij} r^2}{r}, \frac{p^2}{2m_1}\right]\frac{iZ\alpha r^j}{r^3} - p^i\left[\frac{p^2}{2m_2}, \left[\frac{r^i r^j - 3\delta^{ij} r^2}{r}, \frac{p^2}{2m_1}\right]\right]p^j\right\} + (1\leftrightarrow 2),
\end{aligned}
\tag{37}
$$

$$
\begin{aligned}
\delta H_6^B = & \frac{Z\alpha}{4m_1 m_2}\left\{(1+\kappa_1)\left[\left(\vec{s}_1\times\frac{\vec{r}}{r}\right)^i, \frac{p^2}{2m_1}\right]\frac{iZ\alpha r^i}{r^3} - (1+\kappa_2)\frac{iZ\alpha r^i}{r^3}\left[\frac{p^2}{2m_2}, \left(\vec{s}_2\times\frac{\vec{r}}{r}\right)^i\right] \right. \\
& \left. + (1+\kappa_1)\left[\frac{p^2}{2m_2}, \left[\left(\vec{s}_1\times\frac{\vec{r}}{r}\right)^i, \frac{p^2}{2m_1}\right]\right]p^i + (1+\kappa_2)p^i\left[\frac{p^2}{2m_2}, \left[\left(\vec{s}_2\times\frac{\vec{r}}{r}\right)^i, \frac{p^2}{2m_1}\right]\right]\right\} + (1\leftrightarrow 2),
\end{aligned}
\tag{38}
$$

$$
\delta H_6^C = -\frac{Z\alpha(1+\kappa_1)(1+\kappa_2)}{4m_1^2 m_2^2}\left[p^2, \left[p^2, \vec{s}_1\vec{s}_2\frac{2}{3r} + s_1^i s_2^j\frac{1}{2r}\left(\frac{r^i r^j}{r^2} - \frac{\delta^{ij}}{3}\right)\right]\right],
\tag{39}
$$

$$
\begin{aligned}
\delta H_7 = & \sum_a \frac{e_a^2(1+2\kappa_a)}{2m_a^2}\vec{s}_a\cdot\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a + \frac{ie_a(1+2\kappa_a)}{8m_a^3} \\
& \times [\vec{\mathcal{A}}_a\cdot(\vec{p}_a\times\vec{s}_a) + (\vec{p}_a\times\vec{s}_a)\cdot\vec{\mathcal{A}}_a, p_a^2],
\end{aligned}
\tag{40}
$$

$$
\delta H_8 = -\frac{1}{2}\sum_a\left(\alpha_{Ea} - \frac{s_a(s_a+1)}{3m_a^3}\right)\frac{Z^2\alpha^2}{r^4},
\tag{41}
$$

$$
\delta H_9 = \sum_a \frac{e_a\kappa_a}{4m_a^3}\{\vec{p}_a\cdot\vec{\nabla}_a\times\vec{\mathcal{A}}_a, \vec{p}_a\cdot\vec{s}_a\},
\tag{42}
$$

where summation over $a = 1, 2$ goes over both particles. The static fields $\mathcal{A}_i$ and $\mathcal{E}_i$ are defined as

$$
e_1\mathcal{A}_1^i = -\frac{Z\alpha}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\frac{p_2^j}{m_2} - \frac{Z\alpha}{m_2}\frac{(\vec{s}_2\times\vec{r})^i}{r^3}(1+\kappa_2),
\tag{43}
$$

$$e_2 \mathcal{A}_2^i = -\frac{Z\alpha}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right)\frac{p_1^j}{m_1} + \frac{Z\alpha}{m_1}\frac{(\vec{s}_1 \times \vec{r})^i}{r^3}(1 + \kappa_1),$$
(44)

$$e_1 \vec{\mathcal{E}}_1 = -Z\alpha\frac{\vec{r}}{r^3}, \quad e_2 \vec{\mathcal{E}}_2 = Z\alpha\frac{\vec{r}}{r^3}.$$
(45)

In the case when one of the particles is spinless and the other one has spin 1/2, the effective operators (30)–(42) are changed in such a way that $\vec{s}_1 = s_1 = 0$ in δH_i and also in $e_2 \vec{\mathcal{A}}_2$. Lastly, in the case of two spinless particles, the effective operators (30)–(42) are modified by setting $\vec{s}_1 = \vec{s}_2 = s_1 = s_2 = 0$ and the same applies to static fields $e_a \vec{\mathcal{A}}_a$.

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

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. Defining

$$f^{(6)}(n, j) = -\frac{5}{16n^6} + \frac{3}{2(2j + 1)n^5} - \frac{3}{2(2j + 1)^2 n^4} - \frac{1}{(2j + 1)^3 n^3},$$
(46)

we obtain the correction of the order $m\alpha^6$,

$$E^{(6)} = \mu(Z\alpha)^6 \left[f^{(6)}(n, l) + \frac{\mu^2}{m_1 m_2} \right.$$
$$\times \left(\frac{3}{16n^6} - \frac{8l(l+1) - 3}{2(2l-1)(2l+1)(2l+3)n^5} \right.$$
$$\left. + \frac{6}{(2l-1)(2l+1)(2l+3)n^3} \right)$$
$$- \frac{\mu^4}{16m_1^2 m_2^2 n^6} + \frac{2\mu^3(\alpha_{E1} + \alpha_{E2})}{(2l-1)(2l+1)(2l+3)}$$
$$\left. \times \left(\frac{1}{n^5} - \frac{3}{l(l+1)n^3} \right) \right].$$
(47)

Like for $E^{(4)}$, we can explore particular limiting cases of the general result in Eq. (47). In order to do that we will expand the result (47) in powers of the mass ratio for the case when the mass of the second particle is much heavier than the mass of the first particle,

$$E^{(6)} = E^{(6,0)} + E^{(6,1)} + E^{(6,2)} + \dots,$$
(48)

where $E^{(6,0)}$ is of the order of m, $E^{(6,1)}$ is of the order of m^2/M, etc. First, we obtain the limit where mass $M = m_2$ of the nucleus is infinitely heavy, in agreement with the Klein-Gordon equation:

$$E^{(6,0)} = m(Z\alpha)^6 f^{(6)}(n, l).$$
(49)

We may also expand Eq. (47) up to the order of m^2/M to obtain the first-order recoil correction

$$E^{(6,1)} = (Z\alpha)^6 \frac{m^2}{M} f_0^{(6,1)}(n, l),$$
(50)

where we introduce the function

$$f_0^{(6,1)}(n, l) = \frac{1}{2n^6} + \frac{6 - 10l(l+1)}{(2l-1)(2l+1)(2l+3)n^5}$$
$$+ \frac{3}{2(2l+1)^2 n^4}$$
$$+ \frac{3 + 28l(l+1)}{(2l-1)(2l+1)^3(2l+3)n^3}.$$
(51)

This concludes the evaluation of the correction to energy for a purely spinless two-body system.

B. Two particles with spins $s_1 = 0$ and $s_2 = 1/2$

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 C. 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 $E_{s_1=s_2=0}^{(6)}$, then

$$E^{(6)} = E_{s_1=s_2=0}^{(6)} + \frac{\mu(Z\alpha)^6}{l(l+1)(2l-1)(2l+1)(2l+3)}$$
$$\times [A + B\vec{L} \cdot \vec{s}_2].$$
(52)

With the help of the substitutions

$$\lambda_0 = \frac{(2l-1)(2l+3)}{2l+1} = 2l + 1 - \frac{4}{2l+1},$$
(53)

$$\lambda_1 = \frac{3}{2l(l+1)} + \frac{4}{(2l+1)^2},$$
(54)

$$\lambda_2 = -\frac{3}{4l^2} + \frac{13}{4l(l+1)} - \frac{3}{4(l+1)^2} + \frac{8}{(2l+1)^2}$$
(55)

and the definition

$$X = \frac{X_5}{n^5} + \frac{X_4}{n^4} + \frac{X_3}{n^3}$$
(56)

for $X = A, B$, the coefficients A and B in Eq. (52) can be written as

$$A_5 = \frac{l(l+1)}{2}\left[g_2^2 \frac{\mu^2}{4m_2^2} + \left(-2 - 3g_2 + g_2^2\right)\frac{\mu^3}{2m_2^3} + \frac{\mu^4}{m_2^4}\right],$$

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

$$A_3 = g_2^2\left(\lambda_1 - \frac{9}{2}\right)\frac{\mu^2}{4m_2^2} + \left(3(2 + 5g_2 - g_2^2) - 2g_2\lambda_1\right)\frac{\mu^3}{4m_2^3}$$
$$+ (\lambda_1 - 9)\frac{\mu^4}{4m_2^4}$$
(57)

and

$$
B_5 = (2l+1)\lambda_0 \left[-2g_2 \frac{\mu}{m_2} - 3(g_2+1)\frac{\mu^3}{2m_2^3} + \frac{3\mu^4}{2m_2^4} \right] + \left[8(5+3g_2)l(l+1) - 3\left(10+4g_2+g_2^2\right) \right] \frac{\mu^2}{4m_2^2},
$$

$$
B_4 = \frac{3\lambda_0}{l(l+1)} \left[g_2 l(l+1)\frac{\mu}{m_2} + \frac{g_2^2 - 4l(l+1)}{4}\frac{\mu^2}{m_2^2} - \frac{g_2}{2}\frac{\mu^3}{m_2^3} + \frac{\mu^4}{4m_2^4} \right],
$$

$$
B_3 = 2g_2(3-\lambda_1)\frac{\mu}{m_2} + \left[g_2^2 \lambda_2 - 6(1+g_2) + 2\lambda_1 \right] \frac{\mu^2}{m_2^2} + (3-\lambda_2)\left[2g_2 \frac{\mu^3}{m_2^3} - \frac{\mu^4}{m_2^4} \right]. \tag{58}
$$

In order to verify the correctness of our results we will compare them with known results for limiting cases. We now restrict ourselves to pointlike particles by setting $\alpha_{Ea} = 0$. First, we perform the limit of $m_1 \to \infty$ in Eq. (52), i.e., the limit of an infinitely heavy spinless particle. Defining

$$
k = (l-j)(2j+1), \tag{59}
$$

Eq. (52) leads to the nonrecoil result

$$
E^{(6,0)} = \lim_{m_1 \to \infty} E^{(6)} = m_2 (Z\alpha)^6 \left[f^{(6)}(n,j) + \kappa_2 \left(\frac{-9+19k+16k^2}{2|k|(2k-1)(2k+1)(2k+3)n^5} - \frac{3}{2k^2(2k+1)n^4} \right. \right.
$$

$$
\left. - \frac{-3-5k+37k^2+66k^3+24k^4}{2|k|k^2(k+1)(2k-1)(2k+1)^2(2k+3)n^3} \right) + \kappa_2^2 \left(\frac{3(k+1)}{2|k|(2k-1)(2k+1)(2k+3)n^5} - \frac{3}{2k^2(2k+1)^2 n^4} \right.
$$

$$
\left. \left. - \frac{-3-5k+55k^2+120k^3+60k^4}{2|k|k^2(k+1)(2k-1)(2k+1)^3(2k+3)n^3} \right) \right]. \tag{60}
$$

For $\kappa_2 = 0$ and both $l = j \pm 1/2$ expression (60) coincides with the Dirac result acquired by expanding the expression on the right-hand side of Eq. (12) up to the order of $(Z\alpha)^6$. The leading recoil correction of the order of m_2^2/m_1 can be compared with the result from the literature. Defining the function

$$
f_{1/2}^{(6,1)}(n,k) = \frac{1}{2n^6} - \frac{-3-2k+14k^2+10k^3}{|k|(2k-1)(2k+1)(2k+3)n^5} + \frac{3}{8k^2 n^4} + \frac{-3-2k+12k^2+56k^3}{8|k|k^2(2k-1)(2k+1)(2k+3)n^3} \tag{61}
$$

and then by expanding Eq. (52) for large m_1 up to the order of m_2^2/m_1, we get the leading recoil correction,

$$
E^{(6,1)} = (Z\alpha)^6 \frac{m_2^2}{m_1} \left[f_{1/2}^{(6,1)}(n,k) + \kappa_2 \left(-\frac{-12+27k+22k^2}{|k|(2k-1)(2k+1)(2k+3)n^5} + \frac{3}{k^2(2k+1)n^4} \right. \right.
$$

$$
\left. + \frac{-3-5k+49k^2+96k^3+36k^4}{|k|k^2(k+1)(2k-1)(2k+1)^2(2k+3)n^3} \right) + \kappa_2^2 \left(-\frac{9+11k}{2|k|(2k-1)(2k+1)(2k+3)n^5} + \frac{9}{2k^2(2k+1)^2 n^4} \right.
$$

$$
\left. \left. + \frac{3\left(-3-5k+57k^2+128k^3+68k^4\right)}{2|k|k^2(k+1)(2k-1)(2k+1)^3(2k+3)n^3} \right) \right]. \tag{62}
$$

This is in agreement with the known result from [23] 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. (17) up to the order of $(Z\alpha)^6$ with Eq. (75) from Ref. [24]. The resulting sum can be written as follows:

$$
E^{(6,1)}(n,j,l)\Big|_{\kappa_2=0} = \frac{m_2^2}{m_1}(Z\alpha)^6 \left[\frac{1}{2n^6} - \frac{2}{(2j+1)n^5} + \frac{3}{2(2j+1)^2 n^4} + \frac{1}{(2j+1)^3 n^3} \right] + \frac{m_2^2}{m_1}\frac{(Z\alpha)^2}{2\mu^4}\left\langle \frac{\vec{L}^2}{r^4} \right\rangle, \tag{63}
$$

where $\langle 1/r^4 \rangle$ is given in Eq. (E4). Comparing Eq. (62) for $\kappa_2 = 0$ with (63) for $l = j \pm 1/2$ confirms that they agree.

The next term in the mass ratio expansion, of the order of m_2^3/m_1^2 for $\kappa_2 = 0$, is

$$
E^{(6,2)} = (Z\alpha)^6 \frac{m_2^3}{m_1^2} \left[-\frac{15}{16n^6} + \frac{-9-22k+84k^2+72k^3}{4|k|(2k-1)(2k+1)(2k+3)n^5} - \frac{3(2k-1)}{8k^2(2k+1)n^4} \right.
$$

$$
\left. - \frac{3-k-20k^2+184k^3+480k^4+304k^5}{8|k|k^2(k+1)(2k-1)(2k+1)^2(2k+3)n^3} \right], \tag{64}
$$

which can be considered a new result.

Second, we can verify that in the limiting case of Eq. (52), when the spin-1/2 particle becomes infinitely heavy, we obtain a result in agreement with that obtained from the Klein-Gordon equation, i.e.,

$$
E^{(6,0)} = \lim_{m_2 \to \infty} E^{(6)} = m_1 (Z\alpha)^6 f^{(6)}(n,l). \tag{65}
$$

As in the leading relativistic correction $E^{(4)}$, this coincides with the Dirac result in Eq. (60) after replacing j by l and setting $\kappa_2 = 0$. Last, we also present the next term in the expansion of Eq. (52) in terms of the m_1^2/m_2 ratio. Namely,

$$E^{(6,1)} = (Z\alpha)^6 \frac{m_1^2}{m_2} \left[f_0^{(6,1)}(n,l) + g_2 \vec{L} \cdot \vec{s}_2 \left(-\frac{2}{l(l+1)(2l+1)n^5} + \frac{3}{l(l+1)(2l+1)^2 n^4} + \frac{1+6l(l+1)}{l^2(l+1)^2(2l+1)^3 n^3} \right) \right], \quad (66)$$

where $f_0^{(6,1)}(n,l)$ is defined in Eq. (51).

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 D. We express the result using a set of basic spin-dependent operators. To do that we use the identities presented in Appendix G. Moreover, to keep the formulas compact, we introduce the following symbols:

$$\lambda_3 = -\frac{3}{(2l-1)(2l+3)} + \frac{1}{2(2l+1)^2}, \quad (67)$$

$$\lambda_4 = -\frac{3}{4l(l+1)} - \frac{3}{(2l-1)(2l+3)} - \frac{3}{2(2l+1)^2}, \quad (68)$$

$$\lambda_5 = \frac{3}{2l^2} - \frac{1}{2l(l+1)} + \frac{3}{2(l+1)^2}, \quad (69)$$

$$\lambda_6 = \frac{3}{4l^2} - \frac{9}{4l(l+1)} + \frac{3}{4(l+1)^2} + \frac{4}{(2l-1)(2l+3)} - \frac{6}{(2l+1)^2}, \quad (70)$$

$$\lambda_7 = \frac{4}{(2l-1)(2l+3)} + \frac{2}{3(2l+1)^2}, \quad (71)$$

$$\lambda_8 = -\frac{3}{l^2} + \frac{7}{l(l+1)} - \frac{3}{(l+1)^2} - \frac{72}{(2l-1)(2l+3)} + \frac{20}{(2l+1)^2}, \quad (72)$$

$$\lambda_9 = -\frac{1}{l^2} + \frac{3}{l(l+1)} - \frac{1}{(l+1)^2} - \frac{12}{(2l-1)(2l+3)} + \frac{8}{(2l+1)^2}, \quad (73)$$

$$\lambda_{10} = \frac{3}{l^2} + \frac{13}{l(l+1)} - \frac{3}{(l+1)^2} + \frac{36}{(2l-1)(2l+3)} + \frac{32}{(2l+1)^2}, \quad (74)$$

$$\lambda_{11} = \frac{15}{l^2} - \frac{29}{l(l+1)} + \frac{15}{(l+1)^2} - \frac{12}{(2l-1)^2} + \frac{116}{(2l-1)(2l+3)} - \frac{96}{(2l+1)^2} - \frac{12}{(2l+3)^2}, \quad (75)$$

in addition to λ_0, λ_1, and λ_2 defined in the previous section. The final result for $E^{(6)}$ with two spin-1/2 particles is then

$$E^{(6)} = E^{(6)}_{s_1=s_2=0} + \frac{\mu(Z\alpha)^6}{l(l+1)(2l-1)(2l+1)(2l+3)} \left[A + B \vec{L} \cdot \vec{s}_1 + C \vec{L} \cdot \vec{s}_2 + D \vec{s}_1 \cdot \vec{s}_2 + F (L^i L^j)^{(2)} s_1^i s_2^j \right], \quad (76)$$

where we have again subtracted the spinless result $E^{(6)}_{s_1=s_2=0}$ given by Eq. (47). Using once more the definition (56) for $X = A, B, C, D, F$, we get the following coefficients:

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

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

$$A_3 = \frac{\lambda_1 - 3}{8} + \frac{(g_1-2)}{4} \left(\frac{(g_1+2)}{2}(-9+2\lambda_1)\frac{\mu^2}{m_1^2} - (-9+3g_1+2\lambda_1)\frac{\mu^3}{m_1^3} \right)$$
$$+ \frac{\mu^4}{m_1^2 m_2^2} \frac{1}{2} \left(-\frac{9}{2} + \lambda_3 + \frac{g_1^2 g_2^2 \lambda_4}{16} - \lambda_4 \right) + (1 \leftrightarrow 2), \quad (77)$$

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:

$$B_5 = \frac{\mu^2}{8m_1^2} [24(g_1-1) - 6g_1^2 - 3g_1 g_2(1-g_2) + 16l(l+1)(2-g_1)] + \frac{\mu^2}{8m_1 m_2} g_1 [48 + 3g_2(1-g_2) - 64l(l+1)]$$

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

$$B_4 = \frac{3}{8l(l+1)} \left[\frac{\mu^2}{m_1^2} \lambda_0 [2(g_1^2-1) + g_1 g_2(1-g_2) + 8l(l+1)(g_1-1)] + \frac{\mu^2}{m_1 m_2} g_1 \lambda_0 [g_2(g_2-1) + 8l(l+1)] \right.$$

$$+ \frac{\mu^3}{m_1^3}\lambda_0[4(1-g_1) - g_1g_2(1-g_2)] + \frac{\mu^4}{m_1^2m_2^2}\frac{9g_1^2g_2^2 + (g_1g_2+2)[32l(l+1)-24]}{8(2l+1)}\Bigg],$$

$$B_3 = \frac{\mu^2}{2m_1^2}\{-6 + [2g_1(g_1-1) + g_1g_2(1-g_2)]\lambda_2 + (1-g_1)\lambda_5\} + \frac{\mu^2}{2m_1m_2}g_1\{12 - [2+g_2(1-g_2)]\lambda_2 - \lambda_5\}$$

$$+ \frac{\mu^3}{2m_1^3}\{12(g_1-1) + [4(1-g_1) - g_1g_2(1-g_2)]\lambda_2\} + \frac{\mu^4}{2m_1^2m_2^2}\left(-6 + (2+g_1g_2)\lambda_2 + \frac{3}{8}g_1^2g_2^2\lambda_6\right). \tag{78}$$

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

$$D_5 = \frac{\mu^2}{m_1m_2}\frac{l(l+1)\,g_1g_2}{6} + \frac{\mu^4}{m_1^2m_2^2}\frac{4l(l+1)}{3},$$

$$D_4 = -\frac{\mu^3}{m_1^2m_2}(g_1-2)\lambda_0 - \frac{\mu^2}{2m_1m_2}\lambda_0[2(1-g_1) + g_1g_2] - \frac{\mu^4}{m_1^2m_2^2}\frac{3\left(g_1^2g_2^2 - 16\right) + 64l(l+1)}{32(2l+1)} + (1 \leftrightarrow 2),$$

$$D_3 = \frac{\mu^3}{m_1^2m_2}\frac{2(g_1-2)(\lambda_1-3)}{3} + \frac{\mu^2}{12m_1m_2}\{24(g_1-1) - 15g_1g_2 + 4[2(1-g_1) + g_1g_2]\lambda_1\}$$

$$+ \frac{\mu^4}{2m_1^2m_2^2}\left(\frac{1}{12}\left(g_1^2g_2^2 - 16\right)\lambda_4 - 6 + \lambda_7\right) + (1 \leftrightarrow 2). \tag{79}$$

Finally, the coefficient F of the tensor spin-spin interaction is the most complicated and equals

$$F_5 = \frac{1}{(2l-1)(2l+3)}\Bigg[\frac{\mu^3}{m_1^2m_2}\frac{9}{4}(g_1-2)[4 - 6g_2 + 3g_1g_2 + 16\,l(l+1)]$$

$$+ \frac{\mu^2}{2m_1m_2}\left(18(1-g_1) - \frac{45}{4}g_1g_2 + l(l+1)[47g_1g_2 + 72(1-g_1)]\right)$$

$$+ \frac{\mu^4}{m_1^2m_2^2}\left(\lambda_0(5-3g_1g_2)(2l+1) + 6 + \frac{9}{2}g_1g_2 - \frac{9}{8}g_1^2g_2^2\right)\Bigg] + (1 \leftrightarrow 2), \tag{80}$$

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

$$+ \frac{\mu^2}{m_1m_2}\frac{3}{8l(l+1)(2l+1)}\{48(g_2-1) - 15g_1g_2 + l(l+1)[32(g_2-1) - 28g_1g_2]\}$$

$$+ \frac{3\mu^4}{2m_1^2m_2^2}\left(\frac{48 - 72g_1g_2 + 15g_1^2g_2^2 + l(l+1)(12g_1^2g_2^2 - 64)}{16l(l+1)(2l+1)} - \frac{3g_1^2g_2^2}{4\lambda_0}\right) + (1 \leftrightarrow 2), \tag{81}$$

$$F_3 = \frac{\mu^3}{4m_1^2m_2}(g_1-2)[8\lambda_8 + 9(g_1-2)g_2\lambda_9] + \frac{\mu^2}{8m_1m_2}\left(\frac{300g_1g_2}{\lambda_0(2l+1)} - g_1(7g_2-4)\lambda_{10} - 8(g_1-2)\lambda_8 + 36(g_1-1)g_2\lambda_9\right)$$

$$+ \frac{\mu^4}{2m_1^2m_2^2}\left[-\lambda_{10} - \frac{12}{\lambda_0(2l+1)} + \frac{9}{2}g_1g_2\left(\lambda_9 + \frac{4}{\lambda_0(2l+1)}\right) + \frac{1}{16}g_1^2g_2^2\lambda_{11}\right] + (1 \leftrightarrow 2). \tag{82}$$

The above coefficients can be verified against the positronium limit of (76) by setting $m_1 = m_2$, $Z = 1$, and $\kappa_1 = \kappa_2 = 0$, with both particles being pointlike. The obtained result is in agreement with the former one from Ref. [25]. 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. [26] during the evaluation of Eq. (125) for δE_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 δE_5, affecting results in Eqs. (205), (209), (213), and (217). After correcting this error, the results of Ref. [26] are in accordance with those of Ref. [27] as well as with this work.

Exploring now the limiting case of Eq. (76) for two pointlike particles when a particle of mass m_1 is infinitely heavy, we set $\kappa_2 = 0$ and obtain the Dirac result

$$E^{(6,0)} = m_2(Z\alpha)^6 f^{(6)}(n, j), \tag{83}$$

where we used the total angular momentum $\vec{J} = \vec{L} + \vec{s}_2$. The first-order recoil correction given by expanding Eq. (76) for large

m_1 up to the order of m_2^2/m_1, using Eq. (61), reads

$$
\begin{aligned}
E^{(6,1)} =& (Z\alpha)^6 \frac{m_2^2}{m_1} \Bigg[f_{1/2}^{(6,1)}(n,k) + \frac{g_1}{2} \Bigg\{ \vec{s}_1 \cdot \vec{s}_2 \Bigg(\frac{2}{3(2l-1)(2l+1)(2l+3)\,n^5} - \frac{2}{l(l+1)(2l+1)^2\,n^4} \\
&- \frac{2(-3-11l+25l^2+72l^3+36l^4)}{3l^2(l+1)^2(2l-1)(2l+1)^3(2l+3)\,n^3} \Bigg) + \vec{L}\cdot\vec{s}_1 \Bigg(-\frac{-21+32l+32l^2}{2l(l+1)(2l-1)(2l+1)(2l+3)\,n^5} + \frac{3}{2l^2(l+1)^2\,n^4} \\
&+ \frac{-3-5l+19l^2+48l^3+24l^4}{2l^3(l+1)^3(2l-1)(2l+1)(2l+3)\,n^3} \Bigg) + (L^i L^j)^{(2)} s_1^i s_2^j \Bigg(\frac{-63+116l+116l^2}{l(l+1)(2l-1)^2(2l+1)(2l+3)^2\,n^5} \\
&- \frac{3(3+20l+20l^2)}{l^2(l+1)^2(2l-1)(2l+1)^2(2l+3)\,n^4} - \frac{-9-75l-115l^2+640l^3+2120l^4+2160l^5+720l^6}{l^3(l+1)^3(2l-1)^2(2l+1)^3(2l+3)^2\,n^3} \Bigg) \Bigg\} \Bigg]
\end{aligned}
\tag{84}
$$

and looks very compact in comparison to the general case.

VI. SUMMARY AND CONCLUSIONS

We have studied two-body systems with constituents having arbitrary mass, arbitrary magnetic moment, and spin $s = 0$ or $s = 1/2$ in states with angular momentum $l > 1$. The results in Eqs. (47), (52), and (76) are presented in txt format in Supplemental Material [28]. The expansion of energy levels up to α^6 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. Further, Eqs. (73) and (74) of [29] are in agreement with coefficients of terms with even powers of n in the denominator in Eqs. (47), (52), and (76). 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 a range not accessible in normal atoms, namely, from 1 up to 100 MeV. Although there are no definite plans to study rotational states of, for example, protonium or $\bar{p}\alpha$, the availability of a high-precision result is crucial for planning the corresponding measurements.

One such measurement was considered at NIST [15] which involved rotational states of heavy hydrogenlike 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 $(Z\alpha/n)^6$. If necessary, inclusion of the α^7 contribution for an arbitrary mass ratio is feasible along the lines of Ref. [7]. This means that one may ex-

plore the potential for high-accuracy results for an arbitrary two-body system in the search for physics beyond the standard model.

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 of α^6 for the case of two spin-1/2 particles while omitting all the local terms. The derivation proceeds along the same lines as in Ref. [21]. 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_{NRQED} in Eq. (28) and represents the higher-order relativistic correction to the kinetic energy,

$$
\delta H_0 = \frac{p_1^6}{16m_1^5} + \frac{p_2^6}{16m_2^5}.
\tag{A1}
$$

δH_1 comes from the interaction between particles when one vertex is given by the sixth and seventh terms in H_{NRQED} and the other one is eA_0. It leads to

$$
\begin{aligned}
\delta H_1 =& \sum_a \frac{3}{16m_a^4} \left(1 + \frac{4\kappa_a}{3} \right) \vec{s}_a \cdot \left\{ p_a^2, e_a \vec{\mathcal{E}}_a \times \vec{p}_a \right\} \\
&+ \frac{1}{32m_a^4} \left(1 + \frac{s_a(s_a+1)}{3} \right) \left[p_a^2, [p_a^2, V] \right],
\end{aligned}
\tag{A2}
$$

where the potential V is

$$
V = \frac{e_1 e_2}{r} = -\frac{Z\alpha}{r}
\tag{A3}
$$

and the electrostatic fields $\vec{\mathcal{E}}_a$ are defined in Eq. (45).

δH_2 arises when both particles interact via the fifth term in H_{NRQED}. It leads to the effective operator

$$
\begin{aligned}
\delta H_2 =& \frac{e_1 e_2}{4m_1^2 m_2^2} (1+2\kappa_1)(1+2\kappa_2)(\vec{s}_2 \times \vec{p}_2)^i \\
&\times \frac{1}{r^3} \left(\delta^{ij} - 3\frac{r^i r^j}{r^2} \right) (\vec{s}_1 \times \vec{p}_1)^j.
\end{aligned}
\tag{A4}
$$

δH_3 arises when one of the particles interacts through part of the second term in H_{NRQED},

$$-\frac{e}{m}\,\vec{p}\cdot\vec{A} - \frac{e}{m}\,(1+\kappa)\vec{s}\cdot\vec{B}, \tag{A5}$$

while the other particle interacts through part of the third term in H_{NRQED},

$$-\frac{1}{8m^3}\big(\pi^4 - 2e\vec{s}\cdot\vec{B}\,\pi^2 - 2\pi^2 e\vec{s}\cdot\vec{B}\big). \tag{A6}$$

If we define static vector potentials by Eqs. (43) and (44), then we can write the effective operator δH_3 as

$$\delta H_3 = \frac{1}{4}\sum_{a=1,2}\frac{1}{m_a^3}\big\{p_a^2, \vec{p}_a\cdot e_a\vec{\mathcal{A}}_a + \vec{s}_a\cdot(\vec{\nabla}_a\times e_a\vec{\mathcal{A}}_a)\big\}. \tag{A7}$$

δH_4 comes from the exchange of two transverse photons between particles. One of the particles interacts twice by the term (A5) and the other one interacts 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 $\vec{\mathcal{A}}$,

$$\delta H_4 = \sum_{a=1,2}\frac{e_a^2}{2m_a}\,\vec{\mathcal{A}}_a^2. \tag{A8}$$

δH_5 corresponds to the case when one of the particles interacts through the fifth term in H_{NRQED} and the other one interacts through (A5) and eA_0,

$$\delta H_5 = \sum_{a=1,2}\frac{e_a^2\,(1+2\kappa_a)}{4m_a^2}\,\vec{s}_a\cdot(\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a - \vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a). \tag{A9}$$

δH_6 represents the retardation correction to the single transverse photon exchange between particles when both particles interact through (A5). The corresponding α^6 contribution is

$$\langle\delta H_6\rangle = \sum_{a\neq b}\sum_b -\frac{e_a e_b}{m_a m_b}\int\frac{d^3k}{(2\pi)^3\,2\,k^4}\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right)$$
$$\times\,\langle(\vec{p}_a + \vec{s}_a\times\vec{\nabla}_a)^i\,e^{i\vec{k}\cdot\vec{r}_a}(H_0 - E_0)^2$$
$$\times\,(\vec{p}_b + \vec{s}_b\times\vec{\nabla}_b)^j\,e^{-i\vec{k}\cdot\vec{r}_b}\rangle. \tag{A10}$$

Commuting out the expression $(H_0 - E_0)^2$ and performing the integration, we obtain the effective operator δH_6 in Eq. (36).

δH_7 is a retardation correction in a single transverse photon exchange where one vertex is (A5), and the other one comes from the fifth term in H_{NRQED},

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

The resulting effective operator is then

$$\delta H_7 = \sum_{a=1,2}\frac{e_a^2\,(1+2\kappa_a)}{4m_a^2}\,\vec{s}_a\cdot(\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a - \vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a)$$
$$+\,\frac{ie_a\,(1+2\kappa_a)}{8m_a^3}\big[\vec{\mathcal{A}}_a\cdot(\vec{p}_a\times\vec{s}_a)$$
$$+\,(\vec{p}_a\times\vec{s}_a)\cdot\vec{\mathcal{A}}_a, p_a^2\big]. \tag{A12}$$

δH_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 interacts through eA_0. Then

$$\delta H_8 = -\frac{1}{2}\sum_a\left(\alpha_{Ea} - \frac{s_a(s_a+1)}{3\,m_a^3}\right)\frac{Z^2\alpha^2}{r^4}. \tag{A13}$$

Finally, the effective operator δH_9 arises when one of the particles interacts through part of the third term in H_{NRQED},

$$\frac{e\,\kappa}{4m^3}\{\vec{\pi}\cdot\vec{B}, \vec{\pi}\cdot\vec{s}\}, \tag{A14}$$

and the second particle interacts 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

$$\delta H_9 = \sum_a\frac{e_a\kappa_a}{4m_a^3}\{\vec{p}_a\cdot\vec{\nabla}_a\times\vec{\mathcal{A}}_a, \vec{p}_a\cdot\vec{s}_a\}. \tag{A15}$$

This concludes the derivation of effective operators of the order of α^6 for two spin-1/2 particles for states with $l > 1$.

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-δ-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 δH_2, δH_5, δH_7, and δH_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

$$\delta E_0 = \frac{\mu^2}{2}\left(\frac{1}{m_1^5} + \frac{1}{m_2^5}\right)\left(\mu E_0^3 + 3\mu E_0^2\left\langle\frac{1}{r}\right\rangle\right.$$
$$\left. +\,3\mu E_0\left\langle\frac{1}{r^2}\right\rangle + \mu\left\langle\frac{1}{r^3}\right\rangle + \frac{1}{2}\left\langle\frac{1}{r^4}\right\rangle\right), \tag{B5}$$

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

$$\delta E_1 = -\frac{\mu}{8}\left(\frac{1}{m_1^4} + \frac{1}{m_2^4}\right)\left\langle\frac{1}{r^4}\right\rangle, \tag{B6}$$

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

$$\delta E_4 = \frac{E_0}{m_1 m_2}\left\langle\frac{1}{r^2}\right\rangle + \frac{1}{m_1 m_2}\left\langle\frac{1}{r^3}\right\rangle$$
$$+ \frac{1}{2\mu\, m_1 m_2}\left[1 - \frac{3l(l+1)}{4}\right]\left\langle\frac{1}{r^4}\right\rangle. \tag{B8}$$

The retardation correction due to single transverse photon exchange is

$$\delta E_6 = -\frac{E_0}{2m_1 m_2}\left\langle\frac{1}{r^2}\right\rangle + \frac{1}{m_1 m_2}\left[-\frac{1}{4} + \frac{\mu E_0[1 + l(l+1)]}{m_1 m_2}\right]$$
$$\times \left\langle\frac{1}{r^3}\right\rangle + \frac{1}{m_1 m_2}\left[-\frac{1}{8\mu} + \frac{\mu}{m_1 m_2} + l(l+1)\right.$$
$$\times \left.\left(\frac{3}{8\mu} + \frac{\mu}{m_1 m_2}\right)\right]\left\langle\frac{1}{r^4}\right\rangle + \frac{3}{2m_1^2 m_2^2}\left(1 - \frac{l^2(l+1)^2}{4}\right)$$
$$\times \left\langle\frac{1}{r^5}\right\rangle. \tag{B9}$$

Finally, the correction δE_8 is

$$\delta E_8 = -\frac{1}{2}(\alpha_{E1} + \alpha_{E2})\left\langle\frac{1}{r^4}\right\rangle, \tag{B10}$$

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 of $(Z\alpha)^6$ is induced by the Breit Hamiltonian $H^{(4)}$,

$$\delta_2 E^{(6)} = \left\langle H^{(4)}\frac{1}{(E_0 - H_0)'}H^{(4)}\right\rangle. \tag{B11}$$

In general, such a contribution contains singularities that must be isolated by means of regularization and then canceled when combined with the corresponding first-order contribution. All such singularities are, however, proportional to the Dirac δ 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)

$$H^{(4)} = -A\left[\frac{1}{r}H_0 + H_0\frac{1}{r}\right] - \frac{B}{r^2} + \frac{C}{r^3}, \tag{B12}$$

where

$$A = \frac{\mu}{m_1 m_2} + \frac{\mu^2}{2}\left(\frac{1}{m_1^3} + \frac{1}{m_2^3}\right), \tag{B13}$$

$$B = \frac{2\mu}{m_1 m_2} + \frac{\mu^2}{2}\left(\frac{1}{m_1^3} + \frac{1}{m_2^3}\right), \tag{B14}$$

$$C = \frac{l(l+1)}{2m_1 m_2}. \tag{B15}$$

After elementary calculations we can express the second-order contribution in terms of the first-order operators $\langle 1/r^k\rangle$ listed in Appendix E and $\mathcal{E}_{ij}$ listed in Appendix F. Then,

$$\delta_2 E^{(6)} = 4A^2 E_0\left\langle\frac{1}{r}\right\rangle^2 - 4A^2 E_0\left\langle\frac{1}{r^2}\right\rangle + 2AB\left\langle\frac{1}{r}\right\rangle\left\langle\frac{1}{r^2}\right\rangle$$
$$- 2AB\left\langle\frac{1}{r^3}\right\rangle - 2AC\left\langle\frac{1}{r}\right\rangle\left\langle\frac{1}{r^3}\right\rangle + \left(2AC - \frac{A^2}{2\mu}\right)\left\langle\frac{1}{r^4}\right\rangle$$
$$+ 4A^2 E_0^2\,\mathcal{E}_{11} + 4ABE_0\,\mathcal{E}_{12} + B^2\,\mathcal{E}_{22} - 4ACE_0\,\mathcal{E}_{13}$$
$$- 2BC\,\mathcal{E}_{23} + C^2\,\mathcal{E}_{33}. \tag{B16}$$

Combining the first-order contribution $\delta_1 E^{(6)}$ with the second-order term $\delta_2 E^{(6)}$ and using the expectation values from Appendixes E and F, we obtain the total correction to the energy $E^{(6)}$ for two spinless particles, presented in Eq. (47).

APPENDIX C: EXPECTATION VALUES FOR PARTICLES WITH $s_1 = 0$ AND $s_2 = 1/2$

The next case is when one particle is spinless and the other one has spin $s_2 = 1/2$. In contrast to the case $s_1 = s_2 = 0$ described in Appendix B the effective operators δH_5 and δH_7 do not vanish, and operators δH_1, δH_3, δH_4, and δH_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

$$\delta E_1 = \delta E_1^{s_1=s_2=0} - \mu\left[\frac{1}{32m_2^4} + \frac{\vec{L}\cdot\vec{s}_2}{m_2^4}\left(\frac{3}{4} + \kappa_2\right)\right]\left\langle\frac{1}{r^4}\right\rangle$$
$$- \frac{\mu E_0}{m_2^4}\left(\frac{3}{4} + \kappa_2\right)\vec{L}\cdot\vec{s}_2\left\langle\frac{1}{r^3}\right\rangle. \tag{C1}$$

Here $\delta E_1^{s_1=s_2=0}$ stands for the spinless result (B6). We will use this notation throughout the following Appendixes.

The next term $\delta E_2 = 0$ again vanishes. The remaining non-vanishing contributions are

$$\delta E_3 = \delta E_3^{s_1=s_2=0}$$
$$- \frac{\mu}{m_1 m_2}E_0\left(\frac{(1+\kappa_2)}{m_1^2} + \frac{1}{m_2^2}\right)\vec{L}\cdot\vec{s}_2\left\langle\frac{1}{r^3}\right\rangle$$
$$- \frac{\mu}{m_1 m_2}\left(\frac{(1+\kappa_2)}{m_1^2} + \frac{1}{m_2^2}\right)\vec{L}\cdot\vec{s}_2\left\langle\frac{1}{r^4}\right\rangle, \tag{C2}$$

$$\delta E_4 = \delta E_4^{s_1=s_2=0} + \frac{1}{m_1 m_2}\left[\frac{1}{4m_2}(1+\kappa_2)^2\right.$$
$$\left. - \frac{(1+\kappa_2)}{2m_2}\vec{L}\cdot\vec{s}_2\right]\left\langle\frac{1}{r^4}\right\rangle, \tag{C3}$$

$$\delta E_5 = -\frac{(1+2\kappa_2)}{4m_1 m_2^2} \vec{L} \cdot \vec{s}_2 \left\langle \frac{1}{r^4} \right\rangle, \tag{C4}$$

$$\delta E_6 = E_6^{s_1=s_2=0} + \frac{\mu}{2m_1 m_2^3}(1+\kappa_2)\vec{L} \cdot \vec{s}_2 \left\langle \frac{1}{r^4} \right\rangle, \tag{C5}$$

$$\delta E_7 = -\frac{(1+2\kappa_2)}{4m_1 m_2^2}\left(1+\frac{\mu}{m_2}\right)\vec{L} \cdot \vec{s}_2 \left\langle \frac{1}{r^4} \right\rangle. \tag{C6}$$

Contribution δE_8 can be obtained from the spinless case (B10) with the transition $\alpha_{E2} \to \alpha_{E2} - (4m_2^3)^{-1}$, and $\delta E_9 = 0$.

Second-order contribution $\delta_2 E^{(6)}$. For the second-order contribution we repeat the derivation from the spinless case with one difference. The Breit Hamiltonian is again expressed in the form (B12) with 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 lines leading to the result (B16), where for coefficient C we obtain

$$C = \frac{\vec{L}^2}{2m_1 m_2} + \left(\frac{1+2\kappa_2}{2m_2^2} + \frac{1+\kappa_2}{m_1 m_2}\right)\vec{L} \cdot \vec{s}_2 \tag{C7}$$

instead of (B15). To evaluate the term $(\vec{L} \cdot \vec{s}_2)^2$ we use Eq. (G2).

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 (30)–(42) with both spins being nonzero.

First-order contribution $\delta_1 E^{(6)}$. The contribution to the energy of the order of $(Z\alpha)^6$ for states with $l > 1$ from the first-order operators is again expressed in the form of series (B2). The effective operators δH_i may contain spin-dependent terms from both particles. The first contribution δE_0 is the same as in the spinless case, given by Eq. (B5). The next contribution is

$$\begin{aligned}
\delta E_1 = \delta E_1^{s_1=s_2=0} &- \mu\left[\frac{1}{32m_1^4} + \frac{1}{32m_2^4}\right. \\
&+ \frac{\vec{L} \cdot \vec{s}_1}{m_1^4}\left(\frac{3}{4}+\kappa_1\right) + \left.\frac{\vec{L} \cdot \vec{s}_2}{m_2^4}\left(\frac{3}{4}+\kappa_2\right)\right]\left\langle \frac{1}{r^4}\right\rangle \\
&- \mu E_0 \left[\frac{1}{m_1^4}\left(\frac{3}{4}+\kappa_1\right)\vec{L} \cdot \vec{s}_1 + \frac{1}{m_2^4}\left(\frac{3}{4}+\kappa_2\right)\vec{L} \cdot \vec{s}_2\right] \\
&\times \left\langle \frac{1}{r^3}\right\rangle. \tag{D1}
\end{aligned}$$

Correction δE_2 does not vanish now and is

$$\begin{aligned}
\delta E_2 = \frac{1}{4m_1^2 m_2^2}(1+2\kappa_1)(1+2\kappa_2)&\left[\left(4\mu E_0\left\langle\frac{1}{r^3}\right\rangle\right.\right. \\
&+ \left.4\mu\left\langle\frac{1}{r^4}\right\rangle - 12(l-1)(l+2)\left\langle\frac{1}{r^5}\right\rangle\right)\frac{(L^i L^j)^{(2)} s_1^i s_2^j}{(2l-1)(2l+3)} \\
&+ \left(4\mu E_0\left\langle\frac{1}{r^3}\right\rangle + 4\mu\left\langle\frac{1}{r^4}\right\rangle - 3(l-1)(l+2)\left\langle\frac{1}{r^5}\right\rangle\right) \\
&\times \left.\frac{\vec{s}_1 \cdot \vec{s}_2}{3}\right], \tag{D2}
\end{aligned}$$

where we have used the expectation value identity

$$\left\langle \delta^{ij} - 3\frac{r^i r^j}{r^2}\right\rangle = \frac{6}{(2l-1)(2l+3)}\langle (L^i L^j)^{(2)}\rangle. \tag{D3}$$

The next terms are

$$\begin{aligned}
\delta E_3 = \delta E_3^{s_1=s_2=0} + \frac{\mu}{m_1 m_2}&\left\{\left(-E_0\left\langle\frac{1}{r^3}\right\rangle - \left\langle\frac{1}{r^4}\right\rangle\right)\left[\left(\frac{1+\kappa_2}{m_1^2}+\frac{1}{m_2^2}\right)\vec{L}\cdot\vec{s}_2 + \left(\frac{1+\kappa_1}{m_2^2}+\frac{1}{m_1^2}\right)\vec{L}\cdot\vec{s}_1\right]\right. \\
&+ 6\left.\left(\frac{1+\kappa_2}{m_1^2}+\frac{1+\kappa_1}{m_2^2}\right)\left\langle\frac{1}{r^3}\left(E_0+\frac{1}{r}\right)\frac{(L^i L^j)^{(2)} s_1^i s_2^j}{(2l-1)(2l+3)}\right\rangle\right\}, \tag{D4}
\end{aligned}$$

$$\delta E_4 = \delta E_4^{s_1=s_2=0} + \frac{1}{m_1 m_2}\left[\frac{1}{4m_1}(1+\kappa_1)^2 + \frac{1}{4m_2}(1+\kappa_2)^2 - \frac{(1+\kappa_1)}{2m_1}\vec{L}\cdot\vec{s}_1 - \frac{(1+\kappa_2)}{2m_2}\vec{L}\cdot\vec{s}_2\right]\left\langle\frac{1}{r^4}\right\rangle, \tag{D5}$$

$$\delta E_5 = -\frac{(1+2\kappa_1)}{4m_1^2 m_2}\left[\vec{L}\cdot\vec{s}_1 - 4(1+\kappa_2)\left(\frac{(L^i L^j)^{(2)} s_1^i s_2^j}{(2l-1)(2l+3)} + \frac{\vec{s}_1\cdot\vec{s}_2}{3}\right)\right]\left\langle\frac{1}{r^4}\right\rangle + (1 \leftrightarrow 2), \tag{D6}$$

$$\begin{aligned}
\delta E_6 = \delta E_6^{s_1=s_2=0} + \frac{\mu}{m_1 m_2}&\left[\frac{1}{2m_1^2}(1+\kappa_1)\vec{L}\cdot\vec{s}_1 + \frac{1}{2m_2^2}(1+\kappa_2)\vec{L}\cdot\vec{s}_2\right]\left\langle\frac{1}{r^4}\right\rangle \\
&- \frac{\mu}{m_1^2 m_2^2}(1+\kappa_1)(1+\kappa_2)\left(\frac{2}{3}\vec{s}_1\cdot\vec{s}_2 - \frac{(L^i L^j)^{(2)} s_1^i s_2^j}{(2l-1)(2l+3)}\right)\left\langle\frac{1}{r^4}\right\rangle, \tag{D7}
\end{aligned}$$

$$\delta E_7 = -\frac{\mu(1+2\kappa_1)}{4m_1^3 m_2}\left[\vec{L}\cdot\vec{s}_1 + 4(1+\kappa_2)\left(\frac{(L^i L^j)^{(2)} s_1^i s_2^j}{(2l-1)(2l+3)} + \frac{\vec{s}_1\cdot\vec{s}_2}{3}\right)\right]\left\langle\frac{1}{r^4}\right\rangle + (1 \leftrightarrow 2) + \delta E_5. \tag{D8}$$

Contribution δE_8 is obtained from the spinless case (B10) with the transition $\alpha_{Ej} \to \alpha_{Ej} - (4m_j^3)^{-1}$. Finally,

$$\delta E_9 = \frac{\kappa_1(1+\kappa_2)}{2m_1^3 m_2}\left[\left(8\mu E_0\left\langle\frac{1}{r^3}\right\rangle + 8\mu\left\langle\frac{1}{r^4}\right\rangle - 6(l-1)(l+2)\left\langle\frac{1}{r^5}\right\rangle\right)\frac{(L^i L^j)^{(2)}s_1^i s_2^j}{(2l-1)(2l+3)}\right.$$
$$\left. + \left(-\frac{4}{3}\mu E_0\left\langle\frac{1}{r^3}\right\rangle - \frac{4}{3}\mu\left\langle\frac{1}{r^4}\right\rangle + (l-1)(l+2)\left\langle\frac{1}{r^5}\right\rangle\right)\vec{s}_1\cdot\vec{s}_2\right] + (1\leftrightarrow 2). \tag{D9}$$

The total first-order correction $\delta_1 E^{(6)}$ is the 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 tensorlike term in the Breit Hamiltonian. We write the Hamiltonian $H^{(4)}$ in the form

$$H^{(4)} = -\frac{\mu^2}{2}\left(\frac{1}{m_1^3}+\frac{1}{m_2^3}\right)H_0^2 - \frac{\mu}{r^2}\left[\frac{\mu}{2}\left(\frac{1}{m_1^3}+\frac{1}{m_2^3}\right)+\frac{2}{m_1 m_2}\right] - \mu\left[\frac{\mu}{2}\left(\frac{1}{m_1^3}+\frac{1}{m_2^3}\right)+\frac{1}{m_1 m_2}\right]\left(\frac{1}{r}H_0 + H_0\frac{1}{r}\right)$$
$$+ \frac{1}{r^3}\left[\left(\frac{1+\kappa_1}{m_1 m_2}+\frac{1+2\kappa_1}{2m_1^2}\right)\vec{L}\cdot\vec{s}_1 + \left(\frac{1+\kappa_2}{m_1 m_2}+\frac{1+2\kappa_2}{2m_2^2}\right)\vec{L}\cdot\vec{s}_2 + \frac{\vec{L}^2}{2m_1 m_2}\right] + \frac{3}{m_1 m_2}(1+\kappa_1)(1+\kappa_2)\frac{(n^i n^j)^{(2)}s_1^i s_2^j}{r^3}, \tag{D10}$$

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

$$\left\langle\frac{(n^i n^j)^{(2)}s_1^i s_2^j}{r^3}\frac{1}{(E_0-H_0)'}\frac{(n^k n^l)^{(2)}s_1^k s_2^l}{r^3}\right\rangle. \tag{D11}$$

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 $Q = (n^i n^j)^{(2)}s_1^i s_2^j$ and by $\hat{P}_l$ the projection operator in the subspace with angular momentum l. Assuming that the outer states have the angular momentum l, we get for the diagonal term

$$Q\hat{P}_l Q = \frac{l(l+1)}{24(2l-1)(2l+3)}\left(1+\frac{4}{3}\vec{s}_1\cdot\vec{s}_2\right)$$
$$-\frac{1}{8(2l-1)(2l+3)}\vec{L}\cdot(\vec{s}_1+\vec{s}_2)$$
$$-\frac{(2l-3)(2l+5)}{6(2l-1)^2(2l+3)^2}(L^i L^j)^{(2)}s_1^i s_2^j. \tag{D12}$$

For off-diagonal terms we get

$$Q\hat{P}_{l+2} Q = \frac{(l+1)(l+2)}{16(2l+1)(2l+3)}\left(1+\frac{4}{3}\vec{s}_1\cdot\vec{s}_2\right)$$
$$+\frac{(l+2)}{8(2l+1)(2l+3)}\vec{L}\cdot(\vec{s}_1+\vec{s}_2)$$
$$+\frac{(l+2)}{2(2l+1)(2l+3)^2}(L^i L^j)^{(2)}s_1^i s_2^j \tag{D13}$$

and

$$Q\hat{P}_{l-2} Q = \frac{l(l-1)}{16(2l-1)(2l+1)}\left(1+\frac{4}{3}\vec{s}_1\cdot\vec{s}_2\right)$$
$$-\frac{(l-1)}{8(2l-1)(2l+1)}\vec{L}\cdot(\vec{s}_1+\vec{s}_2)$$
$$+\frac{(l-1)}{2(2l-1)^2(2l+1)}(L^i L^j)^{(2)}s_1^i s_2^j. \tag{D14}$$

The radial part of the second-order contribution (D11) is, in the case of the diagonal term $l' = l$, equal to $\mathcal{E}_{33}$, Eq. (F7). For off-diagonal terms Eqs. (F15) and (F20) are used.

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 [17], and setting $Z\alpha = 1$, they are

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

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

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

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

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

These equations are valid for $l > 1$.

APPENDIX F: THE SECOND-ORDER MATRIX ELEMENTS

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

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

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

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

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

$$\mathcal{E}_{22} = -\mu^3 \left(\frac{6}{(2l+1)^2 n^4} + \frac{4}{(2l+1)^3 n^3} \right), \tag{F4}$$

$$\mathcal{E}_{13} = \frac{\mu}{2l(l+1)} \left(2\mathcal{E}_{12} - \left\langle \frac{1}{r^2} \right\rangle \right), \tag{F5}$$

$$\mathcal{E}_{23} = \frac{\mu}{l(l+1)} \left(\mathcal{E}_{22} - \left\langle \frac{1}{r^3} \right\rangle \right), \tag{F6}$$

$$\mathcal{E}_{33} = \frac{\mu^2}{l^2(l+1)^2} \mathcal{E}_{22} - \frac{\mu^2}{l^2(l+1)^2} \left\langle \frac{1}{r^3} \right\rangle - \frac{3\mu}{2l(l+1)} \left\langle \frac{1}{r^4} \right\rangle. \tag{F7}$$

The second-order expectation values involving the $1/r^3$ operator were derived with the help of the identity

$$\frac{1}{r^3} = \frac{\mu}{l(l+1)} \left(\frac{1}{r^2} - [D_r, H_0] \right), \tag{F8}$$

where $D_r = \partial_r + \frac{1}{r}$. 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

$$\left\langle \frac{1}{r^3} \frac{1}{(E_0 - H_{l+2})'} \frac{1}{r^3} \right\rangle, \tag{F9}$$

in which we defined the radial part of the Hamiltonian as

$$H_l = -\frac{1}{2\mu} \left(\partial_r^2 + \frac{2}{r}\partial_r - \frac{l(l+1)}{r^2} \right) - \frac{1}{r}. \tag{F10}$$

Using the identities

$$\frac{1}{r^3} = H_l \hat{\alpha} - \hat{\alpha} H_{l+2}, \tag{F11}$$

$$\frac{1}{r^3} = \hat{\beta} H_l - H_{l+2} \hat{\beta}, \tag{F12}$$

where operators $\hat{\alpha}$ and $\hat{\beta}$ are defined by

$$\hat{\alpha} = -\frac{\mu}{3(l+1)(l+2)} D_r - \frac{\mu(2l+3)}{3(l+1)(l+2)} \frac{1}{r} + \frac{\mu^2}{3(2l+3)(l+1)(l+2)}, \tag{F13}$$

$$\hat{\beta} = \frac{\mu}{3(l+1)(l+2)} D_r - \frac{\mu(2l+3)}{3(l+1)(l+2)} \frac{1}{r} + \frac{\mu^2}{3(2l+3)(l+1)(l+2)}, \tag{F14}$$

we can simplify the radial part to

$$\left\langle \frac{1}{r^3} \frac{1}{(E_0 - H_{l+2})'} \frac{1}{r^3} \right\rangle = \langle \hat{\alpha} (E_0 - H_{l+2}) \hat{\beta} \rangle$$

$$= -\frac{2\mu^2(2l+3)}{9(l+1)^2(l+2)^2} E_0 \left\langle \frac{1}{r^2} \right\rangle$$

$$- \frac{\mu^2(7+9l+3l^2)}{3(l+1)^2(l+2)^2(2l+3)} \left\langle \frac{1}{r^3} \right\rangle$$

$$- \frac{\mu(27+45l+25l^2+4l^3)}{18(l+1)^2(l+2)^2} \left\langle \frac{1}{r^4} \right\rangle. \tag{F15}$$

For the radial part with the angular momentum of the intermediate states equal to $l' = l - 2$ we repeat the calculation using

$$\frac{1}{r^3} = H_l \hat{\delta} - \hat{\delta} H_{l-2}, \tag{F16}$$

$$\frac{1}{r^3} = \hat{\gamma} H_l - H_{l-2} \hat{\gamma}, \tag{F17}$$

with

$$\hat{\delta} = -\frac{\mu}{3l(l-1)} D_r - \frac{\mu(1-2l)}{3l(l-1)} \frac{1}{r} - \frac{\mu^2}{3l(l-1)(2l-1)}, \tag{F18}$$

$$\hat{\gamma} = \frac{\mu}{3l(l-1)} D_r - \frac{\mu(1-2l)}{3l(l-1)} \frac{1}{r} - \frac{\mu^2}{3l(l-1)(2l-1)}. \tag{F19}$$

Then the radial part is

$$\left\langle \frac{1}{r^3} \frac{1}{(E_0 - H_{l-2})'} \frac{1}{r^3} \right\rangle = \langle \hat{\delta} (E_0 - H_{l-2}) \hat{\gamma} \rangle$$

$$= \frac{2\mu^2(2l-1)}{9(l-1)^2 l^2} E_0 \left\langle \frac{1}{r^2} \right\rangle$$

$$+ \frac{\mu^2(1-3l+3l^2)}{3(l-1)^2 l^2(2l-1)} \left\langle \frac{1}{r^3} \right\rangle$$

$$+ \frac{\mu(-3+7l-13l^2+4l^3)}{18(l-1)^2 l^2} \left\langle \frac{1}{r^4} \right\rangle. \tag{F20}$$

Equations (F15) and (F20) are used for the 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:

$$(\vec{L} \cdot \vec{s}_1)^2 = \frac{l(l+1)}{4} - \frac{1}{2}\vec{L} \cdot \vec{s}_1, \tag{G1}$$

$$(\vec{L} \cdot \vec{s}_2)^2 = \frac{l(l+1)}{4} - \frac{1}{2}\vec{L} \cdot \vec{s}_2, \tag{G2}$$

$$\frac{1}{2}\{\vec{L} \cdot \vec{s}_1, \vec{L} \cdot \vec{s}_2\} = (L^i L^j)^{(2)} s_1^i s_2^j + \frac{l(l+1)}{3}\vec{s}_1 \cdot \vec{s}_2, \tag{G3}$$

$$\frac{1}{2}\{(L^i L^j)^{(2)} s_1^i s_2^j, \vec{L} \cdot \vec{s}_1\} = \frac{(2l-1)(2l+3)}{24}\vec{L} \cdot \vec{s}_2$$
$$- \frac{3}{4}(L^i L^j)^{(2)} s_1^i s_2^j, \tag{G4}$$

$$\frac{1}{2}\{(L^i L^j)^{(2)} s_1^i s_2^j, \vec{s}_1 \cdot \vec{s}_2\} = \frac{1}{4}(L^i L^j)^{(2)} s_1^i s_2^j, \tag{G5}$$

$$(\vec{s}_1 \cdot \vec{s}_2)^2 = \frac{3}{16} - \frac{1}{2}\vec{s}_1 \cdot \vec{s}_2. \tag{G6}$$

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.

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