Eighth-order Foldy-Wouthuysen transformation

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The calculation of higher-order binding corrections to bound systems is a fundamental problem of theoretical physics. For any nonrelativistic expansion, one needs the Foldy-Wouthuysen transformation, which disentangles the particle and the antiparticle degrees of freedom. This transformation is carried out here to eighth order in the momenta or to eighth order in the momentum operators, which is equivalent to the eighth order of the fine-structure constant. Matrix elements of the eighth-order terms are evaluated for $F_{5/2}$ and $F_{7/2}$ states in hydrogenlike ions and compared with the Dirac-Coulomb energy levels.

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I. OVERVIEW

The Foldy-Wouthuysen transformation [1] is one of the most essential ingredients of the bound-state formalism [2]. Specifically, the Foldy-Wouthuysen transformation enables one to disentangle the particle and antiparticle degrees of freedom and write separate particle and antiparticle Hamiltonians for spin-1/2 particles coupled to electromagnetic and gravitational fields [3]. In the case of a free Dirac particle, the Foldy-Wouthuysen transformation can be carried out to all orders in the momentum operators, and the transformed Hamiltonian takes the simple form [see Eq. (11.17) of Ref. [2]]

$$H_{\rm FW} = \begin{pmatrix} \sqrt{\vec{p}^{\,2}+m^2}\cdot \mathbb{1}_{2\times2} & 0 \\ 0 & -\sqrt{\vec{p}^{\,2}+m^2}\cdot \mathbb{1}_{2\times2} \end{pmatrix}, \qquad (1)$$

where $\vec{p}$ is the momentum operator. In other cases, where the electron is subjected to nontrivial couplings to electromagnetic or gravitational fields [3], it is possible to carry out the Foldy-Wouthuysen transformation only up to a finite order in a chosen expansion parameter, which can, in many cases, be chosen as a typical momentum scale of the physical problem. Here we are concerned with an electron coupled to a general electromagnetic field, described by a vector potential $\vec{A}$ and a scalar potential Φ.

For bound systems, including bound Coulomb systems and electrons bound in a Penning trap [4,5], one can identify the typical momentum scale as αmc, where m is the electron mass, c is the speed of light, and α is the fine-structure constant or a generalization thereof. Henceforth, we will use natural units with $\hbar = \epsilon_0 = c = 1$ and $e^2 = 4\pi\alpha$. Specifically, for electrons bound in Penning traps, one can define a generalized cyclotron fine-structure constant according to Eq. (35) of Ref. [5]. We define the kinetic momentum

$$\vec{\pi} = \vec{p} - e\vec{A}, \qquad (2)$$

where e is the electron charge. For the electric field $\vec{E}$ and the magnetic field $\vec{B}$, as well as its time derivative $e\partial_t\vec{E}$, we assume the scaling [see Eq. (47) of Ref. [5]]

$$\vec{\pi} \sim \alpha, \quad e\vec{A} \sim \alpha, \quad e\vec{B} \sim \alpha^2,$$
$$V \equiv e\Phi, \quad e\vec{E} = -\vec{\nabla}V \sim \alpha^3, \quad e\partial_t\vec{E} \sim \alpha^5. \qquad (3)$$

For the fourth-order Foldy-Wouthuysen transformation, a particularly instructive derivation is presented in Ref. [6]. The sixth-order Foldy-Wouthuysen transformation has been considered extensively in the literature [see Eqs. (36)–(38) of Ref. [7], Ref. [8], Eqs. (15) and (20) of Ref. [9], Eq. (7) of Ref. [10], and Ref. [11]].

One might be surprised about the scaling $e\vec{B} \sim \alpha^2$, e.g., when comparing to Eq. (30) of Ref. [12]. Our assumption here is that both terms $\vec{p}$ and $e\vec{A}$ in the relation $\vec{\pi} = \vec{p} - e\vec{A}$ carry the same power of α. Let us consider the vector potential for a homogeneous magnetic trap field in the symmetric gauge, $\vec{A} = \frac{1}{2}(\vec{B}\times\vec{r}\,)$. In view of the fact that the position operator fulfills the scaling $|\vec{r}\,| \sim \alpha^{-1}$, we require that $e\vec{B} \sim \alpha^2$ to restore the scaling of $\vec{\pi}$. This particular scaling is relevant, for example, for the strong field encountered in Penning traps [5,13,14], where the fine-structure constant α finds a natural generalization in terms of a cyclotron fine-structure constant α_c.

Here it is our goal to extend the formalism to the eighth order in the fine-structure constant. We venture to obtain the general Hamiltonian for electromagnetic coupling in Sec. II and apply the obtained results to subsets of bound states in hydrogenlike systems in Sec. III, which leads to a verification of the results against the analytically known Dirac-Coulomb energy. Extensive use is made of computer algebra [15]. Conclusions are given in Sec. IV.

II. DIRECT CALCULATION

A. Unitary transformation

We start with the well-known Dirac Hamiltonian $H_{\rm D}$ coupled to a general electromagnetic field,

$$\mathcal{H}_{\rm D} = \vec{\alpha}\cdot\vec{\pi} + \beta m = \begin{pmatrix} (m+e\Phi)\mathbb{1}_{2\times2} & \vec{\sigma}\cdot\vec{\pi} \\ \vec{\sigma}\cdot\vec{\pi} & (-m+e\Phi)\mathbb{1}_{2\times2} \end{pmatrix},$$

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbb{1}_{2\times2} & 0_{2\times2} \\ 0_{2\times2} & -\mathbb{1}_{2\times2} \end{pmatrix}. \qquad (4)$$

The Dirac Hamiltonian couples upper and lower components of the Dirac bispinor. The aim of the (unitary)

Foldy-Wouthuysen transformation is to separate the upper (particle) from the lower (antiparticle) degrees of freedom, through an iterative procedure. We write the Hamiltonian as a sum of even terms $\mathcal{E}$ and odd terms $\mathcal{O}$ in bispinor space (see also Chap. 11 of Ref. [2]),

$$\mathcal{H}_D = \mathcal{E} + \mathcal{O}, \tag{5a}$$

$$\mathcal{E} = \frac{1}{2}(H + \beta H \beta), \quad \mathcal{O} = \frac{1}{2}(H - \beta H \beta), \tag{5b}$$

$$\mathcal{E} = \beta m + e\Phi = \begin{pmatrix} (m + e\Phi)\mathbb{1}_{2\times2} & 0_{2\times2} \\ 0_{2\times2} & (-m + e\Phi)\mathbb{1}_{2\times2} \end{pmatrix}, \tag{5c}$$

$$\mathcal{O} = \vec{\alpha} \cdot \vec{\pi} = \begin{pmatrix} 0 & \vec{\sigma} \cdot \vec{\pi} \\ \vec{\sigma} \cdot \vec{\pi} & 0 \end{pmatrix}. \tag{5d}$$

The aim is to eliminate the odd terms $\mathcal{O}$ through unitary transformations. These transformations, necessarily, in order to preserve the physical interpretation of the operators, need to conserve parity [see the remarks following Eq. (7.33) of Ref. [16] and the comprehensive discussion in Ref. [17]]. In short, it has been shown in Ref. [17] that, if one uses a unitary transformation which breaks parity, the Dirac Hamiltonian can be disentangled into what seems to be particle and antiparticle Hamiltonians, but the operators inside the disentangled (diagonal) Hamiltonian have changed their physical interpretation. Spurious terms [18] which could otherwise break particle-antiparticle symmetry in gravitational fields were shown to be absent in Ref. [17], if the parity-conserving standard Foldy-Wouthuysen transformation is used (see also Ref. [19]). One defines the Hermitian operator S and the unitary operator $U = \exp(\mathrm{i}S)$ as

$$S = -\mathrm{i}\beta \frac{\mathcal{O}}{2m}, \quad S = S^+, \quad U = \mathrm{e}^{\mathrm{i}S}. \tag{6}$$

The odd operator $\mathcal{O}$ defined in Eq. (5d) is proportional to the kinetic momentum $\vec{\pi}$, and hence the Foldy-Wouthuysen transformation eliminates the odd terms order by order in an expansion in the momenta. The transformed Hamiltonian is written in terms of nested commutators,

$$\begin{aligned}\mathcal{H}_{FW} &= \exp(\mathrm{i}S)(H - \mathrm{i}\partial_t)\exp(-\mathrm{i}S) \\ &= H + [\mathrm{i}S, H - \mathrm{i}\partial_t] + \frac{1}{2!}[\mathrm{i}S, [\mathrm{i}S, H - \mathrm{i}\partial_t]] \\ &\quad + \frac{1}{3!}[\mathrm{i}S, [\mathrm{i}S, [\mathrm{i}S, H - \mathrm{i}\partial_t]]] \\ &\quad + \frac{1}{4!}[\mathrm{i}S, [\mathrm{i}S, [\mathrm{i}S, [\mathrm{i}S, H - \mathrm{i}\partial_t]]]] + \cdots, \end{aligned} \tag{7}$$

where we note the identity $[\mathrm{i}S, H - \mathrm{i}\partial_t] = \mathrm{i}[S, H] - \partial_t S$.

Though the intensive use of computer algebra generalized to the symbolic commutation relations [15] of kinetic momentum operators with the four-vector and scalar potentials, it is possible to carry out the transformation through eighth order in the fine-structure constant, under the proviso of the scaling implied by Eq. (3). The result of the iterative eighth-order transformation [17] can be written as

$$\mathcal{H}_{FW} = \mathcal{H}^{[0]} + \mathcal{H}^{[2]} + \mathcal{H}^{[4]} + \mathcal{H}^{[6]} + \mathcal{H}^{[8]}. \tag{8}$$

The superscript denotes the power of the coupling parameter at which the term becomes relevant. The coupling parameter is usually denoted by α. From the zeroth to the third order in α, the terms read

$$\mathcal{H}^{[0]} = \beta m, \quad \vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0_{2\times2} \\ 0_{2\times2} & \vec{\sigma} \end{pmatrix}, \tag{9}$$

$$\mathcal{H}^{[2]} = \frac{\beta}{2m}(\vec{\Sigma} \cdot \vec{\pi})^2 + V. \tag{10}$$

The α^4 terms can be expressed very compactly and are found to be in agreement with Refs. [6,20],

$$\mathcal{H}^{[4]} = -\beta \frac{1}{8m^3}(\vec{\Sigma} \cdot \vec{\pi})^4 - \frac{\mathrm{i}e}{8m^2}[\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}]. \tag{11}$$

For the α^6 terms, we indicate three alternative representations

$$\begin{aligned}\mathcal{H}^{[6]} &= \frac{\beta(\vec{\Sigma} \cdot \vec{\pi})^6}{16m^5} - \frac{5\mathrm{i}e}{128m^4}[\vec{\Sigma} \cdot \vec{\pi}, [\vec{\Sigma} \cdot \vec{\pi}, [\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}]]] \\ &\quad + \frac{\mathrm{i}e}{8m^4}\{(\vec{\Sigma} \cdot \vec{\pi})^2, [\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}]\} + \beta \frac{e^2 \vec{E}^2}{8m^3} \\ &= \frac{\beta(\vec{\Sigma} \cdot \vec{\pi})^6}{16m^5} + \frac{5\mathrm{i}e}{128m^4}[(\vec{\Sigma} \cdot \vec{\pi})^2, \{\vec{\Sigma} \cdot \vec{E}, \vec{\Sigma} \cdot \vec{\pi}\}] \\ &\quad + \frac{3\mathrm{i}e}{64m^4}\{(\vec{\Sigma} \cdot \vec{\pi})^2, [\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}]\} + \beta \frac{e^2 \vec{E}^2}{8m^3} \\ &= \frac{\beta(\vec{\Sigma} \cdot \vec{\pi})^6}{16m^5} + \frac{3\mathrm{i}e}{32m^4}[(\vec{\Sigma} \cdot \vec{\pi})^3, \vec{\Sigma} \cdot \vec{E}]. \\ &\quad - \frac{\mathrm{i}e}{128m^4}[(\vec{\Sigma} \cdot \vec{\pi})^2, \{\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}\}] + \beta \frac{e^2 \vec{E}^2}{8m^3}. \end{aligned} \tag{12}$$

Here $\{A, B\} = AB + BA$ denotes the anticommutator. The last form of the sixth-order terms in Eq. (12) is in agreement with the sixth-order terms from Eq. (8) of Ref. [11]. The sixth-order terms are also compatible with Eqs. (36)–(38) of Ref. [7], with Eq. (7) of Ref. [10], and with the approach from Ref. [8]. Alternatively, the result in Eq. (18) can be obtained by applying the unitary transformation outlined in Eq. (19) of Ref. [9] to the Hamiltonian given in Eq. (15) of Ref. [9], which is tantamount to the Hamiltonian obtained by adding the terms given in Eqs. (15) and (20) of Ref. [9].

The eighth-order term are naturally written as a sum of a kinetic term $\mathcal{K}$, a term $\mathcal{D}$ involving temporal derivatives of the electric field, terms quadratic in the electric field, denoted by $\mathcal{Q}$, and linear terms in the electric field, which we denote by $\mathcal{L}$. The result is

$$\mathcal{H}^{[8]} = \mathcal{K} + \mathcal{D} + \mathcal{Q} + \mathcal{L}, \quad \mathcal{K} = -\beta \frac{5}{128m^7}(\vec{\Sigma} \cdot \vec{\pi})^8, \quad \mathcal{D} = -\frac{\mathrm{i}e^2}{32m^4}[\vec{\Sigma} \cdot \vec{E}, \vec{\Sigma} \cdot \partial_t \vec{E}] + \frac{e}{48m^5}\beta\{(\vec{\Sigma} \cdot \vec{\pi})^3, \vec{\Sigma} \cdot \partial_t \vec{E}\},$$

$$\mathcal{Q} = \frac{7\beta e^2}{192m^5}[\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}][\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}] - \frac{3\beta e^2}{64m^5}\{\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}\}\{\vec{\Sigma} \cdot \vec{\pi}, \vec{\Sigma} \cdot \vec{E}\} - \frac{\beta e^2}{24m^5}[\vec{\Sigma} \cdot \vec{\pi}, [\vec{\Sigma} \cdot \vec{\pi}, (\vec{\Sigma} \cdot \vec{E})^2]],$$

$$\mathcal{L} = -\frac{5ie}{1024m^6}[\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},\vec{\Sigma}\cdot\vec{E}]]]]] - \frac{ie}{32m^6}\{\vec{\Sigma}\cdot\vec{\pi},\{\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},\vec{\Sigma}\cdot\vec{E}]]]\}\}$$
$$- \frac{ie}{48m^6}\{\vec{\Sigma}\cdot\vec{\pi},\{\vec{\Sigma}\cdot\vec{\pi},\{\vec{\Sigma}\cdot\vec{\pi},\{\vec{\Sigma}\cdot\vec{\pi},[\vec{\Sigma}\cdot\vec{\pi},\vec{\Sigma}\cdot\vec{E}]\}\}\}\}. \tag{13}$$

For alternative representations, we note the identities

$$\mathcal{Q} = -\frac{\beta e^2}{96m^5}\{\vec{\Sigma}\cdot\vec{E}, 4(\vec{\Sigma}\cdot\vec{\pi})^2\vec{\Sigma}\cdot\vec{E} + 4\vec{\Sigma}\cdot\vec{E}(\vec{\Sigma}\cdot\vec{\pi})^2 + \vec{\Sigma}\cdot\vec{\pi}\,\vec{\Sigma}\cdot\vec{E}\,\vec{\Sigma}\cdot\vec{\pi}\}, \tag{14a}$$

$$\mathcal{L} = \frac{65ie}{3072m^6}[(\vec{\Sigma}\cdot\vec{\pi})^4, \{\vec{\Sigma}\cdot\vec{\pi},\vec{\Sigma}\cdot\vec{E}\}] - \frac{77ie}{1536m^6}[(\vec{\Sigma}\cdot\vec{\pi})^5,\vec{\Sigma}\cdot\vec{E}]$$
$$- \frac{43ie}{1536m^6}[(\vec{\Sigma}\cdot\vec{\pi})^3, (\vec{\Sigma}\cdot\vec{\pi})^2\vec{\Sigma}\cdot\vec{E} + \vec{\Sigma}\cdot\vec{E}(\vec{\Sigma}\cdot\vec{\pi})^2 + \vec{\Sigma}\cdot\vec{\pi}\,\vec{\Sigma}\cdot\vec{E}\,\vec{\Sigma}\cdot\vec{\pi}]. \tag{14b}$$

The particle-antiparticle symmetry implies that the terms are invariant when the following transformations are simultaneously applied: (i) multiplication by an overall factor -1, (ii) replacement $\beta \to -\beta$, (iii) replacements $\vec{\pi} \to -\vec{\pi}$ and $\partial_t \to -\partial_t$, (iv) replacement $\vec{\Sigma} \to -\vec{\Sigma}$, and (v) replacements $e \to -e$, $V \to -V$, and $\vec{E} \to -\vec{E}$.

B. General particle Hamiltonian

The upper left 2×2 submatrix of $\mathcal{H}_{\rm FW}$ constitutes the particle Hamiltonian, while the lower left 2×2 submatrix of $\mathcal{H}_{\rm FW}$ constitutes the antiparticle Hamiltonian. Here we concentrate on the particle Hamiltonian. Formally, the particle Hamiltonian can be found from the results given in Eqs. (10)–(13) under the replacements $\vec{\Sigma} \to \vec{\sigma}$ and $\beta \to \mathbb{1}_{2\times 2}$. The general Foldy-Wouthuysen transformed particle Hamiltonian $H_{\rm FW}$ under the presence of the external electric and magnetic fields is obtained as

$$H_{\rm FW} = \beta m + H^{[2]} + H^{[4]} + H^{[6]} + H^{[8]}. \tag{15}$$

We find

$$H^{[2]} = \frac{1}{2m}(\vec{\sigma}\cdot\vec{\pi})^2 + V, \tag{16}$$

$$H^{[4]} = -\frac{1}{8m^3}(\vec{\sigma}\cdot\vec{\pi})^4 - \frac{ie}{8m^2}[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}], \tag{17}$$

$$H^{[6]} = \frac{(\vec{\sigma}\cdot\vec{\pi})^6}{16m^5} + \frac{5ie}{128m^4}[(\vec{\sigma}\cdot\vec{\pi})^2, \{\vec{\sigma}\cdot\vec{E},\vec{\sigma}\cdot\vec{\pi}\}]$$
$$+ \frac{3ie}{64m^4}\{(\vec{\sigma}\cdot\vec{\pi})^2, [\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}]\} + \frac{e^2\vec{E}^2}{8m^3}. \tag{18}$$

In order to fix ideas, we point out that the expression $(\vec{\sigma}\cdot\vec{\pi})^2 = \vec{\pi}^2 - e\vec{\sigma}\cdot\vec{B}$ contains both the orbital and the spin coupling to the magnetic field. If $\vec{A} = \frac{1}{2}(\vec{B}\times\vec{r})$ and the homogeneous trap field $\vec{B}$ is directed along the z axis, we have $(\vec{\sigma}\cdot\vec{\pi})^2 = \vec{p}^{\,2} - e\vec{L}\cdot\vec{B} + \frac{m^2\omega_c^2}{4}\rho^2 - e\vec{\sigma}\cdot\vec{B}$, where $\omega_c = \frac{|e|B}{m}$ is the cyclotron frequency and $\rho^2 = x^2 + y^2$ is the coordinate perpendicular to the axis of the magnetic field.

The eighth-order term comprises the kinetic term K, a term D involving temporal derivatives of the electric field, terms quadratic in the electric field, denoted by Q, and linear terms in the electric field, which we denote by L,

$$H^{[8]} = K + D + Q + L, \quad K = -\frac{5}{128m^7}(\vec{\sigma}\cdot\vec{\pi})^8, \quad D = -\frac{ie^2}{32m^4}[\vec{\sigma}\cdot\vec{E},\vec{\sigma}\cdot\partial_t\vec{E}] + \frac{e}{48m^5}\{(\vec{\sigma}\cdot\vec{\pi})^3,\vec{\sigma}\cdot\partial_t\vec{E}\},$$
$$Q = \frac{7e^2}{192m^5}[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}][\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}] - \frac{3e^2}{64m^5}\{\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}\}\{\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}\} - \frac{e^2}{24m^5}[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},(\vec{\sigma}\cdot\vec{E})^2]],$$
$$L = -\frac{5ie}{1024m^6}[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},\sigma\cdot\vec{E}]]]]] - \frac{ie}{32m^6}\{\vec{\sigma}\cdot\vec{\pi},\{\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},\sigma\cdot\vec{E}]]]\}\}$$
$$- \frac{ie}{48m^6}\{\vec{\sigma}\cdot\vec{\pi},\{\vec{\sigma}\cdot\vec{\pi},\{\vec{\sigma}\cdot\vec{\pi},\{\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},\sigma\cdot\vec{E}]\}\}\}\}. \tag{19}$$

For alternative representations, we note identities analogous to Eqs. (14a) and (14b),

$$Q = -\frac{e^2}{96m^5}\{\vec{\sigma}\cdot\vec{E}, 4(\vec{\sigma}\cdot\vec{\pi})^2\vec{\sigma}\cdot\vec{E} + 4\vec{\sigma}\cdot\vec{E}(\vec{\sigma}\cdot\vec{\pi})^2 + \vec{\sigma}\cdot\vec{\pi}\vec{\sigma}\cdot\vec{E}\vec{\sigma}\cdot\vec{\pi}\}, \tag{20a}$$

$$L = \frac{65ie}{3072m^6}[(\vec{\sigma}\cdot\vec{\pi})^4, \{\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}\}] - \frac{77ie}{1536m^6}[(\vec{\sigma}\cdot\vec{\pi})^5,\vec{\sigma}\cdot\vec{E}]$$
$$- \frac{43ie}{1536m^6}[(\vec{\sigma}\cdot\vec{\pi})^3, (\vec{\sigma}\cdot\vec{\pi})^2\vec{\sigma}\cdot\vec{E} + \vec{\sigma}\cdot\vec{E}(\vec{\sigma}\cdot\vec{\pi})^2 + \vec{\sigma}\cdot\vec{\pi}\vec{\sigma}\cdot\vec{E}\vec{\sigma}\cdot\vec{\pi}]. \tag{20b}$$

III. APPLICATIONS

A. Coulomb field coupling

One of the important applications of the Hamiltonian (15) concerns Coulombic bound states, which are relevant to one-electron ions in the central field of a nucleus of charge number Z. In this case, we have the relations

$$eA^0 = V = -\frac{Z\alpha}{r}, \quad \vec{A} = \vec{0}, \quad \vec{B} = \vec{0}, \tag{21}$$

$$e\vec{E} = -e\vec{\nabla}A^0 = -\vec{\nabla}V, \quad \vec{\pi} = \vec{p}. \tag{22}$$

The scalar potential and electric field are time independent in this case. One ends up with the following leading term, where the subscript C indicates the relevance for the Coulomb field:

$$H_C^{[2]} = \frac{\vec{p}^{\,2}}{2m} + V = \frac{\vec{p}^{\,2}}{2m} - \frac{Z\alpha}{r}. \tag{23}$$

This is the Schrödinger-Coulomb Hamiltonian in the nonrecoil approximation (Chap. 4 of Ref. [2]). For the evaluation of the fourth-order corrections, we need the identities

$$\mathrm{i}e[\vec{\sigma}\cdot\vec{p}, \vec{\sigma}\cdot\vec{E}] = -\vec{\nabla}^2 V - 2\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,), \tag{24a}$$

$$e\{\vec{\sigma}\cdot\vec{p}, \vec{\sigma}\cdot\vec{E}\} = -\{\vec{\sigma}\cdot\vec{p}, \vec{\sigma}\cdot\vec{\nabla}V\} = -\mathrm{i}[\vec{p}^{\,2}, V]. \tag{24b}$$

For the Coulomb field, the well-known leading relativistic correction to the Foldy-Wouthuysen Hamiltonian reads

$$\begin{aligned} H_C^{[4]} &= -\frac{\vec{p}^{\,4}}{8m^3} + \frac{1}{8m^2}\vec{\nabla}^2 V + \frac{1}{4m^2}\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}) \\ &= -\frac{\vec{p}^{\,4}}{8m^3} + \frac{\pi(Z\alpha)}{2m^2}\delta^{(3)}(\vec{r}) + \frac{Z\alpha}{4m^2 r^3}\vec{\sigma}\cdot\vec{L}, \end{aligned} \tag{25}$$

where $\vec{L}$ is the orbital angular momentum operator. The sixth-order corrections attain the form

$$\begin{aligned} H_C^{[6]} &= \frac{\vec{p}^{\,6}}{16m^5} - \frac{3\{\vec{p}^{\,2}, \vec{\nabla}^2 V\}}{64m^4} - \frac{3\{\vec{p}^{\,2}, \vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,)\}}{32m^4} \\ &\quad + \frac{5}{128m^4}[\vec{p}^{\,2}, [\vec{p}^{\,2}, V]] + \frac{(\vec{\nabla}V)^2}{8m^3}. \end{aligned} \tag{26}$$

With $\partial_t\vec{E} = \vec{0}$, we have, for the eighth-order corrections,

$$H_C^{[8]} = K_C + D_C + Q_C + L_C, \quad K_C = -\frac{5}{128m^7}\vec{p}^{\,8}, \quad D_C = 0, \tag{27a}$$

$$Q_C = \frac{7[\vec{\nabla}^2 V + 2\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,)][\vec{\nabla}^2 V + 2\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,)]}{192m^5} + \frac{3[\vec{p}^{\,2}, V][\vec{p}^{\,2}, V]}{64m^5} - \frac{[\vec{\sigma}\cdot\vec{p}, [\vec{\sigma}\cdot\vec{p}, (\vec{\nabla}V)^2]]}{24m^5}, \tag{27b}$$

$$\begin{aligned} L_C &= \frac{5[\vec{\sigma}\cdot\vec{p}, [\vec{\sigma}\cdot\vec{p}, [\vec{\sigma}\cdot\vec{p}, [\vec{\sigma}\cdot\vec{p}, \vec{\nabla}^2 V + 2\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,)]]]]}{1024m^6} + \frac{\{\vec{\sigma}\cdot\vec{p}, \{\vec{\sigma}\cdot\vec{p}, [\vec{\sigma}\cdot\vec{p}, [\vec{\sigma}\cdot\vec{p}, \vec{\nabla}^2 V + 2\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,)]]\}\}}{32m^6} \\ &\quad + \frac{1}{48m^6}\{\vec{\sigma}\cdot\vec{p}, \{\vec{\sigma}\cdot\vec{p}, \{\vec{\sigma}\cdot\vec{p}, \{\vec{\sigma}\cdot\vec{p}, \vec{\nabla}^2 V + 2\vec{\sigma}\cdot(\vec{\nabla}V \times \vec{p}\,)\}\}\}\}. \end{aligned} \tag{27c}$$

B. Application: $F_{5/2}$ states

We now compare the eighth-order corrections to the bound-state energy obtained from Eq. (27a) to the bound-state energies of the Dirac-Coulomb problem. It is well known that the Dirac-Coulomb problem can be solved exactly (Chap. 8 of Ref. [2]), with the result

$$E_{\mathrm{D}} = m\left(1 + \frac{(Z\alpha)^2}{(n_r + \gamma)^2}\right)^{-1/2}, \quad n_r = n - j - \frac{1}{2}, \quad \gamma = \sqrt{\left(j + \frac{1}{2}\right)^2 + (Z\alpha)^2}. \tag{28}$$

For $nF_{5/2}$ states, the presence of large spin-orbit coupling implies the emergence of nontrivial corrections to the energy from the corresponding higher-order terms in Eq. (27a). One expands as follows:

$$\begin{aligned} E_{\mathrm{D}}(nF_{5/2}) &= m - \frac{(Z\alpha)^2 m}{2n^2} + (Z\alpha)^4 m\left(\frac{3}{8n^4} - \frac{1}{6n^3}\right) - (Z\alpha)^6 m\left(\frac{1}{216n^3} + \frac{1}{24n^4} - \frac{1}{4n^5} + \frac{5}{16n^6}\right) \\ &\quad + (Z\alpha)^8 m\left(-\frac{1}{3888n^3} - \frac{1}{432n^4} - \frac{1}{432n^5} + \frac{5}{48n^6} - \frac{5}{16n^7} + \frac{35}{128n^8}\right) + O(Z\alpha)^{10}. \end{aligned} \tag{29}$$

Within the Foldy-Wouthuysen method, the eighth-order terms comprise several effects, namely, the combined effect of the third-order perturbative terms $E^{[8]} = E_c^{[8]}$ generated by the fourth-order Hamiltonian $H^{[4]}$, the mixed fourth- and sixth-order terms $E_m^{[8]}$, and the diagonal element of eighth-order $E_d^{[8]}$,

$$E^{[8]} = E_c^{[8]} + E_m^{[8]} + E_d^{[8]}. \tag{30}$$

The terms will be further examined in the following. Let G' be the reduced Green's function

$$G' = \left(\frac{1}{E_S - H_S}\right)', \tag{31}$$

where E_S is the Schrödinger-Coulomb energy $E_S = -\frac{(Z\alpha)^2 m}{2n^2}$ and $H_S = H_C^{[2]}$ is the Schrödinger-Coulomb Hamiltonian.

Then

$$E_c^{[8]} = \langle H^{[4]} G'(H^{[4]} - \langle H^{[4]}\rangle) G' H^{[4]}\rangle, \quad (32a)$$

$$E_m^{[8]} = 2\langle H^{[4]} G' H^{[6]}\rangle, \quad (32b)$$

$$E_d^{[8]} = \langle H^{[8]}\rangle = \langle K_C\rangle + \langle Q_C\rangle + \langle L_C\rangle. \quad (32c)$$

After lengthy algebra, we obtain the results

$$\frac{\langle K_C\rangle_{nF_{5/2}}}{(Z\alpha)^8 m} = -\frac{2}{693n^3} + \frac{65}{1386n^5} - \frac{1549}{5544n^7} + \frac{35}{128n^8}, \quad (33a)$$

$$\frac{\langle Q_C\rangle_{nF_{5/2}}}{(Z\alpha)^8 m} = -\frac{4}{31\,185n^3} + \frac{131}{99\,792n^5} - \frac{23}{13\,860n^7}, \quad (33b)$$

$$\frac{\langle L_C\rangle_{nF_{5/2}}}{(Z\alpha)^8 m} = -\frac{281}{249\,480n^3} + \frac{5975}{399\,168n^5} - \frac{599}{13\,860n^7}, \quad (33c)$$

$$\frac{E_d^{[8]}(nF_{5/2})}{(Z\alpha)^8 m} = -\frac{1033}{249\,480n^3} + \frac{25\,219}{399\,168n^5} - \frac{8989}{27\,720n^7} + \frac{35}{128n^8}, \quad (33d)$$

For absolutely clarity, we should emphasize the all matrix elements are calculated with nonrelativistic Schrödinger-Pauli two-component reference-state wave functions (Chap. 6 of Ref. [2]). Summing up the results for the combined third-order perturbation theory term and the mixed term, we obtain

$$\frac{E_c^{[8]}(nF_{5/2})}{(Z\alpha)^8 m} = -\frac{169\,721}{23\,950\,080n^3} - \frac{19}{1728n^4} + \frac{4\,560\,727}{41\,912\,640n^5} + \frac{955}{3024n^6} - \frac{1052}{693n^7} + \frac{21}{16n^8}, \quad (34)$$

$$\frac{E_m^{[8]}(nF_{5/2})}{(Z\alpha)^8 m} = \frac{262\,729}{23\,950\,080n^3} + \frac{5}{576n^4} - \frac{3\,652\,871}{20\,956\,320n^5} - \frac{40}{189n^6} + \frac{28271}{18\,480n^7} - \frac{21}{16n^8}, \quad (35)$$

$$\frac{E^{[8]}(nF_{5/2})}{(Z\alpha)^8 m} = -\frac{1}{3888n^3} - \frac{1}{432n^4} - \frac{1}{432n^5} + \frac{5}{48n^6} - \frac{5}{16n^7} + \frac{35}{128n^8}. \quad (36)$$

The latter terms confirm Eq. (29).

C. Application: $F_{7/2}$ states

The calculation proceeds in full analogy with $nF_{5/2}$ states. The Dirac-Coulomb energy finds the expansion

$$E_{\rm D}(nF_{7/2}) = m - \frac{(Z\alpha)^2 m}{2n^2} + (Z\alpha)^4 m\left(\frac{3}{8n^4} - \frac{1}{8n^3}\right) - (Z\alpha)^6 m\left(-\frac{1}{512n^3} - \frac{3}{128n^4} + \frac{3}{16n^5} - \frac{5}{16n^6}\right) + (Z\alpha)^8 m\left(-\frac{1}{16384n^3} - \frac{3}{4096n^4} - \frac{1}{1024n^5} + \frac{15}{256n^6} - \frac{15}{64n^7} + \frac{35}{128n^8}\right) + O(Z\alpha)^{10}. \quad (37)$$

After lengthy algebra, we obtain the results

$$\frac{\langle K_C\rangle_{nF_{7/2}}}{(Z\alpha)^8 m} = -\frac{2}{693n^3} + \frac{65}{1386n^5} - \frac{1549}{5544n^7} + \frac{35}{128n^8}, \quad (38a)$$

$$\frac{\langle Q_C\rangle_{nF_{7/2}}}{(Z\alpha)^8 m} = -\frac{5}{18\,144n^3} + \frac{247}{90\,720n^5} - \frac{1}{315n^7}, \quad (38b)$$

$$\frac{\langle L_C\rangle_{nF_{7/2}}}{(Z\alpha)^8 m} = \frac{13\,261}{7\,983\,360n^3} - \frac{156\,853}{7\,983\,360n^5} + \frac{9589}{221\,760n^7}, \quad (38c)$$

$$\frac{E_d^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} = -\frac{121}{80\,640n^3} + \frac{2417}{80\,640n^5} - \frac{965}{4032n^7} + \frac{35}{128n^8}. \quad (38d)$$

The combined third-order terms $E_c^{[8]}(nF_{7/2})$ and mixed terms $E_m^{[8]}(nF_{7/2})$ find the representations

$$\frac{E_c^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} = -\frac{548\,047}{232\,243\,200n^3} - \frac{253}{61\,440n^4} + \frac{2\,636\,603}{50\,803\,200n^5} + \frac{1427}{8064n^6} - \frac{22\,847}{20\,160n^7} + \frac{21}{16n^8}, \quad (39)$$

$$\frac{E_m^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} = \frac{55\,147}{14\,515\,200n^3} + \frac{13}{3840n^4} - \frac{8\,417\,851}{101\,606\,400n^5} - \frac{1909}{16\,128n^6} + \frac{7649}{6720n^7} - \frac{21}{16n^8}. \quad (40)$$

The sum

$$\frac{E^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} = \frac{E_c^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} + \frac{E_m^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} + \frac{E_d^{[8]}(nF_{7/2})}{(Z\alpha)^8 m} = -\frac{1}{16\,384n^3} - \frac{3}{4096n^4} - \frac{1}{1024n^5} + \frac{15}{256n^6} - \frac{15}{64n^7} + \frac{35}{128n^8} \quad (41)$$

reproduces the terms of order $(Z\alpha)^8$ from the Dirac-Coulomb bound-state energy (37).

IV. CONCLUSION

In this article, we have extended the treatment of the Foldy-Wouthuysen transformation to eighth order, based on the scaling of the operators outlined in Eq. (3). The results were obtained by a straightforward application of the elimination of odd operators by repeated unitary transformations of the form outlined in Eq. (6). The sixth-order terms [Eqs. (12) and (18)] were obtained in full agreement with the literature (Refs. [7–11]). For the eighth-order terms, we gave results in Eqs. (13) and (19). We applied our general results to the relativistic bound Coulomb problem in Sec. III. An application to $nF_{5/2}$ and $nF_{7/2}$ states, which present large spin-orbit couplings, confirms, analytically, that the Dirac-Coulomb bound-state energy can be obtained, within the Foldy-Wouthuysen formalism, as a sum of combined third-order perturbative effects generated by the leading relativistic corrections [Eq. (32a)], mixed fourth-order and sixth-order Hamiltonian terms [Eq. (32b)], and diagonal elements of the eighth-order Hamiltonian [Eq. (32c)]. The latter terms are obtained as diagonal elements of our eighth-order terms for the Coulomb field, evaluated on Schrödinger-Pauli wave functions (Chap. 6 of Ref. [2]). As outlined in Ref. [8], the results are important in a wider context, in view of the fact that the Foldy-Wouthuysen Hamiltonian determines (part of) the matching coefficients in the Hamiltonian of Nonrelativistic Quantum Electrodynamics (NRQED).

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APPENDIX: COMPARISON WITH THE LITERATURE

We compare our results with those of Ref. [11]. We note that the Foldy-Wouthuysen Hamiltonian derived in Ref. [11] is derived based on the Douglas-Kroll-Hess [21,22] approach, which treats the kinetic-energy term in the relativistic Hamiltonian on a special footing and differs from the approach chosen here. The result for the eighth-order terms given in Eq. (8) of Ref. [11] can be written as the sum $H'^{[8]} = \mathcal{K} + \mathcal{D}' + \mathcal{Q}' + \mathcal{L}'$, where

$$\mathcal{D}' = -\frac{\mathrm{i}e^2}{32m^4}[\vec{\sigma}\cdot\vec{E}, \vec{\sigma}\cdot\partial_t\vec{E}], \tag{A1a}$$

$$\mathcal{Q}' = -\frac{e^2}{32m^5}\{\vec{\sigma}\cdot\vec{E}, 2(\vec{\sigma}\cdot\vec{\pi})^2\vec{\sigma}\cdot\vec{E} + 2\vec{\sigma}\cdot\vec{E}(\vec{\sigma}\cdot\vec{\pi})^2 + \vec{\sigma}\cdot\vec{\pi}\vec{\sigma}\cdot\vec{E}\vec{\sigma}\cdot\vec{\pi}\}, \tag{A1b}$$

$$\mathcal{L}' = \frac{11\mathrm{i}e}{1024m^6}[(\vec{\sigma}\cdot\vec{\pi})^4, \{\vec{\sigma}\cdot\vec{\pi}, \vec{\sigma}\cdot\vec{E}\}] - \frac{31\mathrm{i}e}{512m^6}[(\vec{\sigma}\cdot\vec{\pi})^5, \vec{\sigma}\cdot\vec{E}] - \frac{9\mathrm{i}e}{512m^6}[(\vec{\sigma}\cdot\vec{\pi})^3, (\vec{\sigma}\cdot\vec{\pi})^2\vec{\sigma}\cdot\vec{E} + \vec{\sigma}\cdot\vec{E}(\vec{\sigma}\cdot\vec{\pi})^2 + \vec{\sigma}\cdot\vec{\pi}\vec{\sigma}\cdot\vec{E}\vec{\sigma}\cdot\vec{\pi}]. \tag{A1c}$$

Here, $\mathcal{D}'$ is the term from Eq. (8) in Ref. [11] which contains temporal derivatives, $\mathcal{Q}'$ is the term from Eq. (8) in Ref. [11] which is quadratic in the electric fields, and $\mathcal{L}'$ is the term from Eq. (8) in Ref. [11] which is linear in the electric fields. The kinetic term $\mathcal{K}$ of eighth order agrees with the corresponding term from Eq. (13) here.

Specifically, the term $\mathcal{D}'$ lacks the terms proportional to the anticommutator $\{(\vec{\sigma}\cdot\vec{\pi})^3, \vec{\sigma}\cdot\partial_t\vec{E}\}$ in comparison to our result for $\mathcal{D}$ given in Eq. (13). The results for $\mathcal{Q}'$ and $\mathcal{L}'$ differ from those given in Eqs. (14a) and (14b) in the prefactors of the individual terms.

One can easily specialize the four operators given in Eqs. (A1b) and (A1c) to the case of a Coulomb field, on the basis of Eq. (21). This leads to the operators Q'_C and L'_C. The diagonal matrix elements for $nF_{5/2}$ evaluate to

$$\frac{\langle Q'_C\rangle_{nF_{5/2}}}{(Z\alpha)^8 m} = -\frac{37}{249\,480n^3} + \frac{779}{498\,960n^5} - \frac{29}{13\,860n^7}, \tag{A2a}$$

$$\frac{\langle L'_C\rangle_{nF_{5/2}}}{(Z\alpha)^8 m} = -\frac{23}{20\,790n^3} + \frac{1399}{95\,040n^5} - \frac{593}{13\,860n^7}. \tag{A2b}$$

For $nF_{7/2}$ states, we have the results

$$\frac{\langle Q'_C\rangle_{nF_{7/2}}}{(Z\alpha)^8 m} = -\frac{131}{332\,640n^3} + \frac{1301}{332\,640n^5} - \frac{16}{3465n^7}, \tag{A2c}$$

$$\frac{\langle L'_C\rangle_{nF_{7/2}}}{(Z\alpha)^8 m} = \frac{947}{532\,224n^3} - \frac{7921}{380\,160n^5} + \frac{1101}{24\,640n^7}. \tag{A2d}$$

These results differ individually from those given in Eqs. (33) and (38), for the diagonal matrix elements of the operators Q_C and L_C, but their sum reproduces our results for both fine-structure components $F_{5/2}$ and $F_{7/2}$ investigated here. We have carried out similar calculations for states with a different angular symmetry (e.g., G states) and find a similar behavior. These observations support the conjecture that the eighth-order Hamiltonian derived here and in Ref. [11] lead to equivalent diagonal elements for hydrogenic reference states.

However, the Hamiltonians derived here and in Ref. [11] are not equivalent for time-dependent problems. Let us consider a binding Coulomb field added to an external plane-wave laser field (in the length gauge), polarized along the z axis, with

$$eA^0 = -\frac{Z\alpha}{r} - e\frac{E_L}{\omega_L} z\sin(\omega_L t), \tag{A3}$$

where E_L is the peak laser field during a laser period and ω_L is the laser angular frequency. The vector potential still vanishes, so that the relation $\vec{\pi} = \vec{p}$ is retained. The spatially homogeneous, but time-dependent, laser field is $\vec{E}_L(t) = \hat{e}_z E_L\cos(\omega_L t)$. The total $\vec{E}$ field (Coulomb plus laser field) fulfills $e\vec{E} = \vec{\nabla}\frac{Z\alpha}{r} + e\hat{e}_z E_L\cos(\omega_L t)$. The commutator $[\vec{\sigma}\cdot\vec{E}, \vec{\sigma}\cdot\partial_t\vec{E}]$ vanishes, but the term

$$H^{[8]} \sim \mathcal{D} \sim \frac{e}{48m^5}\{(\vec{\sigma}\cdot\vec{p})^3, \vec{\sigma}\cdot\partial_t\vec{E}_L(t)\}, \tag{A4}$$

from the $\mathcal{D}$ term in our Eq. (19), generates a contribution proportional to $\sin(\omega_L t)$, in view of the time derivative of the laser field. Its sinusoidal (as opposed to cosinusoidal) time dependence cannot be compensated by any term proportional to the laser field itself, $\vec{E}_L(t) \propto \cos(\omega_L t)$, i.e., the sinusoidal term cannot be compensated by any other term in $H^{[8]}$ which is free from time derivatives of the electric field. Hence, the Hamiltonians derived here and in Ref. [11] cannot be completely equivalent for time-dependent problems.

The eighth-order Hamiltonians derived here and in Ref. [11] could potentially be equivalent up to a unitary transformation, in a somewhat distant analogy to the unitary transformation given in Eq. (19) of Ref. [9], which was applied in Ref. [9] to different forms of the sixth-order Foldy-Wouthuysen Hamiltonian (see also the nonstandard Foldy-Wouthuysen transformation used in Refs. [20,23]). A potential unitary transformation which brings the results communicated in Ref. [11] and those derived here into agreement would only need to affect the eighth-order terms because the sixth-order terms indicated here and in Ref. [11] are identical. The special form of the S operator, which generates the Foldy-Wouthuysen U transformation via the relation $U = \exp(\mathrm{i}S)$ for the nonstandard approach from Refs. [20,23], was recently highlighted in Eq. (17) of Ref. [24]. In general, when two Hamiltonians are related by a unitary transformation, their matrix elements are identical provided one also applies the unitary transformation to the wave functions. Within this context, we mention that unitary (gauge) transformations of the wave functions can change their physical interpretation. This (perhaps surprising) fact is relevant for the quantum dynamical formulation of laser-induced processes off-resonance (see the footnote on p. 268 of Ref. [25] and the elucidating discussion in Ref. [26]).

Another indication that the Hamiltonians derived here and in Ref. [11] cannot be completely equivalent stems from the calculation of off-diagonal matrix elements of the Hamiltonian. As an example, we calculate off-diagonal elements of the operators Q_C, Q'_C, L_C, and L'_C, sandwiched between $|4F_{5/2}\rangle$ and $|6F_{5/2}\rangle$ states, with the results

$$\frac{\langle 4F_{5/2}|Q_C|6F_{5/2}\rangle}{(Z\alpha)^8 m} = -\frac{761}{1\,417\,500\,000}, \tag{A5a}$$

$$\frac{\langle 4F_{5/2}|Q'_C|6F_{5/2}\rangle}{(Z\alpha)^8 m} = -\frac{23}{40\,500\,000}, \tag{A5b}$$

$$\frac{\langle 4F_{5/2}|L_C|6F_{5/2}\rangle}{(Z\alpha)^8 m} = -\frac{5\,007\,493}{1\,134\,000\,000\,000}, \tag{A5c}$$

$$\frac{\langle 4F_{5/2}|L'_C|6F_{5/2}\rangle}{(Z\alpha)^8 m} = -\frac{1\,627\,151}{378\,000\,000\,000}. \tag{A5d}$$

The sums of these terms are

$$\frac{\langle 4F_{5/2}|Q_C + L_C|6F_{5/2}\rangle}{(Z\alpha)^8 m} = -\frac{5\,616\,293}{1\,134\,000\,000\,000}, \tag{A5e}$$

$$\frac{\langle 4F_{5/2}|Q'_C + L'_C|6F_{5/2}\rangle}{(Z\alpha)^8 m} = -\frac{5\,525\,453}{1\,134\,000\,000\,000}. \tag{A5f}$$

Numerically, the difference between $\langle 4F_{5/2}|Q_C + L_C|6F_{5/2}\rangle = -4.952 \times 10^{-6}(Z\alpha)^8 m$ and $\langle 4F_{5/2}|Q'_C + L'_C|6F_{5/2}\rangle = -4.873 \times 10^{-6}(Z\alpha)^8 m$ is about 1.6%. Because the kinetic terms derived here and in Ref. [11] agree, this observation implies that the off-diagonal matrix elements derived from the total $H^{[8]}$ and $H'^{[8]}$ differ.

For off-diagonal matrix elements of $|4F_{7/2}\rangle$ and $|6F_{7/2}\rangle$ states, the following results are obtained:

$$\frac{\langle 4F_{7/2}|Q_C|6F_{7/2}\rangle}{(Z\alpha)^8 m} = -\frac{3587}{2\,835\,000\,000}, \tag{A6a}$$

$$\frac{\langle 4F_{7/2}|Q'_C|6F_{7/2}\rangle}{(Z\alpha)^8 m} = -\frac{49}{27\,000\,000}, \tag{A6b}$$

$$\frac{\langle 4F_{7/2}|L_C|6F_{7/2}\rangle}{(Z\alpha)^8 m} = \frac{14\,493\,239}{1\,134\,000\,000\,000}, \tag{A6c}$$

$$\frac{\langle 4F_{7/2}|L'_C|6F_{7/2}\rangle}{(Z\alpha)^8 m} = \frac{1\,731\,391}{252\,000\,000\,000}. \tag{A6d}$$

The sums of these terms are

$$\frac{\langle 4F_{7/2}|Q_C + L_C|6F_{7/2}\rangle}{(Z\alpha)^8 m} = \frac{11\,623\,639}{2\,268\,000\,000\,000}, \tag{A6e}$$

$$\frac{\langle 4F_{7/2}|Q'_C + L'_C|6F_{7/2}\rangle}{(Z\alpha)^8 m} = \frac{3\,822\,173}{756\,000\,000\,000}. \tag{A6f}$$

We observe that, numerically, the difference between $\langle 4F_{7/2}|Q_C + L_C|6F_{7/2}\rangle = 5.125 \times 10^{-6}(Z\alpha)^8 m$ and $\langle 4F_{7/2}|Q'_C + L'_C|6F_{7/2}\rangle = 5.056 \times 10^{-6}(Z\alpha)^8 m$ is about 1.4%.

In the very recent paper [24], the standard approach to the Foldy-Wouthuysen transformation was applied to obtain a result for the eighth-order terms communicated in Eq. (16) of Ref. [24]. The result from Ref. [24] differs from our result, given in Eq. (19), in the sign of the term $\frac{e}{48m^5}\beta\{(\vec{\Sigma}\cdot\vec{\pi})^3, \vec{\Sigma}\cdot\partial_t\vec{E}\}$. In view of the aspects discussed in this Appendix, we leave the final clarification of the eighth-order terms derived here to those communicated in Refs. [11,23,24] as an open problem for future investigations.

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