On the spin separation of algebraic two-component relativistic Hamiltonians: Molecular properties

Zhendong Li, Yunlong Xiao, and Wenjian Liu

Citation: The Journal of Chemical Physics **141**, 054111 (2014); doi: 10.1063/1.4891567
View online: http://dx.doi.org/10.1063/1.4891567
View Table of Contents: http://aip.scitation.org/toc/jcp/141/5
Published by the American Institute of Physics

On the spin separation of algebraic two-component relativistic Hamiltonians: Molecular properties

Zhendong Li, Yunlong Xiao, and Wenjian Liu[a)]
Beijing National Laboratory for Molecular Sciences, Institute of Theoretical and Computational Chemistry, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, and Center for Computational Science and Engineering, Peking University, Beijing 100871, People's Republic of China

(Received 9 June 2014; accepted 17 July 2014; published online 6 August 2014)

The idea for separating the algebraic exact two-component (X2C) relativistic Hamiltonians into spin-free (sf) and spin-dependent terms [Z. Li, Y. Xiao, and W. Liu, J. Chem. Phys. **137**, 154114 (2012)] is extended to both electric and magnetic molecular properties. Taking the spin-free terms (which are correct to infinite order in $\alpha \approx 1/137$) as zeroth order, the spin-dependent terms can be treated to any desired order via analytic derivative technique. This is further facilitated by unified Sylvester equations for the response of the decoupling and renormalization matrices to single or multiple perturbations. For practical purposes, explicit expressions of order α^2 in spin are also given for electric and magnetic properties, as well as two-electron spin-orbit couplings. At this order, the response of the decoupling and renormalization matrices is not required, such that the expressions are very compact and completely parallel to those based on the Breit-Pauli (BP) Hamiltonian. However, the former employ sf-X2C wave functions, whereas the latter can only use nonrelativistic wave functions. As the sf-X2C terms can readily be interfaced with any nonrelativistic program, the implementation of the $\mathcal{O}(\alpha^2)$ spin-orbit corrections to sf-X2C properties requires only marginal revisions of the routines for evaluating the BP type of corrections. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4891567]

I. INTRODUCTION

The last decade has witnessed tremendous progresses in the field of relativistic quantum chemistry.[1,2] First of all, a second-quantized relativistic many-electron Hamiltonian in full accordance with the principles of quantum electrodynamics (QED) has been introduced,[3] which can be taken as the basis for the emerging field of "molecular QED." This is particularly so when the electron vacuum polarization and self-energy operators are combined and fitted into a suitable model form.[1,4] Second, four-component relativistic explicit correlations have been made possible based either on the relativistic coalescence conditions[5,6] or on the nonrelativistic cusp conditions.[7,8] The only caveat here is that an extended no-pair projection[9] has to be invoked for minimizing the contamination of negative energy states. Third, the so-called exact two-component (X2C) Hamiltonians[10–17] have been made[18–22] as efficient as the popular approximate two-component (A2C) variants,[23–26] not only for energetics but also for response properties.[27–29] Note in passing that an X2C-QED approach is also possible.[1] Although the evaluation of QED effects in molecular spectroscopies and the implementation of relativistic explicitly correlated methods may still take some time, the X2C Hamiltonians have already become the workhorse for routine relativistic electronic structure calculations. Nevertheless, for systems where spin-orbit couplings are very weak, it is highly desired to separate the X2C Hamiltonians into spin-free (sf) and spin-dependent (sd) terms, such that scalar relativistic effects can be treated variationally to infinite order, whereas spin-orbit couplings can be treated order by order either perturbatively or variationally. The problem lies in that the X2C Hamiltonians are defined only algebraically, meaning that the Dirac identity

$$(\vec{\sigma}\cdot\vec{A})B(\vec{\sigma}\cdot\vec{C}) = \vec{A}\cdot(B\vec{C}) + \mathbb{i}\vec{\sigma}\cdot[\vec{A}\times(B\vec{C})], \qquad (1)$$

for spin separation of operators does not apply here. The way out[30] is to partition *a priori* the Dirac matrix into spin-free and spin-dependent terms. The former defines the non-expanded sf-X2C Hamiltonian $\mathbf{h}_{+,sf}$, whereas the latter can be expanded to any desired order $\mathbf{h}^{\mathrm{X}}_{+,k}$ in spin-orbit coupling, leading to a series of new two-component Hamiltonians $\mathbf{h}^{\mathrm{X}}_{+}$, viz.,

$$\mathbf{h}^{\mathrm{X}}_{+} = \mathbf{h}_{+,sf} + \mathbf{h}^{\mathrm{X}}_{+,sd}, \quad \mathbf{h}^{\mathrm{X}}_{+,sd} = \sum_{k=1}^{\infty}\mathbf{h}^{\mathrm{X}}_{+,k}, \quad \mathrm{X} = \mathrm{DKH, BSS, X2C}. \qquad (2)$$

Here, the spin-dependent terms $\mathbf{h}^{\mathrm{X}}_{+,k}$ can be obtained from three types of expansions in powers of spin-orbit coupling, viz., the multiple-step Douglas-Kroll-Hess (DKH)[23,24,31–37] type of transformation $\mathbf{U} = \cdots\mathbf{U}_2\mathbf{U}_1\mathbf{U}_0$, the two-step Barysz-Sadlej-Snijders (BSS)[38–43] type of transformation $\mathbf{U} = \mathbf{U}_Y\mathbf{U}_0$, and the one-step X2C[10–13] type of transformation $\mathbf{U} = \mathbf{U}_X$. All the three expansions converge very fast because of the common good start, $\mathbf{h}_{+,sf}$. On the practical side, the sf-X2C+so-DKH3 combination[30] is most valuable for electronic

a)Author to whom correspondence should be addressed. Electronic mail: liuwjbdf@gmail.com

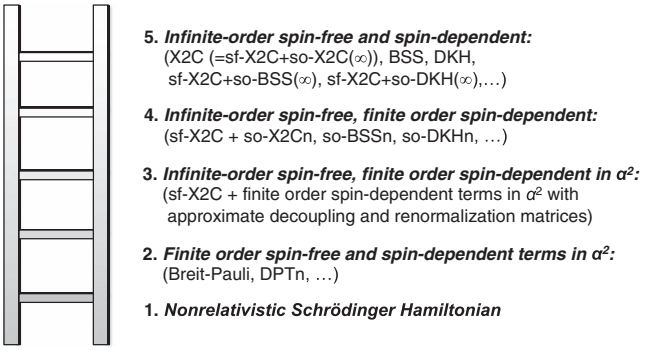

FIG. 1. The two-component Hamiltonian ladder.

structure calculations. Further approximations will give rise to the well-known Breit-Pauli (BP), DKH1, and ZORA (zeroth order regular approximation) spin-orbit terms. At variance with the full "Hamiltonian ladder" discussed before,[1,2] a "two-component Hamiltonian ladder" can be depicted here, see Fig. 1. From bottom to up, the lowest rung is the Schrödinger Hamiltonian. The second rung includes BP and DPT (direct perturbation theory),[44] where both spin-free and spin-dependent terms are of finite orders in α^2. The third rung includes combinations of sf-X2C with spin-dependent terms of order α^2. The fourth rung includes combinations of sf-X2C with the truncated spin-dependent Hamiltonians $\mathbf{h}^{\mathrm{X}}_{+,sd}$ (2) [NB: Although truncated, terms of higher orders in α^2 are still present]. The highest rung includes the original X2C [= sf-X2C+so-X2C(∞)], BSS and DKH Hamiltonians, as well as the sf-X2C+so-BSS(∞) and sf-X2C+so-DKH(∞) combinations. Such partitioning of the two-component Hamiltonians is meaningful not only conceptually but also computationally.

The present work focuses on the third and fourth rungs of the "two-component Hamiltonian ladder" by extending the idea[30] of spin separation to molecular properties. At the fourth rung (Sec. II B), the spin-dependent corrections to sf-X2C properties can be treated to any order via the analytic derivative technique.[45] To this end, unified Sylvester equations are derived in Sec. II B 4 for the response of the decoupling and renormalization matrices to single or multiple perturbations. The spin-dependent terms can then be evaluated straightforwardly by virtue of multiple perturbation theory. For instance, a second order property due to perturbations V^a and V^b can be expressed as

$$E^{ab} = \left(\frac{d^2E}{d\lambda_a d\lambda_b}\right)_{\lambda_a=\lambda_b=0} = \sum_{k=0}^{\infty} E_k^{ab}, \tag{3}$$

where the last expression represents the expansion in spin. The E_0^{ab} term represents the sf-X2C term, while the terms E_k^{ab} ($k \geq 1$) represent the spin-dependent corrections. Thus, similar to the Hamiltonians (2), the property E^{ab} can be separated into spin-free and spin-dependent terms,

$$E^{ab} = E^{ab}_{sf} + E^{ab}_{sd}, \quad E^{ab}_{sf} = E^{ab}_0, \quad E^{ab}_{sd} = \sum_{k=1}^{\infty} E_k^{ab}. \tag{4}$$

The $2n + 1$ rule of perturbation theory may further be invoked to simplify the calculation of E_k^{ab}. It will be shown in Sec. II C that the spin-dependent terms can further be expanded in α^2, with the first order terms being one-to-one correspondent to the BP ones. Since the response of the decoupling and renormalization matrices is not required at this order, the implementation is straightforward.

II. THEORY

A. Spin separation at four-component level

For a given four-component mean-field equation

$$h\psi_p = \epsilon_p \psi_p, \tag{5}$$

with

$$h = \begin{pmatrix} h^{LL} & h^{LS} \\ h^{SL} & h^{SS} \end{pmatrix}, \quad \psi_p = \begin{pmatrix} \psi_p^L \\ \psi_p^S \end{pmatrix}, \tag{6}$$

the 4-spinor ψ_p can generally be expanded as[1]

$$\psi_p = Z\psi_p^M, \quad Z = \begin{pmatrix} Z_{11} & Z_{12} \\ Z_{21} & Z_{22} \end{pmatrix}, \tag{7}$$

$$\psi_p^M = \begin{pmatrix} \bar{\psi}_p^L \\ \bar{\phi}_p^L \end{pmatrix} = \begin{pmatrix} g_\mu \mathbf{A}_{\mu p} \\ g_\mu \mathbf{B}_{\mu p} \end{pmatrix} = \begin{pmatrix} Z_{11} g_\mu \mathbf{A}_{\mu p} + Z_{12} g_\mu \mathbf{B}_{\mu p} \\ Z_{21} g_\mu \mathbf{A}_{\mu p} + Z_{22} g_\mu \mathbf{B}_{\mu p} \end{pmatrix} \tag{8}$$

$$= \begin{pmatrix} Z_{11} g_\mu \\ Z_{21} g_\mu \end{pmatrix} \mathbf{A}_{\mu p} + \begin{pmatrix} Z_{12} g_\mu \\ Z_{22} g_\mu \end{pmatrix} \mathbf{B}_{\mu p}, \tag{9}$$

where it has been assumed that the large ($\bar{\psi}_p^L$) and pseudo-large ($\bar{\phi}_p^L$) components of the modified 4-spinor ψ_p^M are of the same symmetry and can therefore be expanded in the same basis $\{g_\mu\}$. Equation (5) can be rewritten as

$$h^M \psi_p^M = M \psi_p^M \epsilon_p, \quad h^M = Z^\dagger h Z, \quad M = Z^\dagger Z, \tag{10}$$

manifesting the term "modified Dirac equation."[46,47] Its matrix form reads

$$\mathbf{hC} = \mathbf{MC}E, \tag{11}$$

where

$$\mathbf{h} = \begin{pmatrix} \mathbf{h}_{11} & \mathbf{h}_{12} \\ \mathbf{h}_{21} & \mathbf{h}_{22} \end{pmatrix}, \quad \mathbf{M} = \begin{pmatrix} \mathbf{M}_{11} & \mathbf{M}_{12} \\ \mathbf{M}_{21} & \mathbf{M}_{22} \end{pmatrix}, \quad \mathbf{C} = \begin{pmatrix} \mathbf{A} \\ \mathbf{B} \end{pmatrix}, \tag{12}$$

$$(\mathbf{h}_{11})_{\mu\nu} = \langle g_\mu | Z_{11}^\dagger h^{LL} Z_{11} + Z_{11}^\dagger h^{LS} Z_{21} + Z_{21}^\dagger h^{SL} Z_{11} + Z_{21}^\dagger h^{SS} Z_{21} | g_\nu \rangle, \tag{13}$$

$$(\mathbf{h}_{12})_{\mu\nu} = \langle g_\mu | Z_{11}^\dagger h^{LL} Z_{12} + Z_{11}^\dagger h^{LS} Z_{22} + Z_{21}^\dagger h^{SL} Z_{12} + Z_{21}^\dagger h^{SS} Z_{22} | g_\nu \rangle = (\mathbf{h}_{21})_{\nu\mu}^*, \tag{14}$$

$$(\mathbf{h}_{22})_{\mu\nu} = \langle g_\mu | Z_{12}^\dagger h^{LL} Z_{12} + Z_{12}^\dagger h^{LS} Z_{22} + Z_{22}^\dagger h^{SL} Z_{12} + Z_{22}^\dagger h^{SS} Z_{22} | g_\nu \rangle, \tag{15}$$

$$(\mathbf{M}_{11})_{\mu\nu} = \langle g_\mu | Z_{11}^\dagger Z_{11} + Z_{21}^\dagger Z_{21} | g_\nu \rangle, \tag{16}$$

$$(\mathbf{M}_{12})_{\mu\nu} = \langle g_\mu | Z_{11}^\dagger Z_{12} + Z_{21}^\dagger Z_{22} | g_\nu \rangle = (\mathbf{M}_{21})_{\nu\mu}^*, \tag{17}$$

$$(\mathbf{M}_{22})_{\mu\nu} = \langle g_\mu | Z_{12}^\dagger Z_{12} + Z_{22}^\dagger Z_{22} | g_\nu \rangle. \tag{18}$$

Note in passing that Eq. (11) can also be understood as the matrix representation of the unmodified Eq. (5) but in the basis $(Z_{11}g_\mu, Z_{21}g_\mu)^T \cup (Z_{12}g_\mu, Z_{22}g_\mu)^T$, see Eq. (9). A specific model for Eq. (5) is specified by the h (6) and Z (7) operators. For the latter, various choices are possible, e.g., the restricted kinetic balance (RKB),[48] inverse kinetic balance (IKB),[49] or dual kinetic balance (DKB)[50] in the absence of magnetic fields, as well as the corresponding restricted magnetic balance (RMB),[51–53] dual magnetic balance (DMB),[54] orbital decomposition approach (ODA),[55] or external field-dependent unitary transformation (EFUT)[56,57] in the presence of magnetic fields (see Table 1 of Ref. 1 for explicit expressions). The so many choices of Z (7) for the same Hamiltonian h (6) simply mean that the spin separation is not unique at the four-component level.[58] For the purpose of illustration, consider the simplest case, i.e., the one-electron Dirac operator

$$h = \begin{pmatrix} V & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & V - 2c^2 \end{pmatrix} \tag{19}$$

and the RKB *Ansatz* for Z

$$Z = \begin{pmatrix} 1 & 0 \\ 0 & \frac{\vec{\sigma}\cdot\vec{p}}{2c} \end{pmatrix}. \tag{20}$$

The modified Hamiltonian h^M and metric M are then

$$h^M = \begin{pmatrix} V & T \\ T & \frac{\alpha^2}{4}W - T \end{pmatrix}, \quad M = \begin{pmatrix} 1 & 0 \\ 0 & \frac{\alpha^2}{2}T \end{pmatrix}, \tag{21}$$

where

$$T = \frac{\vec{p}^2}{2}, \quad W = (\vec{\sigma}\cdot\vec{p})V(\vec{\sigma}\cdot\vec{p}). \tag{22}$$

The spin separation of h^M (21) can readily be achieved by virtue of the Dirac identity (1), viz.,

$$\begin{aligned} h^M &= h_{sf}^M + h_{sd}^M, \quad h_{sf}^M = \begin{pmatrix} V & T \\ T & \frac{\alpha^2}{4}W_{sf} - T \end{pmatrix}, \\ h_{sd}^M &= \begin{pmatrix} 0 & 0 \\ 0 & \frac{\alpha^2}{4}W_{sd} \end{pmatrix}, \end{aligned} \tag{23}$$

where

$$W_{sf} = \vec{p}\cdot V\vec{p}, \quad W_{sd} = \mathbb{i}\vec{\sigma}\cdot(\vec{p}V\times\vec{p}) = \vec{\sigma}\cdot[(\nabla V)\times\vec{p}]. \tag{24}$$

In the presence of a magnetic field represented by the vector potential $\vec{A}$, the Dirac operator reads

$$h = \begin{pmatrix} V & c\vec{\sigma}\cdot\vec{\pi} \\ c\vec{\sigma}\cdot\vec{\pi} & V - 2c^2 \end{pmatrix}, \quad \vec{\pi} = \vec{p} + \vec{A}. \tag{25}$$

In this case, the RKB *Ansatz* (20) for Z (7) cannot be employed for the purpose of spin separation.[59] Rather, one of the magnetic balance *Ansätze*[53–57] should be employed. Consider the RMB *Ansatz*

$$Z = \begin{pmatrix} 1 & 0 \\ 0 & \frac{\vec{\sigma}\cdot\vec{\pi}}{2c} \end{pmatrix}, \tag{26}$$

the modified Hamiltonian h^M and metric M read

$$h^M = \begin{pmatrix} V & T_\pi \\ T_\pi & \frac{\alpha^2}{4}W_\pi - T_\pi \end{pmatrix}, \quad M = \begin{pmatrix} 1 & 0 \\ 0 & \frac{\alpha^2}{2}T_\pi \end{pmatrix}, \tag{27}$$

where

$$T_\pi = \frac{1}{2}(\vec{\sigma}\cdot\vec{\pi})^2, \quad W_\pi = (\vec{\sigma}\cdot\vec{\pi})V(\vec{\sigma}\cdot\vec{\pi}). \tag{28}$$

Unlike the field-free case (21), the modified metric (27) is now also spin dependent. Nevertheless, the separation of spin is still straightforward, leading to

$$\begin{aligned} h^M &= \begin{pmatrix} V & T_{\pi,sf} \\ T_{\pi,sf} & \frac{\alpha^2}{4}W_{\pi,sf} - T_{\pi,sf} \end{pmatrix} \\ &\quad + \begin{pmatrix} 0 & T_{\pi,sd} \\ T_{\pi,sd} & \frac{\alpha^2}{4}W_{\pi,sd} - T_{\pi,sd} \end{pmatrix}, \\ M &= \begin{pmatrix} 1 & 0 \\ 0 & \frac{\alpha^2}{2}T_{\pi,sf} \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & \frac{\alpha^2}{2}T_{\pi,sd} \end{pmatrix}, \end{aligned} \tag{29}$$

where

$$\begin{aligned} T_{\pi,sf} &= \frac{1}{2}\vec{\pi}^2, \quad T_{\pi,sd} = \frac{1}{2}\mathbb{i}\vec{\sigma}\cdot(\vec{\pi}\times\vec{\pi}), \\ W_{\pi,sf} &= \vec{\pi}\cdot V\vec{\pi}, \quad W_{\pi,sd} = \mathbb{i}\vec{\sigma}\cdot(\vec{\pi}\times V\vec{\pi}). \end{aligned} \tag{30}$$

The RKB (20) and RMB (26) transformations can also be applied to even (diagonal) and odd (off diagonal) property operators, respectively. After separating the transformed operators into spin-free and spin-dependent terms, spin-dependent relativistic corrections to spin-free relativistic properties can be evaluated by multiple perturbation theory, cf. Eqs. (3) and (4) for second order properties.

B. Spin separation at two-component level

1. X2C Hamiltonians

To formulate the X2C counterpart of the matrix Dirac equation (11), we first introduce the following formal relations:

$$\mathbf{B} = \mathbf{X}\mathbf{A}, \quad \tilde{\mathbf{A}} = \tilde{\mathbf{X}}\tilde{\mathbf{B}} \tag{31}$$

between the small and large coefficients for the positive (PES) and negative (NES) energy states, respectively. We then seek a transformation $\mathbf{U}$ that can block-diagonalize both the $\mathbf{h}$ and $\mathbf{M}$ matrices in Eq. (12). It can generally be written as

$$\mathbf{U} = \mathbf{U}_N\mathbf{U}_D, \quad \mathbf{U}_N = \begin{pmatrix} \mathbf{R}_+^\dagger & 0 \\ 0 & \mathbf{R}_-^\dagger \end{pmatrix}, \quad \mathbf{U}_D = \begin{pmatrix} \mathbf{I} & \mathbf{X}^\dagger \\ \tilde{\mathbf{X}}^\dagger & \mathbf{I} \end{pmatrix}, \tag{32}$$

where $\mathbf{U}_D$ achieves the decoupling, whereas $\mathbf{U}_N$ does the renormalization. By requiring that

$$\mathbf{U}\mathbf{h}\mathbf{U}^\dagger = \begin{pmatrix} \mathbf{h}_+^{\mathrm{X}} & 0 \\ 0 & \mathbf{h}_-^{\mathrm{X}} \end{pmatrix}, \tag{33}$$

we obtain

$$\mathbf{h}_+^{\mathrm{X}} = \mathbf{R}_+^\dagger \tilde{\mathbf{L}}_+^{\mathrm{X}} \mathbf{R}_+, \quad \mathrm{X} = \mathrm{NESC}, \mathrm{SESC}, \tag{34}$$

$$\mathbf{h}_-^{\mathrm{X}} = \mathbf{R}_-^\dagger \tilde{\mathbf{L}}_-^{\mathrm{X}} \mathbf{R}_-, \quad \mathrm{X} = \mathrm{NESC}, \mathrm{SESC}, \tag{35}$$

$$\bar{\mathbf{L}}_+ + \tilde{\mathbf{X}}^\dagger \mathbf{L}_+ = 0, \tag{36}$$

where

$$\tilde{\mathbf{L}}_+^{\mathrm{NESC}} = \mathbf{L}_+ + \mathbf{X}^\dagger \bar{\mathbf{L}}_+ = \mathbf{h}_{11} + \mathbf{h}_{12}\mathbf{X} + \mathbf{X}^\dagger \mathbf{h}_{21} + \mathbf{X}^\dagger \mathbf{h}_{22}\mathbf{X}, \tag{37}$$

$$\mathbf{L}_+ = \mathbf{h}_{11} + \mathbf{h}_{12}\mathbf{X}, \quad \bar{\mathbf{L}}_+ = \mathbf{h}_{21} + \mathbf{h}_{22}\mathbf{X}, \tag{38}$$

$$\tilde{\mathbf{L}}_-^{\mathrm{NESC}} = \mathbf{L}_- + \tilde{\mathbf{X}}^\dagger \bar{\mathbf{L}}_- = \mathbf{h}_{22} + \mathbf{h}_{21}\tilde{\mathbf{X}} + \tilde{\mathbf{X}}^\dagger \mathbf{h}_{12} + \tilde{\mathbf{X}}^\dagger \mathbf{h}_{11}\tilde{\mathbf{X}}, \tag{39}$$

$$\mathbf{L}_- = \mathbf{h}_{22} + \mathbf{h}_{21}\tilde{\mathbf{X}}, \quad \bar{\mathbf{L}}_- = \mathbf{h}_{12} + \mathbf{h}_{11}\tilde{\mathbf{X}}. \tag{40}$$

Equation (36) is the state-universal decoupling condition.[11] Similarly, the requirement that

$$\mathbf{U}\mathbf{M}\mathbf{U}^\dagger = \begin{pmatrix} \mathbf{S}_+ & 0 \\ 0 & \mathbf{S}_- \end{pmatrix} \tag{41}$$

gives rise to

$$\mathbf{R}_+^\dagger \tilde{\mathbf{S}}_+ \mathbf{R}_+ = \mathbf{S}_+, \tag{42}$$

$$\mathbf{R}_-^\dagger \tilde{\mathbf{S}}_- \mathbf{R}_- = \mathbf{S}_-, \tag{43}$$

$$\bar{\mathbf{M}}_+ + \tilde{\mathbf{X}}^\dagger \mathbf{M}_+ = 0, \tag{44}$$

where

$$\tilde{\mathbf{S}}_+ = \mathbf{M}_+ + \mathbf{X}^\dagger \bar{\mathbf{M}}_+, \tag{45}$$

$$\mathbf{M}_+ = \mathbf{M}_{11} + \mathbf{M}_{12}\mathbf{X}, \quad \bar{\mathbf{M}}_+ = \mathbf{M}_{21} + \mathbf{M}_{22}\mathbf{X}, \tag{46}$$

$$\tilde{\mathbf{S}}_- = \mathbf{M}_- + \tilde{\mathbf{X}}^\dagger \bar{\mathbf{M}}_-, \tag{47}$$

$$\mathbf{M}_- = \mathbf{M}_{22} + \mathbf{M}_{21}\tilde{\mathbf{X}}, \quad \bar{\mathbf{M}}_- = \mathbf{M}_{12} + \mathbf{M}_{11}\tilde{\mathbf{X}}. \tag{48}$$

Equation (44) shows that $\tilde{\mathbf{X}}$ and $\mathbf{X}$ are not independent but are related as

$$\tilde{\mathbf{X}} = -(\mathbf{M}_+^\dagger)^{-1} \bar{\mathbf{M}}_+^\dagger, \tag{49}$$

in terms of which the decoupling condition (36) can be rewritten as

$$\mathbf{M}_+^{-1} \mathbf{L}_+ = \bar{\mathbf{M}}_+^{-1} \bar{\mathbf{L}}_+. \tag{50}$$

This is a Riccati-like quadratic equation and determines $\mathbf{X}$ uniquely as long as the PES and NES do not get crossed. Since the NESC (normalized elimination of the small components)[10] Hamiltonians $\tilde{\mathbf{L}}_+^{\mathrm{NESC}}$ (37) and $\tilde{\mathbf{L}}_-^{\mathrm{NESC}}$ (39) are manifestly Hermitian, the SESC (symmetrized elimination of the small components)[18,19] counterparts can readily be obtained as

$$\tilde{\mathbf{L}}_+^{\mathrm{SESC}} = \frac{1}{2}[(\mathbf{L}_+ + \mathbf{X}^\dagger \bar{\mathbf{L}}_+) + c.c.] = \frac{1}{2}[\tilde{\mathbf{S}}_+ \mathbf{M}_+^{-1} \mathbf{L}_+ + c.c.], \tag{51}$$

$$\tilde{\mathbf{L}}_-^{\mathrm{SESC}} = \frac{1}{2}[(\mathbf{L}_- + \tilde{\mathbf{X}}^\dagger \bar{\mathbf{L}}_-) + c.c.] = \frac{1}{2}[\tilde{\mathbf{S}}_- \mathbf{M}_-^{-1} \mathbf{L}_- + c.c.], \tag{52}$$

where use of the relations (45) and (50) has been made. Note that both the NESC and SESC are still in the Dirac picture, viz.,

$$\tilde{\mathbf{L}}_+^{\mathrm{X}} \mathbf{A} = \tilde{\mathbf{S}}_+ \mathbf{A} E_+, \quad \mathrm{X} = \mathrm{NESC}, \mathrm{SESC}, \tag{53}$$

$$\tilde{\mathbf{L}}_-^{\mathrm{X}} \tilde{\mathbf{B}} = \tilde{\mathbf{S}}_- \tilde{\mathbf{B}} E_-, \quad \mathrm{X} = \mathrm{NESC}, \mathrm{SESC}. \tag{54}$$

To go to the Schrödinger picture with the $\mathbf{S}_+$ and $\mathbf{S}_-$ matrices defined as

$$(\mathbf{S}_+)_{\mu\nu} = \langle g_\mu | Z_{11}^\dagger Z_{11} | g_\nu \rangle, \tag{55}$$

$$(\mathbf{S}_-)_{\mu\nu} = \langle g_\mu | Z_{22}^\dagger Z_{22} | g_\nu \rangle, \tag{56}$$

the renormalization matrices $\mathbf{R}_+$ and $\mathbf{R}_-$ must be defined properly. The problem lies in that conditions (42) and (43) cannot uniquely determine $\mathbf{R}_+$ and $\mathbf{R}_-$, respectively. One particular choice is to impose the "Hermiticity condition"[13]

$$\mathbf{S}_+ \mathbf{R}_+ = (\mathbf{S}_+ \mathbf{R}_+)^\dagger, \tag{57}$$

$$\mathbf{S}_- \mathbf{R}_- = (\mathbf{S}_- \mathbf{R}_-)^\dagger. \tag{58}$$

As a matter of fact, conditions (42) and (57), as well as (43) and (58), can be unified into a single condition

$$\mathbf{R}_+ \mathbf{S}_+^{-1} \tilde{\mathbf{S}}_+ \mathbf{R}_+ = \mathbf{I}, \quad \mathbf{R}_- \mathbf{S}_-^{-1} \tilde{\mathbf{S}}_- \mathbf{R}_- = \mathbf{I}. \tag{59}$$

The $\mathbf{R}_+$ and $\mathbf{R}_-$ matrices can then be found to be[13]

$$\mathbf{R}_+ = \mathbf{S}_+^{-1/2} [\mathbf{S}_+^{-1/2} \tilde{\mathbf{S}}_+ \mathbf{S}_+^{-1/2}]^{-1/2} \mathbf{S}_+^{1/2}, \tag{60}$$

$$\mathbf{R}_- = \mathbf{S}_-^{-1/2} [\mathbf{S}_-^{-1/2} \tilde{\mathbf{S}}_- \mathbf{S}_-^{-1/2}]^{-1/2} \mathbf{S}_-^{1/2}. \tag{61}$$

With the above quantities, the unitary transformation of Eq. (11), viz.,

$$\mathbf{U}\mathbf{h}\mathbf{U}^\dagger (\mathbf{U}^\dagger)^{-1} \mathbf{C} = \mathbf{U}\mathbf{M}\mathbf{U}^\dagger (\mathbf{U}^\dagger)^{-1} \mathbf{C} E, \tag{62}$$

gives rise to

$$\begin{pmatrix} \mathbf{h}_+^{\mathrm{X}} & 0 \\ 0 & \mathbf{h}_-^{\mathrm{X}} \end{pmatrix} \begin{pmatrix} \mathbf{C}_+ & 0 \\ 0 & \mathbf{C}_- \end{pmatrix} = \begin{pmatrix} \mathbf{S}_+ & 0 \\ 0 & \mathbf{S}_- \end{pmatrix} \begin{pmatrix} \mathbf{C}_+ & 0 \\ 0 & \mathbf{C}_- \end{pmatrix} \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}, \tag{63}$$

or

$$\mathbf{h}_+^{\mathrm{X}} \mathbf{C}_+ = \mathbf{S}_+ \mathbf{C}_+ E_+, \quad \mathrm{X} = \mathrm{NESC}, \mathrm{SESC}, \tag{64}$$

$$\mathbf{h}_{-}^{\mathrm{X}}\mathbf{C}_{-} = \mathbf{S}_{-}\mathbf{C}_{-}E_{-}, \quad \mathrm{X} = \mathrm{NESC, SESC}, \tag{65}$$

which are the desired X2C equations for the PES and NES, respectively. In view of the identity

$$\mathbf{C} = \mathbf{U}^{\dagger}\begin{pmatrix}\mathbf{C}_{+} & 0\\ 0 & \mathbf{C}_{-}\end{pmatrix} = \begin{pmatrix}\mathbf{R}_{+}\mathbf{C}_{+} & \tilde{\mathbf{X}}\mathbf{R}_{-}\mathbf{C}_{-}\\ \mathbf{X}\mathbf{R}_{+}\mathbf{C}_{+} & \mathbf{R}_{-}\mathbf{C}_{-}\end{pmatrix} = \begin{pmatrix}\mathbf{A} & \tilde{\mathbf{X}}\tilde{\mathbf{B}}\\ \mathbf{X}\mathbf{A} & \tilde{\mathbf{B}}\end{pmatrix}, \tag{66}$$

the relationships between $\mathbf{C}_{+}$ and $\mathbf{A}$ and between $\mathbf{C}_{-}$ and $\tilde{\mathbf{B}}$ read

$$\mathbf{C}_{+} = \mathbf{R}_{+}^{-1}\mathbf{A}, \quad \mathbf{C}_{-} = \mathbf{R}_{-}^{-1}\tilde{\mathbf{B}}. \tag{67}$$

A few remarks are in order.

(a) The above formulation of the X2C Hamiltonians is more general than the previous ones[10–17] that were based solely on the RKB condition (20). Here, various kinetic and magnetic balances are incorporated in a unified manner.

(b) No matter how the Z operator (7) is defined, the nonrelativistic metrics (55) and (56) can always be imposed, contrary to the statement[29] that the Z operators with $Z_{12} \neq 0$ (e.g., DKB[50], DMB,[54] and EFUT[57]) do not permit the nonrelativistic metrics. Yet, only for the special cases with $Z_{12} = Z_{21} = 0$, including RKB (20) and RMB (26), the transformation $\mathbf{U}$ (32) satisfies

$$\mathbf{U}\mathbf{M}\mathbf{U}^{\dagger} = \mathbf{M} = \begin{pmatrix}\mathbf{M}_{11} & 0\\ 0 & \mathbf{M}_{22}\end{pmatrix}. \tag{68}$$

(c) The Hermiticity conditions (57) and (58) are in accordance with the Foldy-Wouthuysen (FW) unitary transformation.[60] It is proven in Appendix A that the so-normalized two-component eigenvectors $\psi_{p,+}^{FW} = \sum_{\mu} g_{\mu}(\mathbf{C}_{+})_{\mu p}$ are closest to the large-components ψ_{p}^{L} in the least-squares sense,

$$\min \sum_{p} \|\psi_{p,+}^{FW} - \psi_{p,+}^{L}\|^2 = \min \sum_{p} \langle \psi_{p,+}^{FW} - \psi_{p,+}^{L} | \psi_{p,+}^{FW} - \psi_{p,+}^{L} \rangle. \tag{69}$$

In contrast, the DKH[23,24,31–37] and BSS[38–43] approaches amount to using different renormalizations. However, they share the same decoupling condition (50) as X2C.[15]

2. Spin separation of X2C Hamiltonians

The X2C Hamiltonians (34) are defined algebraically, such that the Dirac identity (1) cannot be applied for spin separation. The way out[30] is to partition *a priori* the matrix Dirac equation (11) into spin-free and spin-dependent terms. For instance, in the case of RKB, the Hamiltonian and metric read explicitly

$$\mathbf{h} = \begin{pmatrix}\mathbf{V} & \mathbf{T}\\ \mathbf{T} & \frac{\alpha^2}{4}\mathbf{W} - \mathbf{T}\end{pmatrix} = \mathbf{h}_{sf} + \mathbf{h}_{sd}, \tag{70}$$

$$\mathbf{h}_{sf} = \begin{pmatrix}\mathbf{V} & \mathbf{T}\\ \mathbf{T} & \frac{\alpha^2}{4}\mathbf{W}_{sf} - \mathbf{T}\end{pmatrix}, \quad \mathbf{h}_{sd} = \begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \frac{\alpha^2}{4}\mathbf{W}_{sd}\end{pmatrix}, \tag{71}$$

$$\mathbf{M} = \begin{pmatrix}\mathbf{S} & \mathbf{0}\\ \mathbf{0} & \frac{\alpha^2}{2}\mathbf{T}\end{pmatrix} = \begin{pmatrix}\mathbf{S}_{+} & 0\\ 0 & \mathbf{S}_{-}\end{pmatrix}, \tag{72}$$

$$S_{\mu\nu} = \langle g_{\mu}|g_{\nu}\rangle, \quad T_{\mu\nu} = \langle g_{\mu}|\frac{1}{2}p^2|g_{\nu}\rangle, \quad V_{\mu\nu} = \langle g_{\mu}|V|g_{\nu}\rangle, \tag{73}$$

$$(W_{sf})_{\mu\nu} = \langle g_{\mu}|\vec{p}\cdot V\vec{p}|g_{\nu}\rangle, \quad (W_{sd})_{\mu\nu} = \langle g_{\mu}|\mathbb{i}\vec{\sigma}\cdot(\vec{p}V\times\vec{p})|g_{\nu}\rangle. \tag{74}$$

The spin-free Hamiltonian $\mathbf{h}_{sf}$ (71), along with the spin-free metric $\mathbf{M}$ (72), can first be block-diagonalized by means of the transformation $\mathbf{U}$ (32) (denoted as $\mathbf{U}_0$), so as to obtain the sf-X2C Hamiltonians $\mathbf{h}_{+,sf}$ ($\triangleq \mathbf{E}_{+,0}$) (34) and $\mathbf{h}_{-,sf}$ ($\triangleq \mathbf{E}_{-,0}$) (35) for the PES and NES, respectively. Hereafter, all quantities with subscript 0 refer to sf-X2C. Two general procedures have been introduced to treat the spin-dependent term $\mathbf{h}_{sd}$ (71) to any order.[30] In practice, the sf-X2C+so-DKH3 Hamiltonian is most valuable. It is defined as

$$\mathbf{h}_{+} = \mathbf{E}_{+,0} + \mathbf{E}_{+,1} + \mathbf{E}_{+,2} + \mathbf{E}_{+,3}, \tag{75}$$

$$\mathbf{E}_{+,0} = \mathbf{h}_{+,sf} = \mathbf{R}_{+,0}^{\dagger}\tilde{\mathbf{L}}_{+,0}^{\mathrm{X}}\mathbf{R}_{+,0}, \quad \mathrm{X} = \mathrm{NESC, SESC}, \tag{76}$$

$$\mathbf{E}_{+,1} = \frac{\alpha^2}{4}\mathbf{R}_{+,0}^{\dagger}\mathbf{X}_0^{\dagger}\mathbf{W}_{sd}\mathbf{X}_0\mathbf{R}_{+,0}, \tag{77}$$

$$\mathbf{E}_{+,2} = \frac{1}{\alpha^2}(\mathbf{W}_1\mathbf{T}^{-1}\mathbf{O}_1^{\dagger} + c.c.), \tag{78}$$

$$\mathbf{E}_{+,3} = \frac{1}{\alpha^2}(\mathbf{W}_1\mathbf{T}^{-1}\mathbf{O}_2^{\dagger} + c.c.), \tag{79}$$

where

$$\tilde{\mathbf{L}}_{+,0}^{\mathrm{NESC}} = \mathbf{V} + \mathbf{T}\mathbf{X}_0 + \mathbf{X}_0^{\dagger}\mathbf{T} + \mathbf{X}_0^{\dagger}\left(\frac{\alpha^2}{4}\mathbf{W}_{sf} - \mathbf{T}\right)\mathbf{X}_0, \tag{80}$$

$$\tilde{\mathbf{L}}_{+,0}^{\mathrm{SESC}} = \frac{1}{2}[\tilde{\mathbf{S}}_{+,0}\mathbf{S}^{-1}(\mathbf{V} + \mathbf{T}\mathbf{X}_0) + c.c.], \tag{81}$$

$$\mathbf{W}_1 = \frac{\alpha^2}{2}\mathbf{S}\mathbf{C}_{+,0}\mathbf{w}_1\mathbf{C}_{-,0}^{\dagger}\mathbf{T}, \tag{82}$$

$$[\mathbf{w}_1]_{pq} = -\frac{[\mathbf{o}_1]_{pq}}{[E_{-,0}]_q - [E_{+,0}]_p}, \quad \mathbf{o}_1 = \mathbf{C}_{+,0}^{\dagger}\mathbf{O}_1\mathbf{C}_{-,0}, \tag{83}$$

$$\mathbf{O}_1 = \frac{\alpha^2}{4}\mathbf{R}_{+,0}^{\dagger}\mathbf{X}_0^{\dagger}\mathbf{W}_{sd}\mathbf{R}_{-,0}, \tag{84}$$

$$\mathbf{O}_2 = \frac{2}{\alpha^2}\mathbf{W}_1\mathbf{T}^{-1}\mathbf{E}_{-,1} - \mathbf{E}_{+,1}\mathbf{S}^{-1}\mathbf{W}_1 = \mathbf{O}_2^{sf} + \mathbf{O}_2^{sd}, \tag{85}$$

$$\mathbf{E}_{-,1} = \frac{\alpha^2}{4}\mathbf{R}_{-,0}^{\dagger}\mathbf{W}_{sd}\mathbf{R}_{-,0}. \tag{86}$$

Here, the coefficients $\mathbf{C}_{+,0}$ and $\mathbf{C}_{-,0}$ are solutions of Eqs. (64) and (65), respectively. The $\mathbf{X}_0$ matrix can readily be obtained by using the efficient algorithms presented before.[15,18] At this

stage, it is to be pointed out that, although both $\mathbf{E}_{+,2}$ (78) and $\mathbf{E}_{+,3}$ (79) stem from the spin-orbit interaction $\mathbf{W}_{sd}$, they are still not yet of the familiar form of $\vec{l}\cdot\vec{s}$. To achieve this, we first note that $\mathbf{W}_{sd}$ (74) in a spin-orbital basis $\{g_\mu = \chi_\mu \vartheta_\mu\}$, with $\{\chi_\mu\}$ being the spatial functions and $\{\vartheta_\mu\}$ being the spin functions α and β, can be written as

$$\mathbf{W}_{sd} = \mathbb{i}(\sigma_x \otimes \mathbf{V}^x + \sigma_y \otimes \mathbf{V}^y + \sigma_z \otimes \mathbf{V}^z) \tag{87}$$

$$= \mathbb{i}\begin{pmatrix} \mathbf{V}^z & \mathbf{V}^x - \mathbb{i}\mathbf{V}^y \\ \mathbf{V}^x + \mathbb{i}\mathbf{V}^y & -\mathbf{V}^z \end{pmatrix} \triangleq \mathbb{i}\vec{\sigma}\cdot\vec{\mathbf{V}}, \tag{88}$$

$$[\mathbf{V}^m]_{\mu\nu} = \langle\chi_\mu|(\vec{p}V\times\vec{p})_m|\chi_\nu\rangle, \quad m = x, y, z, \tag{89}$$

with $\mathbf{V}^m$ being real-valued antisymmetric matrices for real-valued functions $\{\chi_\mu\}$. Since both $\mathbf{X}_0$ and $\mathbf{R}_{+,0}$ are spin free, we can rewrite all the first order spin-dependent terms, including $\mathbf{E}_{+,1}$, $\mathbf{O}_1$, $\mathbf{E}_{-,1}$ and $\mathbf{W}_{+,1}$, in the same form as $\mathbf{W}_{sd}$ (88), e.g., $\mathbf{E}_{+,1} = \mathbb{i}\vec{\sigma}\cdot\vec{\mathbf{E}}^{sd}_{+,1}$ with $\vec{\mathbf{E}}^{sd}_{+,1}$ in place of $\vec{\mathbf{V}}$. In this way, $\mathbf{E}_{+,2}$ (78) can further be separated into two parts by using the Dirac identity (1), viz.,

$$\mathbf{E}^{sf}_{+,2} = \frac{1}{\alpha^2}(\vec{\mathbf{W}}_1\cdot\mathbf{T}^{-1}\vec{\mathbf{O}}_1^T + \vec{\mathbf{O}}_1\cdot\mathbf{T}^{-1}\vec{\mathbf{W}}_1^T), \tag{90}$$

$$\mathbf{E}^{sd}_{+,2} = \frac{\mathbb{i}}{\alpha^2}\vec{\sigma}\cdot(\vec{\mathbf{W}}_1\times\mathbf{T}^{-1}\vec{\mathbf{O}}_1^T + \vec{\mathbf{O}}_1\times\mathbf{T}^{-1}\vec{\mathbf{W}}_1^T). \tag{91}$$

Since $(\vec{\mathbf{W}}_1\times\mathbf{T}^{-1}\vec{\mathbf{O}}_1^T)^T = -(\vec{\mathbf{O}}_1\times\mathbf{T}^{-1}\vec{\mathbf{W}}_1^T)$, the operator in the parenthesis of Eq. (91) is still antisymmetric as it should be. Similarly, $\mathbf{O}_2$ (85) can be separated into

$$\mathbf{O}^{sf}_2 = -(2c^2\vec{\mathbf{W}}_1\cdot\mathbf{T}^{-1}\vec{\mathbf{E}}_{-,1} - \vec{\mathbf{E}}_{+,1}\cdot\mathbf{S}^{-1}\vec{\mathbf{W}}_1), \tag{92}$$

$$\mathbf{O}^{sd}_2 = -\mathbb{i}\vec{\sigma}\cdot(2c^2\vec{\mathbf{W}}_1\times\mathbf{T}^{-1}\vec{\mathbf{E}}_{-,1} - \vec{\mathbf{E}}_{+,1}\times\mathbf{S}^{-1}\vec{\mathbf{W}}_1), \tag{93}$$

such that $\mathbf{E}_{+,3}$ (79) can be rewritten as

$$\mathbf{E}^{sf}_{+,3} = \frac{1}{\alpha^2}(\vec{\mathbf{W}}_1\cdot\mathbf{T}^{-1}\vec{\mathbf{O}}_2^{sd,T} + \vec{\mathbf{O}}_2^{sd}\cdot\mathbf{T}^{-1}\vec{\mathbf{W}}_1^T), \tag{94}$$

$$\mathbf{E}^{sd}_{+,3} = \frac{\mathbb{i}}{\alpha^2}\vec{\sigma}\cdot\big(\vec{\mathbf{W}}_1\mathbf{T}^{-1}\mathbf{O}_2^{sf,T} - \mathbf{O}^{sf}_2\mathbf{T}^{-1}\vec{\mathbf{W}}_1^T + \vec{\mathbf{W}}_1\times\mathbf{T}^{-1}\vec{\mathbf{O}}_2^{sd,T} + \vec{\mathbf{O}}_2^{sd}\times\mathbf{T}^{-1}\vec{\mathbf{W}}_1^T\big). \tag{95}$$

As such, the sf-X2C+so-DKH3 Hamiltonian (75) can be rewritten in a fully spin-separated form

$$\mathbf{h}_+ = \big(\mathbf{E}_{+,0} + \mathbf{E}^{sf}_{+,2} + \mathbf{E}^{sf}_{+,3}\big) + \mathbb{i}\vec{\sigma}\cdot\big(\vec{\mathbf{E}}^{sd}_{+,1} + \vec{\mathbf{E}}^{sd}_{+,2} + \vec{\mathbf{E}}^{sd}_{+,3}\big). \tag{96}$$

It is interesting to note that, while $\mathbf{E}_{0,+} = \mathbf{h}_{+,sf}$ is already infinite order in scalar relativity, the sf-X2C+so-DKH3 Hamiltonian $\mathbf{h}_+$ (96) still has additional scalar terms $\mathbf{E}^{sf}_{+,2}$ and $\mathbf{E}^{sf}_{+,3}$, which stem from the second and third order spin-dependent terms, respectively. This is hardly surprising but just due to the picture change. Note also that the constructions of $\mathbf{E}^{sf/sd}_{+,2}$ and $\mathbf{E}^{sf/sd}_{+,3}$ are essentially free, since all necessary quantities are already available after constructing the sf-X2C Hamiltonian. The high accuracy and compactness of $\mathbf{h}_+$ (96) arise from the sf-sd partitioning of the Dirac matrix (70), the one-step matrix formulation (32) of the sf-X2C Hamiltonian $\mathbf{h}_{+,sf}$ (76), as well as the $2n+1$ rule[32] valid in the DKH type of transformation of the spin-dependent term.

3. Spin separation of X2C first order properties

Introducing a perturbation O^{4C} into the four-component Hamiltonian h (5) leads to

$$h(\epsilon) = h + \epsilon O^{4C}, \tag{97}$$

which can be discretized like $\mathbf{h}$ (12),

$$\mathbf{h}(\epsilon) = \mathbf{h} + \epsilon\mathbf{O}^{4C}. \tag{98}$$

The X2C counterpart $\mathbf{h}^{\mathrm{X}}_+(\epsilon)$ (X = NESC, SESC) (34) of $\mathbf{h}(\epsilon)$ (98) can be formulated in the same way as before. The interest here is the first order $\mathbf{h}^1_+$ term of $\mathbf{h}^{\mathrm{NESC}}_+(\epsilon)$, i.e.,

$$\mathbf{h}^1_+ = \mathbf{O}^{\mathrm{NESC}}_+ + [(\mathbf{R}^\dagger_{+,1}\tilde{\mathbf{L}}^{\mathrm{NESC}}_{+,0}\mathbf{R}_{+,0} + \mathbf{R}^\dagger_{+,0}\mathbf{X}_1^\dagger\bar{\mathbf{L}}_{+,0}\mathbf{R}_{+,0}) + c.c.], \tag{99}$$

$$\mathbf{O}^{\mathrm{NESC}}_+ = [\mathbf{U}_0\mathbf{O}^{4C}\mathbf{U}_0^\dagger]_{++} = \mathbf{R}^\dagger_{+,0}(\mathbf{O}_{11} + \mathbf{O}_{12}\mathbf{X}_0 + \mathbf{X}_0^\dagger\mathbf{O}_{21} + \mathbf{X}_0^\dagger\mathbf{O}_{22}\mathbf{X}_0)\mathbf{R}_{+,0}. \tag{100}$$

It is a bit tedious but straightforward to show that the second term of (99) does not contribute to the first order energy of state p, $E^1_p = (\mathbf{C}^\dagger_{+,0}\mathbf{h}^1_+\mathbf{C}_{+,0})_{pp}$. Alternatively, this can be seen as follows:

$$E^1_p = (\mathbf{C}_0^\dagger\mathbf{O}^{4C}\mathbf{C}_0)_{pp} = \{[\mathbf{U}_0^\dagger\begin{pmatrix}\mathbf{C}_{+,0}\\ 0\end{pmatrix}]^\dagger\mathbf{O}^{4C}[\mathbf{U}_0^\dagger\begin{pmatrix}\mathbf{C}_{+,0}\\ 0\end{pmatrix}]\}_{pp} = (\mathbf{C}^\dagger_{+,0}\mathbf{O}^{\mathrm{NESC}}_+\mathbf{C}_{+,0})_{pp}, \tag{101}$$

where use of the relation $\mathbf{C}_0 = \mathbf{U}_0^\dagger\mathbf{C}_{+,0}$ for the PES has been made, see Eq. (66). It is therefore clear that only $\mathbf{O}^{\mathrm{NESC}}_+$ (100) is required for the valuation of E^1_p. Note in passing that the orderings of the quantities in Eqs. (99)–(101) refer to the external perturbation ϵO^{4C} instead of spin-orbit coupling. To avoid heavy notation in the subsequent derivation of this section, the field-free $\mathbf{X}_0$, $\mathbf{R}_{+,0}$ and $\mathbf{U}_0$ matrices in Eqs. (99)–(101) will be changed to $\mathbf{X}$, $\mathbf{R}_+$, and $\mathbf{U}$, respectively. For the purpose of spin separation, we assume $\mathbf{O}^{4C}$ can be separated as (cf. Sec. II A)

$$\mathbf{O}^{4C} = \mathbf{O}^{4C}_{sf} + \mathbf{O}^{4C}_{sd}. \tag{102}$$

In the case of one-step X2C, the $\mathbf{O}^{4C}$ operator (102) is to be transformed directly to the two-component operator $\mathbf{O}^{\mathrm{X2C}}_+$. In contrast, in the case of two-step BSS, it is the spin-free $\mathbf{U}_0$-transformed counterpart of $\mathbf{O}^{4C}$, i.e.,

$$\tilde{\mathbf{O}}^{4C} = \mathbf{U}_0\mathbf{O}^{4C}\mathbf{U}_0^\dagger = \mathbf{U}_0\mathbf{O}^{4C}_{sf}\mathbf{U}_0^\dagger + \mathbf{U}_0\mathbf{O}^{4C}_{sd}\mathbf{U}_0^\dagger, \tag{103}$$

that is to be transformed to the two-component operator $\mathbf{O}^{\mathrm{BSS}}_+$. The $\mathbf{X}$ and $\mathbf{R}_+[\mathbf{X}]$ matrices in Eq. (100) should then be understood as the respective $\mathbf{Y}$ and $\mathbf{R}_+[\mathbf{Y}]$ matrices in the two-step BSS approach. Once the perturbative expansion of $\mathbf{X}$ (or $\mathbf{Y}$) is obtained at each order in W_{sd} and O_{sd}, the two-component

operator $\mathbf{O}_+^{\mathrm{X}}$ can be constructed, viz.,

$$\mathbf{O}_+^X = \mathbf{O}_{+,sf} + \mathbf{O}_{+,sd}^X, \quad \mathrm{X} = \mathrm{BSS, X2C}, \tag{104}$$

$$\mathbf{O}_{+,sf} = \left[\mathbf{U}_0 \mathbf{O}_{sf}^{4C} \mathbf{U}_0^\dagger\right]_{++}, \quad \mathbf{O}_{+,sd}^{\mathrm{X}} = \sum_{k=1}^{\infty} \mathbf{O}_{+,k}^{\mathrm{X}}. \tag{105}$$

As for the DKH approach, the $\tilde{\mathbf{O}}^{4C}$ operator (103) can be separated into even and odd terms, i.e.,

$$\tilde{\mathbf{O}}^{4C} = \mathbf{U}_0 \mathbf{O}^{4C} \mathbf{U}_0^\dagger = \boldsymbol{\mathcal{E}}_0 + \boldsymbol{\mathcal{O}}_0 + \boldsymbol{\mathcal{E}}_1 + \boldsymbol{\mathcal{O}}_1, \tag{106}$$

where the subscript counts the order in W_{sd} and O_{sd}. Note that the zeroth order odd term $\boldsymbol{\mathcal{O}}_0$ does not vanish here. In general, the nth order DKH $\mathbf{U}_n$ determines a property also to the nth order,[61] unlike the DKH Hamiltonian where the $2n+1$ rule holds.[32] A general procedure for constructing $\mathbf{U}_n$ of arbitrary n has been discussed before[30] and is not repeated here.

As an illustration of the above schemes for spin separation of first order properties, we take the multiple momenta r^m ($m = -2, -1, 1, 2$) as examples. To simplify the calculation, the coefficient $\mathbf{C}_+$ is not expanded order by order ($\mathbf{C}_{+,k}$, $k = 0, \ldots, n$). Instead, the coefficient $\mathbf{C}_+^{[n]}$ that is correct up to order n is directly evaluated as the eigenvector of $\mathbf{h}_+^{[n]}$, viz.,

$$\mathbf{h}_+^{[n]} \mathbf{C}_+^{[n]} = \mathbf{S}_+ \mathbf{C}_+^{[n]} E_+^{[n]}, \quad \mathbf{h}_+^{[n]} = \sum_{k=0}^{n} \mathbf{h}_{+,k}. \tag{107}$$

The $[n]$th order momenta $\langle r^m \rangle_p^{[n]}$ of state p can then be calculated simply as

$$\langle r^m \rangle_p^{[n]} = (\mathbf{C}_+^{[n]\dagger} [\mathbf{r}^m]_+^{[n]} \mathbf{C}_+^{[n]})_{pp}, \quad [\mathbf{r}^m]_+^{[n]} = \sum_{k=0}^{n} [\mathbf{r}^m]_{+,k}. \tag{108}$$

The one-step X2C formulation is adopted in the actual calculations, yet with two partitions of the Dirac Hamiltonian $\mathbf{h}$. One is the sf-sd partition as shown in Eq. (70). The other is the free-particle (fp) partition, viz.,

$$\mathbf{h} = \begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \frac{\alpha^2}{4}\mathbf{W} - \mathbf{T} \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{T} \\ \mathbf{T} & -\mathbf{T} \end{pmatrix} + \begin{pmatrix} \mathbf{V} & \mathbf{0} \\ \mathbf{0} & \frac{\alpha^2}{4}\mathbf{W} \end{pmatrix}. \tag{109}$$

The calculations are carried out for the $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ states of Rn^{85+} with a value of 137.0359895 a.u. for the speed of light, a point charge distribution for the nucleus, as well as an uncontracted triple-zeta basis set $(30s26p17d11f)$[62] for the matrix representation. The deviations of the $[n]$th order X2C results from the four-component ones are plotted in Fig. 2. For comparison, the deviations of the $[n]$th order X2C energies, $E_p^{[n]} = (\mathbf{C}_+^{[n]\dagger} \mathbf{h}_+^{[n]} \mathbf{C}_+^{[n]})_{pp}$, are also plotted therein. It is clearly seen that the rate of convergence is very much the same for the energies and the momenta. In particular, the sf-sd partition (70) is superior over the fp partition (109) adopted in the original DKH[23,24,31–37] and BSS[38–43] approaches.

4. Spin separation of X2C response theory

What has been achieved so far is the spin separation of the field-free X2C Hamiltonians (34) resulting from the field-free Dirac equation represented in a RKB basis (20). Now we consider the spin separation of X2C response theory. The general framework is multiple perturbation theory, where external electric or magnetic perturbations have specific orders whereas spin-orbit couplings are to be treated to any desired order. The central step for such multiple expansions of the X2C Hamiltonians (34) represented in, e.g., a RMB basis (26), is to determine the response $\mathbf{X}^\lambda$ of the decoupling matrix $\mathbf{X}$, with $\lambda = (a, b, \ldots)$ being the composite index for the perturbations $\{V^a, V^b, \ldots\}$. To achieve this, we spell out Eqs. (36) and (44) explicitly

$$\tilde{\mathbf{X}}^\dagger (\mathbf{h}_{11} + \mathbf{h}_{12}\mathbf{X}) + (\mathbf{h}_{21} + \mathbf{h}_{22}\mathbf{X}) = 0, \tag{110}$$

$$\tilde{\mathbf{X}}^\dagger (\mathbf{M}_{11} + \mathbf{M}_{12}\mathbf{X}) + (\mathbf{M}_{21} + \mathbf{M}_{22}\mathbf{X}) = 0, \tag{111}$$

which can be expanded for $\lambda > 0$ as

$$\tilde{\mathbf{X}}^{\lambda\dagger} \mathbf{L}_{+,0} + \mathbf{L}_{-,0}^\dagger \mathbf{X}^\lambda = -\boldsymbol{\mathcal{L}}^\lambda, \tag{112}$$

$$\tilde{\mathbf{X}}^{\lambda\dagger} \mathbf{M}_{+,0} + \mathbf{M}_{-,0}^\dagger \mathbf{X}^\lambda = -\boldsymbol{\mathcal{M}}^\lambda. \tag{113}$$

Here, $\boldsymbol{\mathcal{L}}^\lambda$ and $\boldsymbol{\mathcal{M}}^\lambda$ collect all the terms that do not depend on $\tilde{\mathbf{X}}^\lambda$ and $\mathbf{X}^\lambda$ on the left hand sides of Eqs. (110) and (111), respectively. The zeroth order terms herein are

$$\mathbf{L}_{+,0} = \mathbf{h}_{11,0} + \mathbf{h}_{12,0}\mathbf{X}_0, \tag{114}$$

$$\mathbf{L}_{-,0} = \mathbf{h}_{22,0} + \mathbf{h}_{21,0}\tilde{\mathbf{X}}_0, \tag{115}$$

$$\mathbf{M}_{+,0} = \mathbf{M}_{11,0} + \mathbf{M}_{12,0}\mathbf{X}_0, \tag{116}$$

$$\mathbf{M}_{-,0} = \mathbf{M}_{22,0} + \mathbf{M}_{21,0}\tilde{\mathbf{X}}_0. \tag{117}$$

Use of Eq. (113) can be made to eliminate $\tilde{\mathbf{X}}^\lambda$ in Eq. (112), so as to obtain a Sylvester equation for $\mathbf{X}^\lambda$ only,

$$\mathbf{X}^\lambda \left(\mathbf{M}_{+,0}^{-1}\mathbf{L}_{+,0}\right) - \left(\mathbf{L}_{-,0}\mathbf{M}_{-,0}^{-1}\right)^\dagger \mathbf{X}^\lambda = (\mathbf{M}_{-,0}^\dagger)^{-1}[\boldsymbol{\mathcal{L}}^\lambda - \boldsymbol{\mathcal{M}}^\lambda \mathbf{M}_{+,0}^{-1}\mathbf{L}_{+,0}]. \tag{118}$$

Further in view of the zeroth order equations (cf. Eqs. (11) and (31))

$$\mathbf{L}_{+,0}\mathbf{A}_{+,0} = \mathbf{M}_{+,0}\mathbf{A}_{+,0}E_{+,0}, \tag{119}$$

$$\mathbf{L}_{-,0}\mathbf{B}_{-,0} = \mathbf{M}_{-,0}\mathbf{B}_{-,0}E_{-,0}, \tag{120}$$

Eq. (118) can readily be solved by multiplying $\mathbf{B}_{-,0}^\dagger \mathbf{M}_{-,0}^\dagger$ from the left and $\mathbf{A}_{+,0}$ from the right, viz.,

$$\mathbf{x}^\lambda E_{+,0} - E_{-,0}\mathbf{x}^\lambda = \mathbf{o}^\lambda, \tag{121}$$

where

$$\mathbf{x}^\lambda = \mathbf{B}_{-,0}^\dagger \mathbf{M}_{-,0}^\dagger \mathbf{X}^\lambda \mathbf{A}_{+,0}, \tag{122}$$

$$\mathbf{o}^\lambda = \mathbf{B}_{-,0}^\dagger \boldsymbol{\mathcal{L}}^\lambda \mathbf{A}_{+,0} - \mathbf{B}_{-,0}^\dagger \boldsymbol{\mathcal{M}}^\lambda \mathbf{A}_{+,0} E_{+,0}. \tag{123}$$

Since $E_{+,0}$ and $E_{-,0}$ are diagonal, we have

$$[\mathbf{x}^\lambda]_{pq} = \frac{[\mathbf{o}^\lambda]_{pq}}{[E_{+,0}]_q - [E_{-,0}]_p}, \tag{124}$$

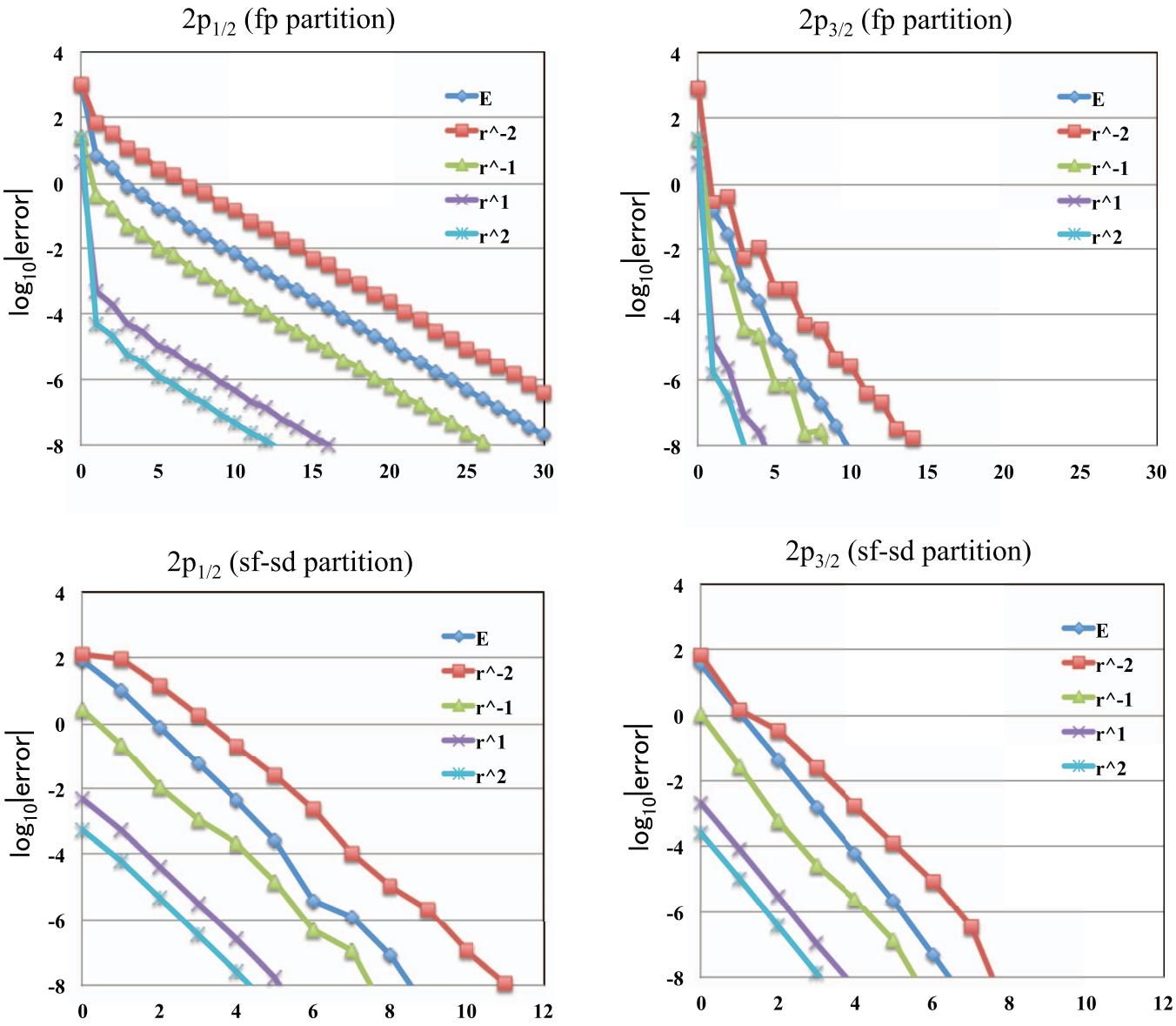

FIG. 2. Deviations of the $[n]$th order energy $\langle \mathbf{h}_+^{[n]} \rangle$ and momenta $\langle \mathbf{r}^m \rangle^{[n]}$ ($m = -2, -1, 1, 2$) from the four-component results for the $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ states of Rn^{85+} by the one-step X2C formulation with the free-particle (fp) (109) and spin-free and spin-dependent (sf-sd) (70) partitions of the Dirac Hamiltonian.

and therefore

$$\mathbf{X}^\lambda = (\mathbf{B}_{-,0}^\dagger \mathbf{M}_{-,0}^\dagger)^{-1} \mathbf{x}^\lambda \mathbf{A}_{+,0}^{-1} \tag{125}$$

in view of Eq. (122).

The response $\mathbf{R}_+^\lambda$ of the renormalization matrix $\mathbf{R}_+$ can be found by expanding Eq. (59). Its zeroth order term is just

$$\mathbf{R}_{+,0} \mathbf{S}_+^{-1} \tilde{\mathbf{S}}_{+,0} \mathbf{R}_{+,0} = \mathbf{I}, \tag{126}$$

which gives rise to

$$\mathbf{R}_{+,0} = \mathbf{S}_+^{-1/2} [\mathbf{S}_+^{-1/2} \tilde{\mathbf{S}}_{+,0} \mathbf{S}_+^{-1/2}]^{-1/2} \mathbf{S}_+^{1/2} \tag{127}$$

$$= \mathbf{z}_0 \omega_0^{-\frac{1}{2}} \mathbf{z}_0^{-1}, \quad \mathbf{z}_0^{-1} = \mathbf{z}_0^\dagger \mathbf{S}_+. \tag{128}$$

Here, $\mathbf{z}_0$ and $\omega_0 = \mathrm{diag}\{\omega_p\}$ are eigenpairs of $\tilde{\mathbf{S}}_{+,0}$, viz.,

$$\tilde{\mathbf{S}}_{+,0} \mathbf{z}_0 = \mathbf{S}_+ \mathbf{z}_0 \omega_0. \tag{129}$$

For $\lambda > 0$, $\mathbf{R}_+^\lambda$ can be determined by the condition

$$[\mathbf{R}_+ \mathbf{S}_+^{-1} \tilde{\mathbf{S}}_+ \mathbf{R}_+]^\lambda = 0, \tag{130}$$

which can again be reexpressed in a Sylvester form

$$\mathbf{R}_+^\lambda (\mathbf{S}_+^{-1} \tilde{\mathbf{S}}_{+,0}) \mathbf{R}_{+,0} + \mathbf{R}_{+,0} (\mathbf{S}_+^{-1} \tilde{\mathbf{S}}_{+,0}) \mathbf{R}_+^\lambda$$
$$= \mathbf{R}_+^\lambda \mathbf{R}_{+,0}^{-1} + \mathbf{R}_{+,0}^{-1} \mathbf{R}_+^\lambda = -\mathcal{G}^\lambda \tag{131}$$

by collecting all the terms independent of $\mathbf{R}_+^\lambda$ into $\mathcal{G}^\lambda$. Equation (131) is readily solved in the basis spanned by $\mathbf{z}_0$ (129), viz.,

$$\mathbf{R}_+^\lambda = \mathbf{z}_0 \mathbf{r}_+^\lambda \mathbf{z}_0^{-1}, \quad [\mathbf{r}_+^\lambda]_{pq} = -\frac{[\mathbf{g}^\lambda]_{pq}}{\sqrt{\omega_p} + \sqrt{\omega_q}},$$
$$\mathbf{g}^\lambda = \mathbf{z}_0^{-1} \mathcal{G}^\lambda \mathbf{z}_0. \tag{132}$$

The above formulations of $\mathbf{X}^\lambda$ (125) and $\mathbf{R}_+^\lambda$ (132) for multiple perturbations are a generalization of our previous formulations[30] of kth order $\mathbf{X}_k$ and $\mathbf{R}_{+,k}$ for a single perturbation (i.e., spin-orbit coupling). In terms of $\mathbf{X}^\lambda$ and $\mathbf{R}_+^\lambda$, as well as the lower order terms, the X2C $\mathbf{h}_+$ (34) can be expanded up to order $\mathbf{h}_+^\lambda$. Of course, the response of the wave function should further be taken into account for the evaluation of a given property but this goes beyond the scope of the present work. We just mention that two "extremal" X2C formulations of NMR (nuclear magnetic resonance) shielding have been made in the past. One is the full X2C-NMR[27,28] that can be represented by $E^\lambda = E^{11\infty}$ in the present notation. That is, the mixed second order energy is of first order in both the external magnetic field $\vec{B}$ and the nuclear magnetic moment $\vec{\mu}_N$, but is of infinite order in spin-orbit coupling. Here, only the first order responses of $\mathbf{X}$ and $\mathbf{R}_+$ to $\vec{B}$ are necessary because of the exchange theorem on one hand and the non-expansion of spin-orbit coupling on the other. The other extreme is the sf-X2C-NMR[29] that can be represented by $E^\lambda = E^{110}$ which is zeroth order in spin-orbit coupling. An intermediate case of $E^\lambda = E^{111}$ will be discussed in Sec. II C 3.

C. Spin-dependent terms of order α^2

The schemes presented in Sec. II B aim to treat the spin- and field-dependent terms to any desired order and therefore belong to the fourth rung of the two-component Hamiltonian ladder shown in Fig. 1. Note in particular that, even at a truncated order, terms of higher orders in α^2 are still present. For practical purposes, we now derive the spin- and field-dependent terms that are $\mathcal{O}(\alpha^2)$. The results belong to the third rung of the Hamiltonian ladder and are akin to those based on the BP Hamiltonian. However, the present results are infinite order, whereas those BP-based ones are zeroth order in scalar relativity. Since the DKH type of formulation is too complicated for multiple perturbations, it is not considered here. On the other hand, for lowest order terms, the BSS type of formulation is somewhat simpler[30] than the X2C approach, for the zeroth order term of the BSS decoupling matrix $\mathbf{Y}$ vanishes as a result of the spin- and field-free transformation $\mathbf{U}_0$, whereas the zeroth order of the X2C decoupling matrix $\mathbf{X}$ does not vanish. Specifically, the BSS transformation $\mathbf{U} = \mathbf{U}_Y\mathbf{U}_0$ of the matrix Dirac equation (11) gives rise to

$$\mathbf{h}_+\mathbf{C}_+ = \mathbf{S}_+\mathbf{C}_+E_+, \tag{133}$$

$$\mathbf{h}_+ = [\mathbf{U}_Y\tilde{\mathbf{h}}\mathbf{U}_Y^\dagger]_{++} = \bar{\mathbf{R}}_+^\dagger\tilde{\mathbf{L}}_+\bar{\mathbf{R}}_+, \tag{134}$$

$$= \mathbf{h}_+^{(00)} + \sum_{n=1}\mathbf{h}_+^{(0n)} + \sum_{m=1}\mathbf{h}_+^{(m0)} + \sum_{m,n=1}\mathbf{h}_+^{(mn)}, \tag{135}$$

$$\tilde{\mathbf{L}}_+ = \tilde{\mathbf{h}}_{11} + \tilde{\mathbf{h}}_{12}\mathbf{Y} + \mathbf{Y}^\dagger\tilde{\mathbf{h}}_{21} + \mathbf{Y}^\dagger\tilde{\mathbf{h}}_{22}\mathbf{Y}, \tag{136}$$

$$\tilde{\mathbf{h}} = \mathbf{U}_0\mathbf{h}\mathbf{U}_0^\dagger. \tag{137}$$

The task here is to identify the field- and spin-dependent terms in $\mathbf{h}_+$ (134) that are $\mathcal{O}(\alpha^2)$. It is to be shown that, at this order, the response of the decoupling matrix $\mathbf{Y}$ is not required, so as to result in very compact expressions for electric and magnetic properties, as well as two-electron spin-orbit couplings.

1. Electric operators

The spin- and field-free transformation of the perturbed Hamiltonian $\mathbf{h}(\epsilon)$ (98) leads to

$$\begin{aligned}\tilde{\mathbf{h}} &= \mathbf{U}_0(\mathbf{h} + \epsilon\mathbf{O}^{4C})\mathbf{U}_0^\dagger \\ &= (\boldsymbol{\mathcal{E}}^{(00)} + \boldsymbol{\mathcal{E}}^{(01)} + \boldsymbol{\mathcal{O}}^{(01)}) + \epsilon(\boldsymbol{\mathcal{E}}^{(10)} + \boldsymbol{\mathcal{O}}^{(10)} \\ &\quad + \boldsymbol{\mathcal{E}}^{(11)} + \boldsymbol{\mathcal{O}}^{(11)}),\end{aligned} \tag{138}$$

where the superscript (mn) indicates mth order in the perturbation and nth order in spin $\vec{\sigma}$. The terms in the first parenthesis arise from the transformed Hamiltonian discussed previously, while those in the second parenthesis from the transformed property operator, viz.,

$$\mathbf{U}_0\mathbf{O}^{4C}\mathbf{U}_0^\dagger = \begin{pmatrix} \mathbf{R}_{+,0}^\dagger\big(\mathbf{O}^{LL} + \frac{\alpha^2}{4}\mathbf{X}_0^\dagger\mathbf{O}^{SS}\mathbf{X}_0\big)\mathbf{R}_{+,0} & \mathbf{R}_{+,0}^\dagger\big(\mathbf{O}^{LL}\tilde{\mathbf{X}}_0 + \frac{\alpha^2}{4}\mathbf{X}_0^\dagger\mathbf{O}^{SS}\big)\mathbf{R}_{-,0} \\ \mathbf{R}_{-,0}^\dagger\big(\tilde{\mathbf{X}}_0^\dagger\mathbf{O}^{LL} + \frac{\alpha^2}{4}\mathbf{O}^{SS}\mathbf{X}_0\big)\mathbf{R}_{+,0} & \mathbf{R}_{-,0}^\dagger\big(\frac{\alpha^2}{4}\mathbf{O}^{SS} + \tilde{\mathbf{X}}_0^\dagger\mathbf{O}^{LL}\tilde{\mathbf{X}}_0\big)\mathbf{R}_{-,0} \end{pmatrix}. \tag{139}$$

Here, it has been assumed that the operator O^{4C} is diagonal

$$O^{4C} = \begin{pmatrix} O^{LL} & 0 \\ 0 & O^{LL} \end{pmatrix} \tag{140}$$

and represented in a RKB basis, viz.,

$$\mathbf{O}^{4C} = \begin{pmatrix} \mathbf{O}^{LL} & 0 \\ 0 & \frac{\alpha^2}{4}\mathbf{O}^{SS} \end{pmatrix}, \quad \mathbf{O}^{SS} = \mathbf{O}_{sf}^{SS} + \mathbf{O}_{sd}^{SS}, \tag{141}$$

$$\begin{aligned}(\mathbf{O}^{LL})_{\mu\nu} &= \langle g_\mu|O^{LL}|g_\nu\rangle, \quad (\mathbf{O}_{sf}^{SS})_{\mu\nu} = \langle g_\mu|\vec{p}\cdot O^{LL}\vec{p}|g_\nu\rangle, \\ (\mathbf{O}_{sd}^{SS})_{\mu\nu} &= \langle g_\mu|\mathbb{i}\vec{\sigma}\cdot(\vec{p}O^{LL}\times\vec{p})|g_\nu\rangle.\end{aligned} \tag{142}$$

As a special case of Eq. (49), the $\tilde{\mathbf{X}}_0$ matrix in Eq. (139) is simply

$$\tilde{\mathbf{X}}_0 = -\frac{\alpha^2}{2}\mathbf{S}^{-1}\mathbf{X}_0^\dagger\mathbf{T}, \quad \mathbf{S} = \mathbf{S}_+. \tag{143}$$

The operators in the second parenthesis of Eq. (138) can then readily be identified from Eq. (139), viz.,

$$\begin{aligned}
\boldsymbol{\mathcal{E}}^{(10)} &= \begin{pmatrix} \mathbf{R}_{+,0}^{\dagger}\big(\mathbf{O}_{sf}^{LL} + \frac{\alpha^2}{4}\mathbf{X}_0^{\dagger}\mathbf{O}_{sf}^{SS}\mathbf{X}_0\big)\mathbf{R}_{+,0} & \mathbf{0} \\ \mathbf{0} & \mathbf{R}_{-,0}^{\dagger}\big(\frac{\alpha^2}{4}\mathbf{O}_{sf}^{SS} + \tilde{\mathbf{X}}_0^{\dagger}\mathbf{O}_{sf}^{LL}\tilde{\mathbf{X}}_0\big)\mathbf{R}_{-,0} \end{pmatrix}, \\
\boldsymbol{\mathcal{E}}^{(11)} &= \begin{pmatrix} \frac{\alpha^2}{4}\mathbf{R}_{+,0}^{\dagger}\mathbf{X}_0^{\dagger}\mathbf{O}_{sd}^{SS}\mathbf{X}_0\mathbf{R}_{+,0} & \mathbf{0} \\ \mathbf{0} & \frac{\alpha^2}{4}\mathbf{R}_{-,0}^{\dagger}\mathbf{O}_{sd}^{SS}\mathbf{R}_{-,0} \end{pmatrix}, \\
\boldsymbol{\mathcal{O}}^{(10)} &= \begin{pmatrix} \mathbf{0} & \mathbf{R}_{+,0}^{\dagger}\big(\mathbf{O}_{sf}^{LL}\tilde{\mathbf{X}}_0 + \frac{\alpha^2}{4}\mathbf{X}_0^{\dagger}\mathbf{O}_{sf}^{SS}\big)\mathbf{R}_{-,0} \\ \mathbf{R}_{-,0}^{\dagger}\big(\tilde{\mathbf{X}}_0^{\dagger}\mathbf{O}_{sf}^{LL} + \frac{\alpha^2}{4}\mathbf{O}_{sf}^{SS}\mathbf{X}_0\big)\mathbf{R}_{+,0} & \mathbf{0} \end{pmatrix}, \\
\boldsymbol{\mathcal{O}}^{(11)} &= \begin{pmatrix} \mathbf{0} & \frac{\alpha^2}{4}\mathbf{R}_{+,0}^{\dagger}\mathbf{X}_0^{\dagger}\mathbf{O}_{sd}^{SS}\mathbf{R}_{-,0} \\ \frac{\alpha^2}{4}\mathbf{R}_{-,0}^{\dagger}\mathbf{O}_{sd}^{SS}\mathbf{X}_0\mathbf{R}_{+,0} & \mathbf{0} \end{pmatrix}.
\end{aligned} \tag{144}$$

Note that the leading order of $\boldsymbol{\mathcal{E}}^{(11)}$, $\boldsymbol{\mathcal{O}}^{(10)}$, and $\boldsymbol{\mathcal{O}}^{(11)}$ is $\mathcal{O}(\alpha^2)$, for all quantities therein are $\mathcal{O}(\alpha^0)$, except that $\tilde{\mathbf{X}}_0$ is $\mathcal{O}(\alpha^2)$. To get the perturbed operators (135) that can be used for first order electric properties, we need to first consider the expansion of $\mathbf{Y}$,

$$\mathbf{Y} = \mathbf{Y}^{(00)} + \mathbf{Y}^{(01)} + \mathbf{Y}^{(10)} + \mathbf{Y}^{(11)} + \cdots, \tag{145}$$

where $\mathbf{Y}^{(00)}$ actually vanishes, for the $\mathbf{U}_0$-transformation has decoupled the zeroth order Hamiltonian. It can readily be deduced from Eq. (118) that $\mathbf{Y}^{\lambda}$ (in place of $\mathbf{X}^{\lambda}$), $\boldsymbol{\mathcal{L}}^{\lambda}$, and $\boldsymbol{\mathcal{O}}^{\lambda}$ have the same ordering in α^2. That is, the leading order of a particular $\mathbf{Y}^{\lambda}$ can be deduced from that of the corresponding $\boldsymbol{\mathcal{O}}^{\lambda}$. For instance, the $\boldsymbol{\mathcal{O}}^{(10)}$ and $\boldsymbol{\mathcal{O}}^{(11)}$ in Eq. (144) reveal that both $\mathbf{Y}^{(10)}$ and $\mathbf{Y}^{(11)}$ are $\mathcal{O}(\alpha^2)$. So is $\mathbf{Y}^{(01)}$.

Since both the metric $\mathbf{M}$ (72) and $\mathbf{U}_0\mathbf{M}\mathbf{U}_0^{\dagger}$ are in this case independent of the field and spin, the expansion of $\tilde{\mathbf{S}}_+$ defined in terms of $\mathbf{Y}$ leads to

$$\begin{aligned}
&\tilde{\mathbf{S}}_+ = \mathbf{S} + \frac{\alpha^2}{4}\mathbf{Y}^{\dagger}\mathbf{T}\mathbf{Y} = \tilde{\mathbf{S}}_+^{(00)} + \tilde{\mathbf{S}}_+^{(01)} + \tilde{\mathbf{S}}_+^{(10)} + \tilde{\mathbf{S}}_+^{(11)} + \cdots, \\
&\tilde{\mathbf{S}}_+^{(00)} = \mathbf{S}, \quad \tilde{\mathbf{S}}_+^{(01)} = \tilde{\mathbf{S}}_+^{(01)} = \mathbf{0}, \\
&\tilde{\mathbf{S}}_+^{(11)} = \frac{\alpha^2}{4}(\mathbf{Y}^{(10)\dagger}\mathbf{T}\mathbf{Y}^{(01)} + c.c.),
\end{aligned} \tag{146}$$

in terms of which the expansion of condition (59) gives rise to (cf. Eq. (131))

$$\begin{aligned}
&\bar{\mathbf{R}}_+^{(00)} = \mathbf{I}, \quad \bar{\mathbf{R}}_+^{(01)} = \bar{\mathbf{R}}_+^{(10)} = \mathbf{0}, \\
&\bar{\mathbf{R}}_+^{(11)} = -\frac{1}{2}\mathbf{S}^{-1}\tilde{\mathbf{S}}_+^{(11)} = -\frac{\alpha^2}{4}\mathbf{S}^{-1}(\mathbf{Y}^{(10)\dagger}\mathbf{T}\mathbf{Y}^{(01)} + c.c.) \sim \mathcal{O}(\alpha^6).
\end{aligned} \tag{147}$$

The $\mathbf{h}_+^{(10)}$ and $\mathbf{h}_+^{(11)}$ terms in Eq. (135) can then be evaluated as

$$\mathbf{h}_+^{(10)} = [\bar{\mathbf{R}}_+^{\dagger}\tilde{\mathbf{L}}_+\bar{\mathbf{R}}_+]^{(10)} = \tilde{\mathbf{L}}_+^{(10)} = \tilde{\mathbf{h}}_{11}^{(10)} = \boldsymbol{\mathcal{E}}_{11}^{(10)}, \tag{148}$$

$$\mathbf{h}_+^{(11)} = [\bar{\mathbf{R}}_+^{\dagger}\tilde{\mathbf{L}}_+\bar{\mathbf{R}}_+]^{(11)} = \tilde{\mathbf{L}}_+^{(11)} + \big(\boldsymbol{\mathcal{E}}_{11}^{(00)}\bar{\mathbf{R}}_+^{(11)} + c.c.\big), \tag{149}$$

where

$$\begin{aligned}
\tilde{\mathbf{L}}_+^{(11)} &= \tilde{\mathbf{h}}_{11}^{(11)} + \big(\tilde{\mathbf{h}}_{12}^{(10)}\mathbf{Y}^{(01)} + \tilde{\mathbf{h}}_{12}^{(01)}\mathbf{Y}^{(10)} + c.c.\big) \\
&\quad + \big(\mathbf{Y}^{(10)\dagger}\tilde{\mathbf{h}}_{22}^{(00)}\mathbf{Y}^{(01)} + c.c.\big) \\
&= \boldsymbol{\mathcal{E}}_{11}^{(11)} + \big(\boldsymbol{\mathcal{O}}_{12}^{(10)}\mathbf{Y}^{(01)} + \boldsymbol{\mathcal{O}}_{12}^{(01)}\mathbf{Y}^{(10)} + c.c.\big) \\
&\quad + \big(\mathbf{Y}^{(10)\dagger}\boldsymbol{\mathcal{E}}_{22}^{(00)}\mathbf{Y}^{(01)} + c.c.\big).
\end{aligned} \tag{150}$$

Note in passing that use of the relation $\tilde{\mathbf{h}}_{12}^{(00)} = \boldsymbol{\mathcal{O}}_{12}^{(00)} = 0$ has been made to arrive at Eq. (150). Here, the terms involving $\mathbf{Y}^{(01)}$ or $\mathbf{Y}^{(10)}$ are $\mathcal{O}(\alpha^4)$. The second term of $\mathbf{h}_+^{(11)}$ (149) is $\mathcal{O}(\alpha^6)$. The next lowest order term in Eq. (135) is $\mathbf{h}_+^{(12)}$, which is quadratic in spin $\vec{\sigma}$ and hence $\mathcal{O}(\alpha^4)$. Therefore, the wanted $\mathcal{O}(\alpha^2)$ terms in Eq. (135) are simply

$$\mathbf{h}_+^{(10)} = \boldsymbol{\mathcal{E}}_{11}^{(10)} = \mathbf{R}_{+,0}^{\dagger}\left(\mathbf{O}_{sf}^{LL} + \frac{\alpha^2}{4}\mathbf{X}_0^{\dagger}\mathbf{O}_{sf}^{SS}\mathbf{X}_0\right)\mathbf{R}_{+,0}, \tag{151}$$

$$\mathbf{h}_+^{(11)} = \boldsymbol{\mathcal{E}}_{11}^{(11)} = \frac{\alpha^2}{4}\mathbf{R}_{+,0}^{\dagger}\mathbf{X}_0^{\dagger}\mathbf{O}_{sd}^{SS}\mathbf{X}_0\mathbf{R}_{+,0}. \tag{152}$$

The similarity of $\mathbf{h}_+^{(11)}$ (152) with $\mathbf{E}_{+,1}$ (77), i.e., $\mathbf{h}_+^{(01)}$ in the notation here, is obvious. Note in passing that, if $V^a = V^b = \mathbf{h}_+^{(10)} + \mathbf{h}_+^{(11)}$ is adopted for the second order property E^{ab} (4), the term quadratic in $\mathbf{h}_+^{(11)}$ can be neglected for it is $\mathcal{O}(\alpha^4)$. If the spin-free $\mathbf{X}_0$ and $\mathbf{R}_{+,0}$ are also expanded in powers of α^2, viz.,

$$\mathbf{X}_0 = \mathbf{I} + \mathcal{O}(\alpha^2), \tag{153}$$

$$\mathbf{R}_{+,0} = \mathbf{I} - \frac{\alpha^2}{4}\mathbf{S}^{-1}\mathbf{T} + \mathcal{O}(\alpha^4), \tag{154}$$

Eqs. (151) and (152) would reduce to

$$\mathbf{h}_+^{(10)} = \mathbf{O}_{sf}^{LL} - \frac{\alpha^2}{4}(\mathbf{T}\mathbf{S}^{-1}\mathbf{O}_{sf}^{LL} + c.c.) + \frac{\alpha^2}{4}\mathbf{O}_{sf}^{SS} + \mathcal{O}(\alpha^4), \tag{155}$$

$$\mathbf{h}_+^{(11)} = \frac{\alpha^2}{4}\mathbf{O}_{sd}^{SS} + \mathcal{O}(\alpha^4), \tag{156}$$

which are just the matrix counterparts of the BP operators for electric properties, e.g., $\frac{\alpha^2}{4}\mathbf{TS}^{-1}\mathbf{O}_{sf}^{LL}$ is the matrix representation of the BP operator $\frac{1}{2}\nabla^2 O^{LL}$ in the RKB basis. Moreover, if the free-particle $\mathbf{X}_0$ and $\mathbf{R}_{+,0}$ are used, Eqs. (151) and (152) would be the matrix counterparts of the fpFW transformed electric operators[63] by noting the following relations:[30]

$$X_0 = \frac{2c^2}{E_p + c^2}, \quad E_p = \sqrt{c^4 + c^2\vec{p}^2},$$
$$R_{+,0} = \sqrt{\frac{E_p + c^2}{2E_p}} \equiv \mathcal{A}, \quad \mathcal{Q} \equiv \frac{1}{2}X_0 R_{+,0}. \tag{157}$$

Since Eqs. (151) and (152) can readily be implemented, both the BP and fpFW formulations should be regarded as outdated.

2. Magnetic operators: A single magnetic field

The extension of the previous formulation to a magnetic perturbation is straightforward. The only complexity arises from the dependence of the metric on the spin and field, cf. Eq. (29). Suppose the magnetic field is uniform

$$\vec{A} = \vec{A}^{10} = \frac{1}{2}(\vec{B} \times \vec{r}_O), \quad \vec{r}_O = \vec{r} - \vec{R}_O, \tag{158}$$

where $\vec{R}_O$ denotes the gauge origin. The terms in Eq. (30) can be decomposed as

$$T_{\pi,sf} = \frac{1}{2}\vec{\pi}^2 = T + \frac{1}{2}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{1}{2}A^2$$
$$= T + \frac{1}{2}\vec{B}\cdot\vec{l}_O + \frac{1}{2}A^2, \tag{159}$$

$$T_{\pi,sd} = \frac{1}{2}\mathbb{i}\vec{\sigma}\cdot(\vec{\pi}\times\vec{\pi}) = \frac{1}{2}\mathbb{i}\vec{\sigma}\cdot(\vec{p}\times\vec{A} + \vec{A}\times\vec{p}) = \frac{1}{2}\vec{\sigma}\cdot\vec{B}, \tag{160}$$

$$W_{\pi,sf} = \vec{\pi}\cdot V\vec{\pi} = W_{sf} + (\vec{p}\cdot V\vec{A} + \vec{A}\cdot V\vec{p}) + VA^2, \tag{161}$$

$$W_{\pi,sd} = \mathbb{i}\vec{\sigma}\cdot(\vec{\pi}\times V\vec{\pi}) = W_{sd} + \mathbb{i}\vec{\sigma}\cdot(\vec{p}\times V\vec{A} + \vec{A}\times V\vec{p}). \tag{162}$$

Then, the $\mathbf{U}_0$-transformed Hamiltonian $\tilde{\mathbf{h}}$ and metric $\tilde{\mathbf{M}}$ can be written as

$$\tilde{\mathbf{h}} = \mathbf{U}_0\mathbf{h}\mathbf{U}_0^\dagger = \tilde{\mathbf{h}}^{(00)} + \tilde{\mathbf{h}}^{(01)} + \tilde{\mathbf{h}}^{(10)} + \tilde{\mathbf{h}}^{(11)} + \tilde{\mathbf{h}}^{(20)}, \tag{163}$$

$$\tilde{\mathbf{M}} = \mathbf{U}_0\mathbf{M}\mathbf{U}_0^\dagger = \begin{pmatrix} \mathbf{S} & 0 \\ 0 & \frac{\alpha^2}{2}\mathbf{T} \end{pmatrix} + \mathbf{U}_0\begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \frac{\alpha^2}{2}\left(\mathbf{T}^{(1)}_{\pi,sf} + \mathbf{T}^{(1)}_{\pi,sd} + \mathbf{T}^{(2)}_{\pi,sf}\right) \end{pmatrix}\mathbf{U}_0^\dagger, \tag{164}$$
$$= \tilde{\mathbf{M}}^{(00)} + \tilde{\mathbf{M}}^{(10)} + \tilde{\mathbf{M}}^{(11)} + \tilde{\mathbf{M}}^{(20)}, \tag{165}$$

where

$$\left[\mathbf{T}^{(1)}_{\pi,sf}\right]_{\mu\nu} = \langle g_\mu|\frac{1}{2}\vec{B}\cdot\vec{l}_O|g_\nu\rangle, \tag{166}$$

$$\left[\mathbf{T}^{(1)}_{\pi,sd}\right]_{\mu\nu} = \langle g_\mu|\frac{1}{2}\vec{\sigma}\cdot\vec{B}|g_\nu\rangle, \tag{167}$$

$$\left[\mathbf{T}^{(2)}_{\pi,sf}\right]_{\mu\nu} = \langle g_\mu|\frac{1}{2}A^2|g_\nu\rangle. \tag{168}$$

In view of Eq. (131), the expansion of condition (59) leads to

$$\bar{\mathbf{R}}_+^{(00)} = \mathbf{I}, \quad \bar{\mathbf{R}}_+^{(01)} = \mathbf{0}, \tag{169}$$

$$\bar{\mathbf{R}}_+^{(10)} = -\frac{1}{2}\mathbf{S}^{-1}\tilde{\mathbf{S}}_+^{(10)} = -\frac{1}{2}\mathbf{S}^{-1}\tilde{\mathbf{M}}_{11}^{(10)} + \mathcal{O}(\alpha^4), \tag{170}$$

$$\tilde{\mathbf{M}}_{11}^{(10)} = \frac{\alpha^2}{2}\mathbf{R}_{+,0}^\dagger\mathbf{X}_0^\dagger\mathbf{T}^{(1)}_{\pi,sf}\mathbf{X}_0\mathbf{R}_{+,0}, \tag{171}$$

$$\bar{\mathbf{R}}_+^{(11)} = -\frac{1}{2}\mathbf{S}^{-1}\tilde{\mathbf{S}}_+^{(11)} = -\frac{1}{2}\mathbf{S}^{-1}\tilde{\mathbf{M}}_{11}^{(11)} + \mathcal{O}(\alpha^4), \tag{172}$$

$$\tilde{\mathbf{M}}_{11}^{(11)} = \frac{\alpha^2}{2}\mathbf{R}_{+,0}^\dagger\mathbf{X}_0^\dagger\mathbf{T}^{(1)}_{\pi,sd}\mathbf{X}_0\mathbf{R}_{+,0}. \tag{173}$$

The $\mathbf{h}_+^{(10)}$ and $\mathbf{h}_+^{(11)}$ terms in Eq. (135) can then be evaluated as

$$\mathbf{h}_+^{(10)} = [\bar{\mathbf{R}}_+^\dagger\tilde{\mathbf{L}}_+\bar{\mathbf{R}}_+]^{(10)}$$
$$= \tilde{\mathbf{L}}_+^{(10)} + \left(\tilde{\mathbf{L}}_+^{(00)}\bar{\mathbf{R}}_+^{(10)} + c.c.\right) + \mathcal{O}(\alpha^4) \tag{174}$$

$$= \tilde{\mathbf{h}}_{11}^{(10)} + \left(\mathbf{h}_{+,sf}^{(00)}\bar{\mathbf{R}}_+^{(10)} + c.c.\right) + \mathcal{O}(\alpha^4), \tag{175}$$

$$\mathbf{h}_+^{(11)} = [\bar{\mathbf{R}}_+^\dagger\tilde{\mathbf{L}}_+\bar{\mathbf{R}}_+]^{(11)}$$
$$= \tilde{\mathbf{L}}_+^{(11)} + \left(\mathbf{h}_{+,sf}\bar{\mathbf{R}}_+^{(11)} + c.c.\right) + \mathcal{O}(\alpha^4) \tag{176}$$

$$= \tilde{\mathbf{h}}_{11}^{(11)} + \left(\mathbf{h}_{+,sf}^{(00)}\bar{\mathbf{R}}_+^{(11)} + c.c.\right) + \mathcal{O}(\alpha^4). \tag{177}$$

where

$$\tilde{\mathbf{h}}_{11}^{(10)} = \mathbf{R}_{+,0}^\dagger\Big[\mathbf{T}^{(1)}_{\pi,sf}\mathbf{X}_0 + \mathbf{X}_0^\dagger\mathbf{T}^{(1)}_{\pi,sf} + \mathbf{X}_0^\dagger\left(\frac{\alpha^2}{4}\mathbf{W}^{(1)}_{\pi,sf} - \mathbf{T}^{(1)}_{\pi,sf}\right)\mathbf{X}_0\Big]\mathbf{R}_{+,0}, \tag{178}$$

$$\tilde{\mathbf{h}}_{11}^{(11)} = \mathbf{R}_{+,0}^\dagger\Big[\mathbf{T}^{(1)}_{\pi,sd}\mathbf{X}_0 + \mathbf{X}_0^\dagger\mathbf{T}^{(1)}_{\pi,sd} + \mathbf{X}_0^\dagger\left(\frac{\alpha^2}{4}\mathbf{W}^{(1)}_{\pi,sd} - \mathbf{T}^{(1)}_{\pi,sd}\right)\mathbf{X}_0\Big]\mathbf{R}_{+,0}, \tag{179}$$

$$\left[\mathbf{W}^{(1)}_{\pi,sf}\right]_{\mu\nu} = \langle g_\mu|\vec{p}\cdot V\vec{A} + \vec{A}\cdot V\vec{p}|g_\nu\rangle,$$
$$\left[\mathbf{W}^{(1)}_{\pi,sd}\right]_{\mu\nu} = \langle g_\mu|\mathbb{i}\vec{\sigma}\cdot(\vec{p}\times V\vec{A} + \vec{A}\times V\vec{p})|g_\nu\rangle. \tag{180}$$

Therefore, the wanted $\mathcal{O}(\alpha^2)$ terms are

$$\begin{aligned}\mathbf{h}_+^{(10)} = \mathbf{R}_{+,0}^\dagger\Big[&\mathbf{T}_{\pi,sf}^{(1)}\mathbf{X}_0 + \mathbf{X}_0^\dagger\mathbf{T}_{\pi,sf}^{(1)} \\ &+\mathbf{X}_0^\dagger\left(\frac{\alpha^2}{4}\mathbf{W}_{\pi,sf}^{(1)} - \mathbf{T}_{\pi,sf}^{(1)}\right)\mathbf{X}_0\Big]\mathbf{R}_{+,0} \\ &-\frac{\alpha^2}{4}\left[\mathbf{h}_{+,sf}^{(0)}\mathbf{S}^{-1}\left(\mathbf{R}_{+,0}^\dagger\mathbf{X}_0^\dagger\mathbf{T}_{\pi,sf}^{(1)}\mathbf{X}_0\mathbf{R}_{+,0}\right) + c.c.\right],\end{aligned} \tag{181}$$

$$\begin{aligned}\mathbf{h}_+^{(11)} = \mathbf{R}_{+,0}^\dagger\Big[&\mathbf{T}_{\pi,sd}^{(1)}\mathbf{X}_0 + \mathbf{X}_0^\dagger\mathbf{T}_{\pi,sd}^{(1)} \\ &+\mathbf{X}_0^\dagger\left(\frac{\alpha^2}{4}\mathbf{W}_{\pi,sd}^{(1)} - \mathbf{T}_{\pi,sd}^{(1)}\right)\mathbf{X}_0\Big]\mathbf{R}_{+,0} \\ &-\frac{\alpha^2}{4}\left[\mathbf{h}_{+,sf}^{(0)}\mathbf{S}^{-1}\left(\mathbf{R}_{+,0}^\dagger\mathbf{X}_0^\dagger\mathbf{T}_{\pi,sd}^{(1)}\mathbf{X}_0\mathbf{R}_{+,0}\right) + c.c.\right].\end{aligned} \tag{182}$$

If the expansions of $\mathbf{X}_0$ (153) [NB: The terms of $\mathcal{O}(\alpha^2)$ in $\mathbf{X}_0$ makes no contribution due to cancelations in Eq. (181) or (182)] and $\mathbf{R}_{+,0}$ (154), as well as

$$\mathbf{h}_{+,sf}^{(0)} = \mathbf{T} + \mathbf{V} + \mathcal{O}(\alpha^2), \tag{183}$$

are invoked, Eqs. (181) and (182) will reduce to the BP counterparts, viz.,

$$\begin{aligned}\mathbf{h}_+^{(10)} &= \mathbf{T}_{\pi,sf}^{(1)} + \frac{\alpha^2}{4}\mathbf{W}_{\pi,sf}^{(1)} - \frac{\alpha^2}{4}\left[\mathbf{T}\mathbf{S}^{-1}\mathbf{T}_{\pi,sf}^{(1)} + c.c.\right] \\ &\quad -\frac{\alpha^2}{4}\left[(\mathbf{T}+\mathbf{V})\mathbf{S}^{-1}\mathbf{T}_{\pi,sf}^{(1)} + c.c.\right], \\ &= \mathbf{T}_{\pi,sf}^{(1)} + \frac{\alpha^2}{4}\left[\mathbf{W}_{\pi,sf}^{(1)} - \left(\mathbf{V}\mathbf{S}^{-1}\mathbf{T}_{\pi,sf}^{(1)} + c.c.\right)\right] \\ &\quad -\frac{\alpha^2}{2}\left[\mathbf{T}\mathbf{S}^{-1}\mathbf{T}_{\pi,sf}^{(1)} + c.c.\right],\end{aligned} \tag{184}$$

$$\begin{aligned}\mathbf{h}_+^{(11)} &= \mathbf{T}_{\pi,sd}^{(1)} + \frac{\alpha^2}{4}\mathbf{W}_{\pi,sd}^{(1)} - \frac{\alpha^2}{4}\left[\mathbf{T}\mathbf{S}^{-1}\mathbf{T}_{\pi,sd}^{(1)} + c.c.\right] \\ &\quad -\frac{\alpha^2}{4}\left[(\mathbf{T}+\mathbf{V})\mathbf{S}^{-1}\mathbf{T}_{\pi,sd}^{(1)} + c.c.\right], \\ &= \mathbf{T}_{\pi,sd}^{(1)} + \frac{\alpha^2}{4}\left[\mathbf{W}_{\pi,sd}^{(1)} - \left(\mathbf{V}\mathbf{S}^{-1}\mathbf{T}_{\pi,sd}^{(1)} + c.c.\right)\right] \\ &\quad -\frac{\alpha^2}{2}\left[\mathbf{T}\mathbf{S}^{-1}\mathbf{T}_{\pi,sd}^{(1)} + c.c.\right].\end{aligned} \tag{185}$$

The physical meanings of these terms are as follows. The first terms of $\mathbf{h}_+^{(10)}$ and $\mathbf{h}_+^{(11)}$ are $\mathcal{O}(\alpha^0)$ and represent the orbital Zeeman (OZ) ($H^{OZ} = \frac{1}{2}\vec{B}\cdot\vec{l}_O$) and spin Zeeman (SZ) ($H^{SZ} = \vec{B}\cdot\vec{s}$) terms, respectively. The second term of Eq. (184) vanishes in the complete basis set (CBS) limit in view of the following operator identity:

$$\begin{aligned}&(\vec{p}\cdot V\vec{A} + \vec{A}\cdot V\vec{p}) - \left(\frac{1}{2}[V(\vec{B}\cdot\vec{l}_O) + (\vec{B}\cdot\vec{l}_O)V]\right) \\ &\quad = ([\vec{p},V]\cdot\vec{A} + \vec{A}\cdot[V,\vec{p}] + V(\vec{A}\cdot\vec{p}) + (\vec{A}\cdot\vec{p})V) \\ &\qquad -\left(\frac{1}{2}[V(\vec{B}\cdot\vec{l}_O) + (\vec{B}\cdot\vec{l}_O)V]\right) \\ &\quad = (V(\vec{A}\cdot\vec{p}) + (\vec{A}\cdot\vec{p})V) \\ &\qquad -\left(\frac{1}{2}[V(\vec{B}\cdot\vec{l}_O) + (\vec{B}\cdot\vec{l}_O)V]\right) = 0.\end{aligned} \tag{186}$$

However, the second term of Eq. (185) does not vanish in the CBS limit, but yields the field-dependent spin-orbit interaction H_B^{SO}

$$\begin{aligned}H_B^{SO} &= (\mathbb{i}\vec{\sigma}\cdot(\vec{p}\times V\vec{A} + \vec{A}\times V\vec{p})) \\ &\qquad -\left(V\left(\frac{1}{2}\vec{\sigma}\cdot\vec{B}\right) + \left(\frac{1}{2}\vec{\sigma}\cdot\vec{B}\right)V\right) \\ &= (\mathbb{i}\vec{\sigma}\cdot([\vec{p},V]\times\vec{A} + V(\vec{p}\times\vec{A} + \vec{A}\times\vec{p}))) \\ &\qquad -V\left(\frac{1}{2}\vec{\sigma}\cdot\vec{B}\right) \\ &= \frac{1}{2}\sum_A\frac{Z_A}{r_A^3}[(\vec{\sigma}\cdot\vec{B})(\vec{r}_A\cdot\vec{r}_O) - (\vec{\sigma}\cdot\vec{r}_O)(\vec{r}_A\cdot\vec{B})].\end{aligned} \tag{187}$$

The third terms of Eqs. (184) and (185) are the kinetic energy corrections to the orbital Zeeman (OZ-KE) operator ($H^{OZ-KE} = \frac{\alpha^2}{4}(\vec{B}\cdot\vec{l}_O)\nabla^2$) and the spin Zeeman (SZ-KE) operator ($H^{SZ-KE} = \frac{\alpha^2}{4}(\vec{B}\cdot\vec{\sigma})\nabla^2$), respectively. As such, all the leading order spin-dependent corrections[64,65] to the otherwise sf-X2C terms are included in Eqs. (181) and (182). Note in passing that the g-tensor can be evaluated with $\frac{\partial\mathbf{h}_+^{(10)}}{\partial B_m}$ and $\frac{\partial\mathbf{h}_+^{(11)}}{\partial B_m}$ $(m = x, y, z)$.

The above formulation can also be applied to the magnetic field created by a nuclear magnetic moment $\vec{\mu}_N$, by just replacing the vector potential $\vec{A}$ (158) with

$$\vec{A} = \vec{A}^{01} = \alpha^2\frac{\vec{\mu}_N\times\vec{r}_N}{r_N^3}, \quad \vec{r}_N = \vec{r} - \vec{R}_N, \tag{188}$$

where $\vec{R}_N$ denotes the position of the active nucleus. The counterpart of Eq. (166) then represents the paramagnetic nuclear spin-electron orbit (PSO) interaction, while that of Eq. (167) represents the sum of the Fermi contact (FC) and spin-dipole (SD) interactions in the nonrelativistic limit if the turn over rule is invoked. The kinetic energy corrections to PSO, FC, and SD (PSO-KE, FC-KE, SD-KE) as well as the field-dependent spin-orbit interaction[64,65] can all be identified in the same way.

3. Magnetic operators: Uniform and nuclear magnetic fields

The previous formulation for a single magnetic field requires some extensions for two magnetic fields represented

by

$$\vec{A} = \vec{A}^{01} + \vec{A}^{10}, \tag{189}$$

with $\vec{A}^{10}$ and $\vec{A}^{01}$ given in Eqs. (158) and (188), respectively. The interest here is to find the mixed term $\frac{\partial^2 \mathbf{h}_+}{\partial B_m \partial \mu_{N,n}}$ that is $\mathcal{O}(\alpha^2)$ in spin. Note that the factor α^2 in $\vec{A}^{01}$ is not counted here. In this section, an operator $\mathbf{O}^{(mn)}$, which is of order m in $\vec{B}$ and order n in $\vec{\mu}$, will be denoted as

$$\mathbf{O}^{(mn)} = \mathbf{O}^{(mn)}_{sf} + \mathbf{O}^{(mn)}_{sd}, \quad \mathbf{O}^{(mn)}_{sd} = \sum_{k=1} \mathbf{O}^{(mn)}_{sd\,k}. \tag{190}$$

That is, the ordering k in spin $\vec{\sigma}$ is denoted with subscript instead of superscript as done in Secs. II C 1 and II C 2. Under this notation, the expansion of the decoupling matrix $\mathbf{Y}$ reads

$$\mathbf{Y} = \mathbf{Y}^{(00)}_1 + \mathbf{Y}^{(01)} + \mathbf{Y}^{(10)} + \mathbf{Y}^{(11)} + \cdots. \tag{191}$$

The leading order of every term here is $\mathcal{O}(\alpha^2)$ in view of Eq. (118), implying that their contributions to $\bar{\mathbf{R}}^{(mn)}_+$ will be $\mathcal{O}(\alpha^6)$, see Eq. (147). Therefore, the $\mathcal{O}(\alpha^2)$ terms of $\bar{\mathbf{R}}^{(mn)}_+$ arise solely from the $\mathbf{U}_0$-transformed metric, see $\bar{\mathbf{R}}^{(10)}_+$ (170) and $\bar{\mathbf{R}}^{(11)}_+$ (172). Due to the particular structure of the quadratic term $A^2 = (\vec{A}^{10} + \vec{A}^{01})^2$ in T_π (159), the lowest order of $\bar{\mathbf{R}}^{(11)}_+$ is actually spin free

$$\begin{aligned}\bar{\mathbf{R}}^{(11)}_+ &= -\frac{\alpha^2}{2}\mathbf{S}^{-1}\tilde{\mathbf{S}}^{(11)}_+ + \mathcal{O}(\alpha^4) = -\frac{\alpha^2}{2}\mathbf{S}^{-1}\tilde{\mathbf{M}}^{(11)}_{11} + \mathcal{O}(\alpha^4)\\ &= -\frac{\alpha^2}{4}\mathbf{S}^{-1}\big(\mathbf{R}^\dagger_{+,0}\mathbf{X}^\dagger_0\mathbf{T}^{(11)}_{\pi,sf}\mathbf{X}_0\mathbf{R}_{+,0}\big) + \mathcal{O}(\alpha^4),\end{aligned} \tag{192}$$

$$\big[\mathbf{T}^{(11)}_{\pi,sf}\big]_{\mu\nu} = \langle g_\mu|\vec{A}^{10}\cdot\vec{A}^{01}|g_\nu\rangle. \tag{193}$$

Keeping these in mind, $\mathbf{h}^{(11)}_+$ can be derived as

$$\begin{aligned}\mathbf{h}^{(11)}_+ &= [\bar{\mathbf{R}}^\dagger_+\tilde{\mathbf{L}}_+\bar{\mathbf{R}}_+]^{(11)}\\ &= \bar{\mathbf{R}}^{(00)\dagger}_+\tilde{\mathbf{L}}^{(11)}_+\bar{\mathbf{R}}^{(00)}_+ + (\bar{\mathbf{R}}^{(00)\dagger}_+\tilde{\mathbf{L}}^{(00)}_+\bar{\mathbf{R}}^{(11)}_+ + c.c.)\\ &\quad +(\bar{\mathbf{R}}^{(00)\dagger}_+[\tilde{\mathbf{L}}^{(10)}_+\bar{\mathbf{R}}^{(01)}_+ + \tilde{\mathbf{L}}^{(01)}_+\bar{\mathbf{R}}^{(10)}_+] + c.c.)\\ &\quad +(\bar{\mathbf{R}}^{(10)\dagger}_+\tilde{\mathbf{L}}^{(00)}_+\bar{\mathbf{R}}^{(01)}_+ + c.c.)\end{aligned} \tag{194}$$

$$\begin{aligned}&= (\tilde{\mathbf{L}}^{(11)}_{+,sf} + \tilde{\mathbf{L}}^{(11)}_{+,sd}) + (\tilde{\mathbf{L}}^{(00)}_{+,sf}\bar{\mathbf{R}}^{(11)}_{+,sf} + c.c.)\\ &\quad +\big[(\tilde{\mathbf{L}}^{(10)}_{+,sf} + \tilde{\mathbf{L}}^{(10)}_{+,sd})(\bar{\mathbf{R}}^{(01)}_{+,sf} + \bar{\mathbf{R}}^{(01)}_{+,sd})\\ &\quad +(\tilde{\mathbf{L}}^{(01)}_{+,sf} + \tilde{\mathbf{L}}^{(01)}_{+,sd})(\bar{\mathbf{R}}^{(10)}_{+,sf} + \bar{\mathbf{R}}^{(10)}_{+,sd}) + c.c.\big] + \mathcal{O}(\alpha^4)\end{aligned} \tag{195}$$

$$\begin{aligned}&= \tilde{\mathbf{h}}^{(11)}_{11,sf} + (\mathbf{h}_{+,sf}\bar{\mathbf{R}}^{(11)}_{+,sf} + c.c.)\\ &\quad +\big[(\tilde{\mathbf{h}}^{(10)}_{11,sf} + \tilde{\mathbf{h}}^{(10)}_{11,sd1})(\bar{\mathbf{R}}^{(01)}_{+,sf} + \bar{\mathbf{R}}^{(01)}_{+,sd1}) + c.c.\big]\\ &\quad +\big[(\tilde{\mathbf{h}}^{(01)}_{11,sf} + \tilde{\mathbf{h}}^{(01)}_{11,sd1})(\bar{\mathbf{R}}^{(10)}_{+,sf} + \bar{\mathbf{R}}^{(10)}_{+,sd1}) + c.c.\big] + \mathcal{O}(\alpha^4),\end{aligned} \tag{196}$$

where both $\tilde{\mathbf{h}}^{(11)}_{11,sd1}$ and $\bar{\mathbf{R}}^{(11)}_{sd1}$ vanish for A^2 is spin free. Equation (196) can be reexpressed as

$$\mathbf{h}^{(11)}_+ = \mathbf{h}^{(11)}_{+,sf} + \mathbf{h}^{(11)}_{+,sd1} + \mathbf{h}^{(11)}_{+,sd2} + \mathcal{O}(\alpha^4), \tag{197}$$

$$\begin{aligned}\mathbf{h}^{(11)}_{+,sf} &= \tilde{\mathbf{h}}^{(11)}_{11,sf} + (\mathbf{h}_{+,sf}\bar{\mathbf{R}}^{(11)}_{+,sf} + c.c.)\\ &\quad +(\tilde{\mathbf{h}}^{(10)}_{11,sf}\bar{\mathbf{R}}^{(01)}_{+,sf} + c.c.) + (\tilde{\mathbf{h}}^{(01)}_{11,sf}\bar{\mathbf{R}}^{(10)}_{+,sf} + c.c.),\end{aligned} \tag{198}$$

$$\begin{aligned}\mathbf{h}^{(11)}_{+,sd1} &= (\tilde{\mathbf{h}}^{(10)}_{11,sf}\bar{\mathbf{R}}^{(01)}_{+,sd1} + \tilde{\mathbf{h}}^{(10)}_{11,sd1}\bar{\mathbf{R}}^{(01)}_{+,sf} + c.c.)\\ &\quad +(\tilde{\mathbf{h}}^{(01)}_{11,sf}\bar{\mathbf{R}}^{(10)}_{+,sd1} + \tilde{\mathbf{h}}^{(01)}_{11,sd1}\bar{\mathbf{R}}^{(10)}_{+,sf} + c.c.),\end{aligned} \tag{199}$$

$$\mathbf{h}^{(11)}_{+,sd2} = (\tilde{\mathbf{h}}^{(10)}_{11,sd1}\bar{\mathbf{R}}^{(01)}_{+,sd1} + c.c.) + (\tilde{\mathbf{h}}^{(01)}_{11,sd1}\bar{\mathbf{R}}^{(10)}_{+,sd1} + c.c.). \tag{200}$$

All the terms here have been given before, except for $\tilde{\mathbf{h}}^{(11)}_{11,sf}$. For instance, $\tilde{\mathbf{h}}^{(10)}_{11,sf}$ and $\tilde{\mathbf{h}}^{(10)}_{11,sd1}$ are just Eqs. (178) and (179), respectively, denoted differently though. $\tilde{\mathbf{h}}^{(01)}_{11,sf}$ and $\tilde{\mathbf{h}}^{(01)}_{11,sd1}$ are obtained from $\tilde{\mathbf{h}}^{(10)}_{11,sf}$ and $\tilde{\mathbf{h}}^{(10)}_{11,sd1}$ by replacing A^{10} with A^{01}. The expression for $\tilde{\mathbf{h}}^{(11)}_{11,sf}$ can be obtained simply as

$$\begin{aligned}\tilde{\mathbf{h}}^{(11)}_{11,sf} &= [\mathbf{U}_0\mathbf{h}\mathbf{U}^\dagger_0]^{(11)}_{++} = \mathbf{R}^\dagger_{+,0}\Big[\mathbf{T}^{(11)}_{\pi,sf}\mathbf{X}_0 + \mathbf{X}^\dagger_0\mathbf{T}^{(11)}_{\pi,sf}\\ &\quad +\mathbf{X}^\dagger_0\Big(\frac{\alpha^2}{4}\mathbf{W}^{(11)}_{\pi,sf} - \mathbf{T}^{(11)}_{\pi,sf}\Big)\mathbf{X}_0\Big]\mathbf{R}_{+,0},\end{aligned} \tag{201}$$

with

$$\big[\mathbf{W}^{(11)}_{\pi,sf}\big]_{\mu\nu} = \langle g_\mu|2V\vec{A}^{10}\cdot\vec{A}^{01}|g_\nu\rangle. \tag{202}$$

Note that $\mathbf{h}^{(11)}_{+,sd2}$ (200) arises from products of spin-dependent matrices and can further be decomposed into a spin-free and a spin-dependent term as going from $\mathbf{E}_{+,2}$ (78) to $\mathbf{E}^{sf}_{+,2}$ (90) and $\mathbf{E}^{sd1}_{+,2}$ (91).

The physical meanings of the terms in Eq. (197) can be made clear by considering the expansions (153), (154), and (183),

$$\begin{aligned}\mathbf{h}^{(11)}_{+,sf} &= \Big[\mathbf{T}^{(11)}_{\pi,sf} + \frac{\alpha^2}{4}\mathbf{W}^{(11)}_{\pi,sf} - \frac{\alpha^2}{4}(\mathbf{T}\mathbf{S}^{-1}\mathbf{T}^{(11)}_{\pi,sf} + c.c.)\Big]\\ &\quad -\frac{\alpha^2}{4}[(\mathbf{T}+\mathbf{V})\mathbf{S}^{-1}\mathbf{T}^{(11)}_{\pi,sf} + c.c.]\\ &\quad -\frac{\alpha^2}{4}(\mathbf{T}^{(10)}_{\pi,sf}\mathbf{S}^{-1}\mathbf{T}^{(01)}_{\pi,sf} + c.c.)\\ &\quad -\frac{\alpha^2}{4}(\mathbf{T}^{(01)}_{\pi,sf}\mathbf{S}^{-1}\mathbf{T}^{(10)}_{\pi,sf} + c.c.)\end{aligned} \tag{203}$$

$$\begin{aligned}&= \mathbf{T}^{(11)}_{\pi,sf} + \frac{\alpha^2}{4}[\mathbf{W}^{(11)}_{\pi,sf} - (\mathbf{V}\mathbf{S}^{-1}\mathbf{T}^{(11)}_{\pi,sf} + c.c.)]\\ &\quad -\frac{\alpha^2}{2}(\mathbf{T}\mathbf{S}^{-1}\mathbf{T}^{(11)}_{\pi,sf} + c.c.)\\ &\quad -\frac{\alpha^2}{2}(\mathbf{T}^{(10)}_{\pi,sf}\mathbf{S}^{-1}\mathbf{T}^{(01)}_{\pi,sf} + c.c.),\end{aligned} \tag{204}$$

$$\mathbf{h}^{(11)}_{+,sd1} = -\frac{\alpha^2}{2}(\mathbf{T}^{(10)}_{\pi,sf}\mathbf{S}^{-1}\mathbf{T}^{(01)}_{\pi,sd} + \mathbf{T}^{(10)}_{\pi,sd}\mathbf{S}^{-1}\mathbf{T}^{(01)}_{\pi,sf} + c.c.), \tag{205}$$

$$\mathbf{h}^{(11)}_{+,sd2} = -\frac{\alpha^2}{2}(\mathbf{T}^{(10)}_{\pi,sd}\mathbf{S}^{-1}\mathbf{T}^{(01)}_{\pi,sd} + c.c.). \tag{206}$$

The first term of Eq. (204) is nothing but the sf-X2C diamagnetic shielding (DS), where the remaining terms represent the $\mathcal{O}(\alpha^2)$ corrections. Specifically, the third term is a kinetic energy correction to the DS (DS-KE), while the fourth term is the cross between PSO and OZ (PSO-OZ). In contrast, the second term will vanish in the CBS limit in view of Eqs. (193) and (202). The $\mathbf{h}^{(11)}_{+,sd1}$ (205) term is composed of the OZ-FC, OZ-SD, and SZ-PSO cross terms, which do not contribute to the NMR shielding of a closed-shell system at $\mathcal{O}(\alpha^2)$, for the expectation value of the Pauli matrix is zero. By applying the Dirac identity (1) to $\mathbf{h}^{(11)}_{+,sd2}$ (206), a spin-free contribution can be identified from the spin-dependent SZ-FC and SZ-SD cross terms.[64,65] The remaining term linear in $\vec{\sigma}$ again does not contribute to the NMR shielding of a closed-shell system at $\mathcal{O}(\alpha^2)$.

At this stage, the spin separation of X2C properties has fully been achieved. The present results of order α^2 in spin are superior over the BP-based formulations because of three reasons. First, scalar relativity is not expanded here but is treated variationally through the sf-X2C Hamiltonian. Second, the presence of $\mathbf{X}_0$ and $\mathbf{R}_{+,0}$ in the spin-dependent perturbation operators brings in some scalar relativistic effects of high orders in α^2. This is to some extent similar to the spin-dependent perturbation operators in the ZORA approach,[25,26] which include some high order scalar relativistic effects through the decoupling matrix[30]

$$\begin{aligned}\mathbf{X}_0^{\mathrm{ZORA}} &= \left(\mathbf{T} - \frac{\alpha^2}{4}\mathbf{W}_{sf}\right)^{-1}\mathbf{T} \\ &= \mathbf{I} - \frac{\alpha^2}{4}\mathbf{T}^{-1}\mathbf{W}_{sf}\left(\mathbf{T} - \frac{\alpha^2}{4}\mathbf{W}_{sf}\right)^{-1}\mathbf{T}. \end{aligned} \tag{207}$$

However, the renormalization of ZORA is simply $\mathbf{R}^{\mathrm{ZORA}}_{0,+} = \mathbf{I}$, thereby losing the kinetic energy corrections to the property operators. Third, the present matrix formulations allow for easy implementations for only matrix multiplications are required.

4. Two-electron spin-orbit operators: Operator-like formulation

Applying the RKB transformation (20) to the Coulomb and Gaunt interactions

$$G^C_{ij} = \frac{1}{r_{ij}}, \quad G^G_{ij} = -\frac{\vec{\alpha}_i \cdot \vec{\alpha}_j}{r_{ij}} \tag{208}$$

leads[66] to

$$\begin{aligned}\tilde{g}^C_{ij} &= (Z_i \otimes Z_j)^\dagger G^C_{ij}(Z_i \otimes Z_j) \\ &= \begin{pmatrix} g^{C,00}_{ij} & 0 & 0 & 0 \\ 0 & \frac{\alpha^2}{4}g^{C,02}_{ij} & 0 & 0 \\ 0 & 0 & \frac{\alpha^2}{4}g^{C,20}_{ij} & 0 \\ 0 & 0 & 0 & \frac{\alpha^4}{16}g^{C,22}_{ij} \end{pmatrix},\end{aligned}$$

$$\begin{aligned}\tilde{g}^G_{ij} &= (Z_i \otimes Z_j)^\dagger G^G_{ij}(Z_i \otimes Z_j) \\ &= \begin{pmatrix} 0 & 0 & 0 & \frac{\alpha^2}{4}g^{G,++}_{ij} \\ 0 & 0 & \frac{\alpha^2}{4}g^{G,+-}_{ij} & 0 \\ 0 & \frac{\alpha^2}{4}g^{G,-+}_{ij} & 0 & 0 \\ \frac{\alpha^2}{4}g^{G,--}_{ij} & 0 & 0 & 0 \end{pmatrix},\end{aligned} \tag{209}$$

where

$$\begin{aligned} &g^{C,00}_{ij} = g^C_{ij}, \quad g^{C,02}_{ij} = \Pi_j g^C_{ij}\Pi_j, \quad g^{C,20}_{ij} = \Pi_i g^C_{ij}\Pi_i, \\ &g^{C,22}_{ij} = \Pi_i\Pi_j g^C_{ij}\Pi_i\Pi_j, \end{aligned} \tag{210}$$

$$\begin{aligned} g^{G,++}_{ij} &= g^G_{ij}\Pi_i\Pi_j, \quad g^{G,+-}_{ij} = \Pi_j g^G_{ij}\Pi_i, \\ g^{G,-+}_{ij} &= \Pi_i g^G_{ij}\Pi_j, \quad g^{G,--}_{ij} = \Pi_i\Pi_j g^G_{ij}, \end{aligned} \tag{211}$$

$$g^C_{ij} = \frac{1}{r_{12}}, \quad g^G_{ij} = -\frac{\vec{\sigma}_1 \cdot \vec{\sigma}_2}{r_{12}}, \quad \Pi_i = \vec{\sigma}_i \cdot \vec{p}_i. \tag{212}$$

It is clear that, in the transformed Coulomb operators (210), there is always a pair of σ in Π for the same electron, while in the transformed Gaunt terms (211), the σ in Π is paired with that in g^G_{ij}. Therefore, the spin separation can be achieved by using the Dirac identity (1). To go to the two-component formulation, the following transformation:[15]

$$\begin{aligned} U &= \begin{pmatrix} R^\dagger_+ & 0 \\ 0 & R^\dagger_- \end{pmatrix}\begin{pmatrix} 1 & X^\dagger \\ \tilde{X}^\dagger & 1 \end{pmatrix}, \quad \tilde{X} = -X^\dagger S_-, \\ S_- &= \frac{\alpha^2}{2}T, \end{aligned} \tag{213}$$

$$\begin{aligned} R^\dagger_+ &= (1 + X^\dagger S_- X)^{-\frac{1}{2}}, \\ R^\dagger_- &= S_-^{\frac{1}{2}}(1 + S_-^{-\frac{1}{2}}\tilde{X}^\dagger\tilde{X}S_-^{-\frac{1}{2}})^{-\frac{1}{2}}S_-^{-\frac{1}{2}}, \end{aligned} \tag{214}$$

should further be applied to the $\tilde{g}^C_{ij}$ and $\tilde{g}^G_{ij}$ operators (209). For the present purpose, only the spin-free transformation U_0 is considered, which leads to

$$\begin{aligned} g_{++}(i,j) &= [(U_0(i) \otimes U_0(j))(\tilde{g}^C_{ij} + \tilde{g}^G_{ij})(U_0(i) \otimes U_0(j))^\dagger]_{++} \\ &= g^C_{++}(i,j) + g^G_{++}(i,j), \end{aligned} \tag{215}$$

$$\begin{aligned} g^C_{++}(i,j) = {} & R^\dagger_{+,0}(i)R^\dagger_{+,0}(j)[g^{C,00}_{ij} \\ & + \frac{\alpha^2}{4}X^\dagger_0(i)g^{C,20}_{ij}X_0(i) + \frac{\alpha^2}{4}X^\dagger_0(j)g^{C,02}_{ij}X_0(j) \\ & + \frac{\alpha^4}{16}X^\dagger_0(i)X^\dagger_0(j)g^{C,22}_{ij}X_0(i)X_0(j)]R_{+,0}(i)R_{+,0}(j), \end{aligned} \tag{216}$$

$$\begin{aligned} g^G_{++}(i,j) = {} & \frac{\alpha^2}{4}R^\dagger_{+,0}(i)R^\dagger_{+,0}(j)[g^{G,++}_{ij}X_0(i)X_0(j) \\ & + X^\dagger_0(i)g^{G,-+}_{ij}X_0(j) + X^\dagger_0(j)g^{G,+-}_{ij}X_0(i) \\ & + X^\dagger_0(i)X^\dagger_0(j)g^{G,--}_{ij}]R_{+,0}(i)R_{+,0}(j). \end{aligned} \tag{217}$$

It has been a common exercise that the spin-free part of g_{++} (215) is approximated simply as the bare Coulomb term g_{ij}^{C}, resulting in the following spin-free many-electron Hamiltonian:

$$H_{sf} = \sum_{pq}[\mathbf{C}_+^\dagger \mathbf{h}_{+,sf}^{\mathrm{X2C}} \mathbf{C}_+]_{pq} a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle a_p^\dagger a_q^\dagger a_s a_r,$$
$$\psi_p = \sum_\mu g_\mu (\mathbf{C}_+)_{\mu p}, \tag{218}$$

which has been employed in various correlation/excitation calculations.[67–69] To find the spin-dependent part of g_{++} (215), we first extract the spin-dependent terms of $g_{ij}^{C,xy}$ (210) and $g_{ij}^{G,xy}$ (211),

$$\begin{aligned}
g_{ij,SO}^{C,20} &= \left[\Pi_i g_{ij}^C \Pi_i\right]_{SO} = \mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_i\right),\\
g_{ij,SO}^{C,02} &= \left[\Pi_j g_{ij}^C \Pi_j\right]_{SO} = \mathbb{i}\vec{\sigma}_j \cdot \left(\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_j\right),\\
g_{ij,SO}^{G,++} &= \left[g_{ij}^G \Pi_i \Pi_j\right]_{SO} = -\mathbb{i}(\vec{\sigma}_j - \vec{\sigma}_i)\cdot\frac{1}{r_{ij}}(\vec{p}_i \times \vec{p}_j),\\
g_{ij,SO}^{G,-+} &= \left[\Pi_i g_{ij}^G \Pi_j\right]_{SO} = -\mathbb{i}(\vec{\sigma}_i + \vec{\sigma}_j)\cdot\left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_j\right),\\
g_{ij,SO}^{G,+-} &= \left[\Pi_j g_{ij}^G \Pi_i\right]_{SO} = -\mathbb{i}(\vec{\sigma}_i + \vec{\sigma}_j)\cdot\left(\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_i\right),\\
g_{ij,SO}^{G,--} &= \left[\Pi_i \Pi_j g_{ij}^G\right]_{SO} = -\mathbb{i}(\vec{\sigma}_i - \vec{\sigma}_j)\cdot(\vec{p}_i \times \vec{p}_j)\frac{1}{r_{ij}},
\end{aligned} \tag{219}$$

which are first order in both $\vec{\sigma}$ and α^2. The spin-same-orbit (SSO) and spin-other-orbit (SOO) parts of g_{++} (215) can hence be written as

$$H_{SSO,2e} = \frac{\alpha^2}{4}\sum_{i\neq j} R_{+,0}^\dagger(i) R_{+,0}^\dagger(j) X_0^\dagger(i) \times\left[\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_i\right)\right] X_0(i) R_{+,0}(j) R_{+,0}(i), \tag{220}$$

$$\begin{aligned}
H_{SOO,2e} &= \frac{\alpha^2}{4}\sum_{i\neq j} R_{+,0}^\dagger(i) R_{+,0}^\dagger(j)\left\{\left[\mathbb{i}\vec{\sigma}_i \cdot \frac{1}{r_{ij}}(\vec{p}_i \times \vec{p}_j)\right] X_0(i) X_0(j)\right.\\
&+ X_0^\dagger(i)\left[-\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_j\right)\right] X_0(j)\\
&+ X_0^\dagger(j)\left[-\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_i\right)\right] X_0(i)\\
&\left.+ X_0^\dagger(i) X_0^\dagger(j)\left[-\mathbb{i}\vec{\sigma}_i \cdot (\vec{p}_i \times \vec{p}_j)\frac{1}{r_{ij}}\right]\right\} R_{+,0}(j) R_{+,0}(i).
\end{aligned} \tag{221}$$

By means of the approximations $X_0 \approx 1$ and $R_{+,0} \approx 1$, as well as the following identities:

$$\begin{aligned}
\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_j &= -\left(\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_j\right) + \frac{1}{r_{ij}}(\vec{p}_i \times \vec{p}_j),\\
\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_i &= -\left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_i\right) - \frac{1}{r_{ij}}(\vec{p}_i \times \vec{p}_j),\\
(\vec{p}_i \times \vec{p}_j)\frac{1}{r_{ij}} &= \frac{1}{r_{ij}}(\vec{p}_i \times \vec{p}_j) + \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_i\right)\\
&\quad -\left(\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_j\right),
\end{aligned} \tag{222}$$

both $H_{SSO,2e}$ (220) and $H_{SOO,2e}$ (221) will reduce to their BP counterparts, the sum of which is simply the familiar form

$$\begin{aligned}
H_{SO,2e}^{\mathrm{BP}} &= \frac{\alpha^2}{4}\sum_{i\neq j}\left[\mathbb{i}(\vec{\sigma}_i + 2\vec{\sigma}_j)\cdot\left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_i\right)\right]\\
&= -\frac{\alpha^2}{2}\sum_{i\neq j}\frac{(\vec{s}_i + 2\vec{s}_j)\cdot(\vec{r}_{ij} \times \vec{p}_i)}{r_{ij}^3}.
\end{aligned} \tag{223}$$

If the free-particle X_0 and $R_{+,0}$ (157) are used, Eqs. (220) and (221) will reduce to the DKH1 type of SSO and SOO operators

$$H_{SSO,2e}^{\mathrm{DKH1}} = \alpha^2\sum_{i\neq j}\mathcal{Q}_i\mathcal{A}_j\left[\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_i\right)\right]\mathcal{Q}_i\mathcal{A}_j, \tag{224}$$

$$\begin{aligned}
H_{SOO,2e}^{\mathrm{DKH1}} &= \alpha^2\sum_{i\neq j}\left\{\mathcal{A}_i\mathcal{A}_j\left[\mathbb{i}\vec{\sigma}_i \cdot \frac{1}{r_{ij}}(\vec{p}_i \times \vec{p}_j)\right]\mathcal{Q}_i\mathcal{Q}_j\right.\\
&+\mathcal{Q}_i\mathcal{A}_j\left[-\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_j\right)\right]\mathcal{A}_i\mathcal{Q}_j\\
&+\mathcal{A}_i\mathcal{Q}_j\left[-\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_j \times \frac{1}{r_{ij}}\vec{p}_i\right)\right]\mathcal{Q}_i\mathcal{A}_j\\
&\left.+\mathcal{Q}_i\mathcal{Q}_j\left[-\mathbb{i}\vec{\sigma}_i \cdot (\vec{p}_i \times \vec{p}_j)\frac{1}{r_{ij}}\right]\mathcal{A}_i\mathcal{A}_j\right\}.
\end{aligned} \tag{225}$$

It should be pointed out that, while the present SSO operator $H_{SSO,2e}^{\mathrm{DKH1}}$ (224) agrees with Eq. (47) in Ref. 70, the present SOO operator $H_{SOO,2e}^{\mathrm{DKH1}}$ (225) is somewhat different from Eqs. (48) and (49) in Ref. 70

$$\begin{aligned}
\tilde{H}_{SOO,2e}^{\mathrm{DKH1}} &= \alpha^2\sum_{i\neq j} 2\mathcal{Q}_i\mathcal{A}_j\left[\mathbb{i}\vec{\sigma}_i \cdot \left(\vec{p}_i \times \frac{1}{r_{ij}}\vec{p}_j\right)\right]\mathcal{A}_i\mathcal{Q}_j\\
&= \alpha^2\sum_{i\neq j} 2\mathcal{Q}_i\mathcal{A}_j\left[\vec{\sigma}_i \cdot \left(\frac{\vec{r}_{ij}}{r_{ij}^3} \times \vec{p}_j\right)\right]\mathcal{A}_i\mathcal{Q}_j.
\end{aligned} \tag{226}$$

Only by assuming that the operator $\vec{P}_i = \frac{\vec{p}_i}{E_i + c^2}$ used in Ref. 70 shares similar properties (222) as $\vec{p}_i$, which is equivalent to assuming $[\frac{1}{E_i+c^2}, \frac{1}{r_{ij}}] \approx 0$, Eq. (226) can be derived from Eq. (225). The practical implication of such approximations may not be significant, since the leading term $\frac{1}{2c^2}$ of the denominator $\frac{1}{E_i+c^2}$ ($\approx \frac{1}{2c^2} - \frac{p_i^2}{8c^4}$) is commutable with $\frac{1}{r_{ij}}$. However, since the required integrals are the same for

Eqs. (225) and (226), the approximations do not introduce any advantages.

At this stage, Eqs. (220) and (221) are only formal since the decoupling operator X_0 is not known in closed form. However, they can be made useful by going to the matrix representation.[13] Actually, the operator U (213) subject to

$$UMU^\dagger = \begin{pmatrix} R_+^\dagger(1+X^\dagger S_- X)R_+ & 0 \\ 0 & R_-^\dagger(S_- + \tilde{X}^\dagger \tilde{X})R_- \end{pmatrix} = M, \quad M = \begin{pmatrix} 1 & 0 \\ 0 & S_- \end{pmatrix} \tag{227}$$

is nothing but the operator counterpart of the matrix $\mathbf{U}$ (32) satisfying Eq. (68). To see this, we have to recall the formal relations[15]

$$\bar{\psi}_i^L = X\psi_i^L, \quad i \in \text{PES}; \quad \psi_{\tilde{i}}^L = \tilde{X}\bar{\psi}_{\tilde{i}}^L, \quad \tilde{i} \in \text{NES} \tag{228}$$

that are behind the transformation U (213). In view of Eq. (31), the matrix representations of X and $\tilde{X}$ in the basis $\{g_\mu\}$ are simply $\mathbf{SX}$ and $\mathbf{S}\tilde{\mathbf{X}}$, respectively. The matrix representations $\bar{\mathbf{R}}_+$ of R_+ and $\bar{\mathbf{R}}_-$ of R_- can be found from the identities implied in Eq. (227). Specifically,

$$\begin{aligned} &R_+^\dagger(1+X^\dagger S_- X)R_+ \\ &= 1 \to \bar{\mathbf{R}}_+^\dagger \mathbf{S}^{-1}\tilde{\mathbf{S}}_+\mathbf{S}^{-1}\bar{\mathbf{R}}_+ = \mathbf{S} = \mathbf{S}_+ \\ &\to [\mathbf{S}_+^{-1/2}\bar{\mathbf{R}}_+\mathbf{S}_+^{-1/2}]^\dagger[\mathbf{S}_+^{-1/2}\tilde{\mathbf{S}}_+\mathbf{S}_+^{-1/2}][\mathbf{S}_+^{-1/2}\bar{\mathbf{R}}_+\mathbf{S}_+^{-1/2}] = \mathbf{I} \\ &\to \bar{\mathbf{R}}_+ = \mathbf{S}_+^{1/2}[\mathbf{S}_+^{-1/2}\tilde{\mathbf{S}}_+\mathbf{S}_+^{-1/2}]^{-1/2}\mathbf{S}_+^{1/2}, \end{aligned} \tag{229}$$

$$\begin{aligned} &R_-^\dagger(S_- + \tilde{X}^\dagger\tilde{X})R_- \\ &= S_- \to \bar{\mathbf{R}}_-^\dagger \mathbf{S}_+^{-1}\tilde{\mathbf{S}}_-\mathbf{S}_+^{-1}\bar{\mathbf{R}}_- = \mathbf{S}_-^{-1}, \quad \mathbf{S}_- = \frac{\alpha^2}{2}\mathbf{T} \\ &\to [\mathbf{S}_-^{1/2}\mathbf{S}_+^{-1}\bar{\mathbf{R}}_-\mathbf{S}_-^{-1/2}]^\dagger[\mathbf{S}_-^{-1/2}\tilde{\mathbf{S}}_-\mathbf{S}_-^{-1/2}][\mathbf{S}_-^{1/2}\mathbf{S}_+^{-1}\bar{\mathbf{R}}_-\mathbf{S}_-^{-1/2}] = \mathbf{I} \\ &\to \bar{\mathbf{R}}_- = \mathbf{S}_+\mathbf{S}_-^{-1/2}[\mathbf{S}_-^{-1/2}\tilde{\mathbf{S}}_-\mathbf{S}_-^{-1/2}]^{-1/2}\mathbf{S}_-^{1/2}. \end{aligned} \tag{230}$$

The $\mathbf{R}_+$ (60) and $\mathbf{R}_-$ (61) matrices can hence be recovered by the relations $\mathbf{R}_+ = \mathbf{S}_+^{-1}\bar{\mathbf{R}}_+$ and $\mathbf{R}_- = \mathbf{S}_+^{-1}\bar{\mathbf{R}}_-$, respectively. Therefore, Eqs. (220) and (221) can be rewritten in a second-quantized form

$$H_{SSO,2e} = \sum_{pqrs}\frac{\alpha^2}{4}\langle pq|G_{SSO}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r, \tag{231}$$

$$\begin{aligned} \langle pq|G_{SSO}|rs\rangle = &\sum_{\mu\nu\kappa\lambda}(\mathbf{X}_0\mathbf{A})_{\mu p}^*(\mathbf{A})_{\kappa q}^*\langle\mu\kappa|\mathbb{i}\vec{\sigma}_1 \\ &\cdot\left(\vec{p}_1 \times \frac{1}{r_{12}}\vec{p}_1\right)|\nu\lambda\rangle(\mathbf{X}_0\mathbf{A})_{\nu r}\mathbf{A}_{\lambda s}, \\ \mathbf{A} = &\mathbf{R}_{+,0}\mathbf{C}_+, \end{aligned} \tag{232}$$

$$H_{SOO,2e} = \sum_{pqrs}\frac{\alpha^2}{4}\langle pq|G_{SOO}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r, \tag{233}$$

$$\begin{aligned} &\langle pq|G_{SOO}|rs\rangle \\ &= \sum_{\mu\nu\kappa\lambda}\Bigg[\mathbf{A}_{\mu p}^*\mathbf{A}_{\kappa q}^*\langle\mu\kappa|\mathbb{i}\vec{\sigma}_1\cdot\frac{1}{r_{12}}(\vec{p}_1\times\vec{p}_2)|\nu\lambda\rangle(\mathbf{X}_0\mathbf{A})_{\nu r}(\mathbf{X}_0\mathbf{A})_{\lambda s} \\ &+(\mathbf{X}_0\mathbf{A})_{\mu p}^*\mathbf{A}_{\kappa q}^*\langle\mu\kappa|-\mathbb{i}\vec{\sigma}_1\cdot\left(\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_2\right)|\nu\lambda\rangle\mathbf{A}_{\nu r}(\mathbf{X}_0\mathbf{A})_{\lambda s} \\ &+\mathbf{A}_{\mu p}^*(\mathbf{X}_0\mathbf{A})_{\kappa q}^*\langle\mu\kappa|-\mathbb{i}\vec{\sigma}_1\cdot\left(\vec{p}_2\times\frac{1}{r_{12}}\vec{p}_1\right)|\nu\lambda\rangle(\mathbf{X}_0\mathbf{A})_{\nu r}\mathbf{A}_{\lambda s} \\ &+(\mathbf{X}_0\mathbf{A})_{\mu p}^*(\mathbf{X}_0\mathbf{A})_{\kappa q}^*\langle\mu\kappa|-\mathbb{i}\vec{\sigma}_1\cdot(\vec{p}_1\times\vec{p}_2)\frac{1}{r_{12}}|\nu\lambda\rangle\mathbf{A}_{\nu r}\mathbf{A}_{\lambda s}\Bigg]. \end{aligned} \tag{234}$$

Once the spin-free decoupling matrix $\mathbf{X}_0$ is made available,[15,18] the operators $H_{SSO,2e}$ (231) and $H_{SOO,2e}$ (233) can be constructed.

5. Effective one-electron spin-orbit operator

Due to the weak interplay with electron correlation, the two-electron spin-orbit operators (231) and (233) can further be simplified by invoking a mean-field approximation,[71,72] thereby leading to an effective one-electron spin-orbit operator

$$H_{SO,2e} = \sum_{pq}(\mathbf{C}_+^\dagger\mathbf{F}_{SO,2e}\mathbf{C}_+)_{pq}a_p^\dagger a_q. \tag{235}$$

As a matter of fact, the operator $\mathbf{F}_{SO,2e}$ arises more naturally from the two-electron spin-orbit part of $\mathbf{h}_+^{\text{NESC}}$ (34) transformed from $\mathbf{h}$ (12),

$$\mathbf{F}_{SO,2e} = \mathbf{R}_+^\dagger\tilde{\mathbf{L}}_{SO,2e}^{\text{NESC}}\mathbf{R}_+, \tag{236}$$

$$\tilde{\mathbf{L}}_{SO,2e}^{\text{NESC}} = \frac{\alpha^2}{4}\left[\mathbf{G}_{SO}^{LL} + \mathbf{G}_{SO}^{LS}\mathbf{X} + \mathbf{X}^\dagger\mathbf{G}_{SO}^{SL} + \mathbf{X}^\dagger\mathbf{G}_{SO}^{SS}\mathbf{X}\right], \tag{237}$$

where

$$\begin{aligned} \left[\mathbf{G}_{SO}^{LL}\right]_{\mu\nu} = &\sum_i\left[\langle\mu\bar{i}|\left[\Pi_2 g_{12}^C\Pi_2\right]_{SO}|\nu\bar{i}\rangle\right. \\ &\left.-\langle\mu\bar{i}|\left[\Pi_2 g_{12}^G\Pi_1\right]_{SO}|\bar{i}\nu\rangle\right] \end{aligned} \tag{238}$$

$$\begin{aligned} = &\sum_{\kappa\lambda}P_{\lambda\kappa}^{SS}\left[\langle\mu\kappa|\left[\Pi_2 g_{12}^C\Pi_2\right]_{SO}|\nu\lambda\rangle\right. \\ &\left.-\langle\mu\kappa|\left[\Pi_2 g_{12}^G\Pi_1\right]_{SO}|\lambda\nu\rangle\right], \end{aligned} \tag{239}$$

$$\begin{aligned} \left[\mathbf{G}_{SO}^{LS}\right]_{\mu\nu} = &\sum_i\left[\langle\mu i|\left[g_{12}^G\Pi_1\Pi_2\right]_{SO}|\nu\bar{i}\rangle\right. \\ &\left.-\langle\mu i|\left[g_{12}^G\Pi_1\Pi_2\right]_{SO}|\bar{i}\nu\rangle\right] \\ &+\sum_i\left[\langle\mu\bar{i}|\left[\Pi_2 g_{12}^G\Pi_1\right]_{SO}|\nu i\rangle\right. \\ &\left.-\langle\mu\bar{i}|\left[\Pi_2 g_{12}^C\Pi_2\right]_{SO}|i\nu\rangle\right] \end{aligned} \tag{240}$$

$$= \sum_{\kappa\lambda} P^{SL}_{\lambda\kappa}\big[\langle\mu\kappa|\big[g^G_{12}\Pi_1\Pi_2\big]_{SO}|\nu\lambda\rangle - \langle\mu\kappa|\big[g^G_{12}\Pi_1\Pi_2\big]_{SO}|\lambda\nu\rangle\big] + \sum_{\kappa\lambda} P^{LS}_{\lambda\kappa}\big[\langle\mu\kappa|\big[\Pi_2 g^G_{12}\Pi_1\big]_{SO}|\nu\lambda\rangle - \langle\mu\kappa|\big[\Pi_2 g^C_{12}\Pi_2\big]_{SO}|\lambda\nu\rangle\big], \quad (241)$$

$$\big[\mathbf{G}^{SL}_{SO}\big]_{\mu\nu} = \sum_i \big[\langle\mu\bar{i}|\big[\Pi_1\Pi_2 g^G_{12}\big]_{SO}|\nu i\rangle - \langle\mu\bar{i}|\big[\Pi_1\Pi_2 g^G_{12}\big]_{SO}|i\nu\rangle\big] + \sum_i \big[\langle\mu i|\big[\Pi_1 g^G_{12}\Pi_2\big]_{SO}|\nu\bar{i}\rangle - \langle\mu i|\big[\Pi_1 g^C_{12}\Pi_1\big]_{SO}|\bar{i}\nu\rangle\big] \quad (242)$$

$$= \sum_{\kappa\lambda} P^{LS}_{\lambda\kappa}\big[\langle\mu\kappa|\big[\Pi_1\Pi_2 g^G_{12}\big]_{SO}|\nu\lambda\rangle - \langle\mu\kappa|\big[\Pi_1\Pi_2 g^G_{12}\big]_{SO}|\lambda\nu\rangle\big] + \sum_{\kappa\lambda} P^{SL}_{\lambda\kappa}\big[\langle\mu\kappa|\big[\Pi_1 g^G_{12}\Pi_2\big]_{SO}|\nu\lambda\rangle - \langle\mu\kappa|\big[\Pi_1 g^C_{12}\Pi_1\big]_{SO}|\lambda\nu\rangle\big], \quad (243)$$

$$\big[\mathbf{G}^{SS}_{SO}\big]_{\mu\nu} = \sum_i \big[\langle\mu i|\big[\Pi_1 g^C_{12}\Pi_1\big]_{SO}|\nu i\rangle - \langle\mu i|\big[\Pi_1 g^G_{12}\Pi_2\big]_{SO}|i\nu\rangle\big] + \frac{\alpha^2}{4}\sum_i \big[\langle\mu\bar{i}|\big[\Pi_1\Pi_2 g^C_{12}\Pi_1\Pi_2\big]_{SO}|\nu\bar{i}\rangle - \langle\mu\bar{i}|\big[\Pi_1\Pi_2 g^C_{12}\Pi_1\Pi_2\big]_{SO}|\bar{i}\nu\rangle\big] \quad (244)$$

$$= \sum_{\kappa\lambda} P^{LL}_{\lambda\kappa}\big[\langle\mu\kappa|\big[\Pi_1 g^C_{12}\Pi_1\big]_{SO}|\nu\lambda\rangle - \langle\mu\kappa|\big[\Pi_1 g^G_{12}\Pi_2\big]_{SO}|\lambda\nu\rangle\big] + \frac{\alpha^2}{4}\sum_{\kappa\lambda} P^{SS}_{\lambda\kappa}\big[\langle\mu\kappa|\big[\Pi_1\Pi_2 g^C_{12}\Pi_1\Pi_2\big]_{SO}|\nu\lambda\rangle - \langle\mu\kappa|\big[\Pi_1\Pi_2 g^C_{12}\Pi_1\Pi_2\big]_{SO}|\lambda\nu\rangle\big]. \quad (245)$$

Here, the indices i and $\bar{i}$ representing the respective large and pseudo-large components of the occupied 4-spinors (7). The last term of $\mathbf{G}^{SS}_{SO}$ (245) can be neglected to make $\mathbf{F}_{SO,2e}$ (236) correct to $\mathcal{O}(\alpha^2)$. The density matrices $\mathbf{P}^{XY}$ can be constructed as

$$\mathbf{P}^{LL} = \mathbf{R}_+\mathbf{P}\mathbf{R}_+^\dagger, \quad \mathbf{P} = \mathbf{C}_+\mathbf{n}\mathbf{C}_+^\dagger, \qquad \mathbf{P}^{LS} = \mathbf{P}^{LL}\mathbf{X}^\dagger = \mathbf{P}^{SL\dagger}, \quad \mathbf{P}^{SS} = \mathbf{X}\mathbf{P}^{LL}\mathbf{X}^\dagger. \quad (246)$$

At this stage, all the quantities have been represented in the atomic spin-orbital basis. In particular, the density matrix $\mathbf{P}$ is generally nonzero in the $\alpha\beta$ block. Further approximations are possible. First, staying within the spirit of Sec. II C 4, the two-component $\mathbf{X}$, $\mathbf{R}_+$, and $\mathbf{P}$ matrices are to be replaced by the corresponding spin-free ones. The $\alpha\beta$ block of $\mathbf{P}$ is then zero. Second, for open-shell systems, $\mathbf{P}$ can be approximated by the spin-averaged density matrix $\mathbf{P} = \frac{1}{2}(\mathbf{P}_\alpha + \mathbf{P}_\beta)$. Under these two approximations, the $\mathbf{G}^{XY}_{SO}$ matrices can be made very simple after integrations over spin. As shown in Appendix B, they become the matrix representations of the following operators:

$$G^{XY}_{SO} = \mathbb{i}\vec{\sigma}\cdot\vec{g}^{XY} = \mathbb{i}\sigma_l g^{XY,l}, \quad l \in \{x, y, z\}, \quad (247)$$

$$g^{LL,l}_{\mu\nu} = \sum_{\kappa\lambda} g^{G,LL,l}_{\mu\nu,\kappa\lambda} P^{SS}_{\lambda\kappa}, \quad g^{G,LL,l}_{\mu\nu,\kappa\lambda} = -2K^l_{\lambda\mu,\kappa\nu}, \quad (248)$$

$$g^{LS,l}_{\mu\nu} = \sum_{\kappa\lambda} g^{C,LS,l}_{\mu\nu,\kappa\lambda} P^{LS}_{\lambda\kappa}, \quad g^{C,LS,l}_{\mu\nu,\kappa\lambda} = -K^l_{\mu\lambda,\kappa\nu} - K^l_{\lambda\mu,\kappa\nu}, \quad (249)$$

$$g^{SL,l}_{\mu\nu} = \sum_{\kappa\lambda} g^{C,SL,l}_{\mu\nu,\kappa\lambda} P^{SL}_{\lambda\kappa} = -g^{LS,l}_{\nu\mu}, \qquad g^{C,SL,l}_{\mu\nu,\kappa\lambda} = K^l_{\mu\lambda,\kappa\nu} + K^l_{\mu\lambda,\nu\kappa}, \quad (250)$$

$$g^{SS,l}_{\mu\nu} = \sum_{\kappa\lambda}\big(g^{C,SS,l}_{\mu\nu,\kappa\lambda} + g^{G,SS,l}_{\mu\nu,\kappa\lambda}\big)P^{SS}_{\lambda\kappa}, \qquad g^{C,SS,l}_{\mu\nu,\lambda\kappa} = -2\big(K^l_{\mu\nu,\kappa\lambda} + K^l_{\mu\nu,\lambda\kappa}\big), \quad g^{G,SS,l}_{\mu\nu,\lambda\kappa} = 2K^l_{\mu\lambda,\nu\kappa}, \quad (251)$$

where the antisymmetric K integrals are defined as

$$K^l_{\mu\nu,\kappa\lambda} = \varepsilon_{lmn}(\mu_m\nu|\kappa_n\lambda) = -K^l_{\kappa\lambda,\mu\nu}, \qquad \mu_m = \partial_m\mu, \quad l, m, n \in \{x, y, z\}. \quad (252)$$

It is seen that $g^{LS,l}_{\mu\nu}/g^{SL,l}_{\mu\nu}$ and $g^{LL,l}_{\mu\nu}$ are due entirely to the Coulomb-exchange and Gaunt-exchange interactions, respectively, while $g^{SS,l}_{\mu\nu}$ (251) is a mixture of the Coulomb-direct and Gaunt-exchange interactions. The Gaunt-direct interaction vanishes due to spin averaging. Again, if the approximations $\mathbf{X}_0 \approx \mathbf{I}$ and $\mathbf{R}_{+,0} \approx \mathbf{I}$ are introduced, the $\mathbf{F}_{SO,2e}$ operator (236) will reduce to the mean-field BP spin-orbit Hamiltonian,[71] viz.,

$$\big[\mathbf{F}^{BP}_{SO,2e}\big]_{\mu\nu} = \sum_{\kappa\lambda}\mathbb{i}\sigma^l_{\mu\nu}\big[g^{C,SS,l}_{\mu\nu,\lambda\kappa} + \big(g^{G,LL,l}_{\mu\nu,\kappa\lambda} + g^{G,SS,l}_{\mu\nu,\kappa\lambda}\big) + \big(g^{C,LS,l}_{\mu\nu,\kappa\lambda} + g^{C,SL,l}_{\mu\nu,\kappa\lambda}\big)\big]P_{\lambda\kappa} \quad (253)$$

$$= \sum_{\kappa\lambda}\mathbb{i}\sigma^l_{\mu\nu}\big[g^{C,SS,l}_{\mu\nu,\lambda\kappa} + 3\big(g^{C,LS,l}_{\mu\nu,\kappa\lambda} + g^{C,SL,l}_{\mu\nu,\kappa\lambda}\big)\big]P_{\lambda\kappa}. \quad (254)$$

At this level, the Gaunt-exchange interaction is just twice the Coulomb-exchange interaction. Since Eqs. (236) and (254) share the same kind of integrals $K^l_{\mu\nu,\kappa\lambda}$ (252), their computational costs are virtually the same, for the additional matrix multiplications involved in the former are very cheap. The computational cost for the evaluation of $K^l_{\mu\nu,\kappa\lambda}$ can substantially be reduced by employing the local nature of spin-orbit interactions. For instance, the one-center approximation for $K^l_{\mu\nu,\kappa\lambda}$ is already sufficiently accurate.[68,71,72]

The extension of spin separation to density functional theory (DFT) is straightforward. For a pure density functional,

the Kohn-Sham (KS) Hamiltonian matrix is of form (70), except that the external potential V is replaced by a local effective potential V_{eff}

$$V_{\text{eff}} = V + V_H[\rho] + V_{XC}[\rho], \tag{255}$$

$$V_H[\rho] = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad V_{XC}[\rho] = \frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})}. \tag{256}$$

The first order spin-orbit KS matrix $\mathbf{F}_{SO}$ is readily obtained as

$$\mathbf{F}_{SO} = \frac{\alpha^2}{4} \mathbf{R}_{+,0}^{\dagger} \mathbf{X}_0^{\dagger} \mathbf{W}_{\text{eff},sd} \mathbf{X}_0 \mathbf{R}_{+,0}, \tag{257}$$

where $\mathbf{W}_{\text{eff},sd}$ is the matrix representation of $W_{\text{eff},sd} = \mathbb{i}\vec{\sigma} \cdot (\vec{p} V_{\text{eff}} \times \vec{p})$, similar to W_{sd} (24). If the approximations $\mathbf{X}_0 \approx \mathbf{I}$ and $\mathbf{R}_{+,0} \approx \mathbf{I}$ are adopted in Eq. (257), $\mathbf{F}_{SO}$ (257) will to the Pauli-like spin-orbit operator $\frac{\alpha^2}{4} \mathbf{W}_{\text{eff},sd}$.[73,74] As noticed by Neese,[75] the exchange-correlation contribution to $\mathbf{F}_{SO}$ (257) is of opposite sign from that of the Gaunt-exchange, the second term in Eq. (253), such that the spin-other-orbit coupling, which otherwise cannot be described by pure DFT, can be estimated by multiplying the exchange-correlation contribution by a factor of -2.

The extension to magnetic fields, so as to obtain field-dependent spin-orbit couplings, is also straightforward. Expressions will be reported elsewhere along with numerical results.

III. CONCLUSION

The spin separation of the X2C Hamiltonians is basically a matrix perturbation theory. It is based on the *a priori* partition of the matrix Dirac Hamiltonian into a sum of spin-free and spin-dependent terms. The former defines the non-expanded sf-X2C Hamiltonian, whereas the latter can be expanded to any desired order in spin (and field), thereby leading to a series of new two-component Hamiltonians. Such a matrix formulation has multiple advantages: (1) No new integrals other than those entering the parent Dirac Hamiltonian arise; (2) no singularities arise; (3) given proper representations, electric and magnetic fields can be treated in the same way; (4) scalar relativity is treated variationally to infinite order; (5) taking sf-X2C as a start, the perturbation expansion in spin is guaranteed to converge very fast. The lowest order terms (e.g., so-DKH3) are already very accurate; (6) the $\mathcal{O}(\alpha^2)$ spin-orbit corrections to sf-X2C electric/magnetic properties are one-to-one correspondent to but more accurate than the Breit-Pauli spin-orbit corrections to nonrelativistic electric/magnetic properties; (7) since only matrix multiplications are required, the implementation of the present results is straightforward. Numerical results for NMR shielding, nuclear spin-spin coupling, g-tensor shift, etc., will be reported in future.

ACKNOWLEDGMENTS

The research of this work was supported by grants from the National Natural Science Foundation of China (NNSFC) (Project Nos. 21033001, 21273011, and 21290192).

APPENDIX A: THE LEAST CHANGE PROPERTY OF $\mathbf{R}_+$

To prove Eq. (69), we first introduce the following Lemma:

Lemma 1. The solution of the maximization problem

$$\max_{\mathbf{A}} \text{tr}(\mathbf{A}^{\dagger} + \mathbf{A}), \quad s.t. \quad \mathbf{A}^{\dagger}\mathbf{A} = \mathbf{G} \tag{A1}$$

is given by $\mathbf{A} = \mathbf{G}^{1/2}$, *provided that* $\mathbf{G}$ *is positive definite and Hermitian*.

Proof. Let $\mathbf{A} = \mathbf{U}\mathbf{G}^{1/2}$ with $\mathbf{U}$ being unitary, then

$$\max_{\mathbf{A}} \text{tr}(\mathbf{A}^{\dagger} + \mathbf{A}) = \max_{\mathbf{U}} \text{tr}[\mathbf{G}^{1/2}(\mathbf{U}^{\dagger} + \mathbf{U})]. \tag{A2}$$

By writing $\mathbf{U} = \mathbf{V}\boldsymbol{\lambda}\mathbf{V}^{\dagger}$ with $\mathbf{V}$ being unitary and $|\lambda_i| = 1$, Eq. (A2) becomes

$$\begin{aligned}
&\max_{\mathbf{U}} \text{tr}[\mathbf{G}^{1/2}(\mathbf{U}^{\dagger} + \mathbf{U})] \\
&= \max_{\mathbf{V},\boldsymbol{\lambda}} \text{tr}[\mathbf{V}^{\dagger}\mathbf{G}^{1/2}\mathbf{V}(\boldsymbol{\lambda} + \boldsymbol{\lambda}^*)] \\
&= \max_{\mathbf{V},\boldsymbol{\lambda}} \sum_p [\mathbf{V}^{\dagger}\mathbf{G}^{1/2}\mathbf{V}]_{pp} 2\Re(\lambda_p) \\
&\le 2 \max_{\mathbf{V}} \sum_p [\mathbf{V}^{\dagger}\mathbf{G}^{1/2}\mathbf{V}]_{pp} = 2\text{tr}(\mathbf{G}^{1/2}),
\end{aligned} \tag{A3}$$

where the equality holds for $\lambda_i = 1$. That is, the solution of Eq. (A2) is $\mathbf{U} = \mathbf{I}$. □

Equation (69) can be cast into a constrained minimization problem,

$$\min \sum_p \left\| \psi_p^{FW} - \psi_p^{L} \right\|^2 = \min_{\mathbf{C}} \sum_p (\mathbf{A}_p - \mathbf{C}_p)^{\dagger} \mathbf{S} (\mathbf{A}_p - \mathbf{C}_p), \tag{A4}$$

$$\mathbf{C} = \mathbf{R}_+^{-1}\mathbf{A}, \quad \mathbf{C}^{\dagger}\mathbf{S}\mathbf{C} = \mathbf{I}, \quad \mathbf{R}_+^{\dagger}\tilde{\mathbf{S}}_+\mathbf{R}_+ = \mathbf{S}, \tag{A5}$$

which can further be reformulated as a minimization problem with argument $\mathbf{R}_+$,

$$\begin{aligned}
&\min_{\mathbf{C}} \sum_p (\mathbf{A}_p - \mathbf{C}_p)^{\dagger} \mathbf{S} (\mathbf{A}_p - \mathbf{C}_p) \\
&= \min_{\mathbf{C}} \text{tr}[(\mathbf{I} - \mathbf{R}_+)^{\dagger} \mathbf{S} (\mathbf{I} - \mathbf{R}_+) \mathbf{C}\mathbf{C}^{\dagger}] \\
&= \min_{\mathbf{C}} \text{tr}[(\mathbf{I} - \mathbf{R}_+)^{\dagger} \mathbf{S} (\mathbf{I} - \mathbf{R}_+) \mathbf{S}^{-1}] \\
&= \min_{\mathbf{C}} \text{tr}[\mathbf{I} - \mathbf{R}_+^{\dagger} - \mathbf{S}\mathbf{R}_+\mathbf{S}^{-1} + \mathbf{R}_+^{\dagger}\mathbf{S}\mathbf{R}_+\mathbf{S}^{-1}] \\
&= \min_{\mathbf{C}} \text{tr}[\mathbf{I} - \mathbf{S}^{-1/2}\mathbf{R}_+^{\dagger}\mathbf{S}^{1/2} - \mathbf{S}^{1/2}\mathbf{R}_+\mathbf{S}^{-1/2} \\
&\quad + \mathbf{S}^{-1/2}\mathbf{R}_+^{\dagger}\mathbf{S}^{1/2}\mathbf{S}^{1/2}\mathbf{R}_+\mathbf{S}^{-1/2}] \\
&= \min_{\mathbf{C}} \text{tr}[\mathbf{I} - \mathbf{r}^{\dagger} - \mathbf{r} + \mathbf{r}^{\dagger}\mathbf{r}],
\end{aligned} \tag{A6}$$

where $\mathbf{r} = \mathbf{S}^{1/2}\mathbf{R}_+\mathbf{S}^{-1/2}$, in terms of which the last equation in Eq. (A5) becomes

$$\mathbf{r}^{\dagger}\mathbf{S}^{-1/2}\tilde{\mathbf{S}}_+\mathbf{S}^{-1/2}\mathbf{r} = \mathbf{I}, \tag{A7}$$

or equivalently,

$$\mathbf{r}\mathbf{r}^\dagger = \mathbf{s}^{-1}, \quad \mathbf{s} = \mathbf{S}^{-1/2}\tilde{\mathbf{S}}_+\mathbf{S}^{-1/2}. \tag{A8}$$

Therefore, Eq. (A6) can be rewritten as

$$\begin{aligned}\min_{\mathbf{C}} \sum_p (\mathbf{A}_p - \mathbf{C}_p)^\dagger \mathbf{S}(\mathbf{A}_p - \mathbf{C}_p) \\ = \mathrm{tr}(\mathbf{I} + \mathbf{s}^{-1}) - \max_{\mathbf{r}} \ \mathrm{tr}(\mathbf{r}^\dagger + \mathbf{r}).\end{aligned} \tag{A9}$$

According to the Lemma, we have

$$\mathbf{r} = \mathbf{s}^{-1/2} \quad \Leftrightarrow \quad \mathbf{R}_+ = \mathbf{S}^{-1/2}(\mathbf{S}^{-1/2}\tilde{\mathbf{S}}_+\mathbf{S}^{-1/2})^{-1/2}\mathbf{S}^{1/2}. \tag{A10}$$

APPENDIX B: SPIN INTEGRATION OF G_{SO}^{XY}

To integrate out the spin, we write $\mathbf{G}_{SO}^{LL}$ (239) as

$$\begin{aligned}\left[\mathbf{G}_{SO}^{LL}\right]_{\mu\nu} &= \mathbb{i} \sum_i \langle \mu\bar{i}|\vec{\sigma}_2|\nu\bar{i}\rangle \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_2|\nu\bar{i}\rangle \\ &\quad + \langle \mu\bar{i}|\vec{\sigma}_1 + \vec{\sigma}_2|\bar{i}\nu\rangle \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle \\ &= \mathbb{i} \sum_i \langle \mu\bar{i}|\vec{\sigma}_1 + \vec{\sigma}_2|\bar{i}\nu\rangle \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle \\ &= \mathbb{i} \sum_i \sum_{\tau_i} (\vec{\sigma}_{\mu\bar{i}} I_{\bar{i}\nu} + I_{\mu\bar{i}}\vec{\sigma}_{\bar{i}\nu}) \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle,\end{aligned} \tag{B1}$$

where the symbol $I_{\mu\nu} = \langle \tau_\mu|\tau_\nu\rangle$ represents the overlap between spin functions α and β. The summation over τ_i is for the spins of the occupied orbitals. For open-shell systems, if i is a singly occupied α orbital, the only nonzero contribution is $\sum_{\tau_i} \vec{\sigma}_{\mu\bar{i}} I_{\bar{i}\nu} = \vec{\sigma}_{\mu\alpha} I_{\alpha\nu}$, which requires $\tau_\nu = \alpha$. If the summation is over both α and β, then

$$\begin{aligned}\sum_{\tau_i} \sigma_{\mu i}^l I_{i\nu} &= \langle \tau_\mu|\sigma^l|\alpha\rangle\langle\alpha|\tau_\nu\rangle + \langle \tau_\mu|\sigma^l|\beta\rangle\langle\beta|\tau_\nu\rangle \\ &= \langle \tau_\mu|\sigma^l|\tau_\nu\rangle = \sigma_{\mu\nu}^l,\end{aligned} \tag{B2}$$

which just depends on the spins of μ and ν. Another property to be used below is the zero trace of the Pauli matrices,

$$\sum_{\tau_i} \sigma_{ii}^l = 0. \tag{B3}$$

Since the spin-averaged density matrix $\mathbf{P}$ amounts to using a fractional occupation 1/2 for the singly occupied orbitals and their vacant parts, Eq. (B1) can be written as

$$\begin{aligned}\left[\mathbf{G}_{SO}^{LL}\right]_{\mu\nu} &= \mathbb{i} \sum_{\bar{i}} 2\vec{\sigma}_{\mu\nu} \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle \\ &= \mathbb{i}\vec{\sigma}_{\mu\nu} \cdot \sum_{\bar{i}} 2\langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle \\ &= \mathbb{i}\varepsilon_{lmn}\sigma_{\mu\nu}^l \sum_{\kappa\lambda} 2\langle \mu(\partial_m\kappa)|(\partial_n\lambda)\nu\rangle P_{\lambda\kappa}^{SS} \\ &= \mathbb{i}\varepsilon_{lmn}\sigma_{\mu\nu}^l \sum_{\kappa\lambda} 2[\mu(\partial_n\lambda)|(\partial_m\kappa)\nu] P_{\lambda\kappa}^{SS} \\ &= \mathbb{i}\sigma_{\mu\nu}^l \left(\varepsilon_{lmn} \sum_{\kappa\lambda} -2[\mu(\partial_m\lambda)|(\partial_n\kappa)\nu] P_{\lambda\kappa}^{SS}\right).\end{aligned} \tag{B4}$$

Similarly, we have

$$\begin{aligned}\left[\mathbf{G}_{SO}^{LS}\right]_{\mu\nu} &= \mathbb{i} \sum_i \left[-\langle \mu i|\vec{\sigma}_2 - \vec{\sigma}_1|\nu\bar{i}\rangle \cdot \langle \mu i|\frac{1}{r_{12}}(\vec{p}_1 \times \vec{p}_2)|\nu\bar{i}\rangle + \langle \mu i|\vec{\sigma}_2 - \vec{\sigma}_1|\bar{i}\nu\rangle \cdot \langle \mu i|\frac{1}{r_{12}}(\vec{p}_1 \times \vec{p}_2)|\bar{i}\nu\rangle \right] \\ &\quad + \mathbb{i} \sum_i \left[-\langle \mu\bar{i}|\vec{\sigma}_2 + \vec{\sigma}_1|\nu i\rangle \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\nu i\rangle - \langle \mu\bar{i}|\vec{\sigma}_2|i\nu\rangle \cdot \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_2|i\nu\rangle \right] \\ &= \mathbb{i}\vec{\sigma}_{\mu\nu} \cdot \sum_i \left[2\langle \mu i|\frac{1}{r_{12}}(\vec{p}_1 \times \vec{p}_2)|\nu\bar{i}\rangle - 2\langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_1|\nu i\rangle - \langle \mu\bar{i}|\vec{p}_2 \times \frac{1}{r_{12}}\vec{p}_2|i\nu\rangle \right] \\ &= \mathbb{i}\varepsilon_{lmn}\sigma_{\mu\nu}^l \sum_i [-2\langle \mu i|(\partial_m\nu)(\partial_n\bar{i})\rangle - 2\langle \mu(\partial_m\bar{i})|(\partial_n\nu)i\rangle - \langle \mu(\partial_m\bar{i})|i(\partial_n\nu)\rangle] \\ &= \mathbb{i}\varepsilon_{lmn}\sigma_{\mu\nu}^l \sum_{\kappa\lambda} [-2\langle \mu\kappa|(\partial_m\nu)(\partial_n\lambda)\rangle P_{\lambda\kappa}^{SL} - 2\langle \mu(\partial_m\kappa)|(\partial_n\nu)\lambda\rangle P_{\lambda\kappa}^{LS} - \langle \mu(\partial_m\kappa)|\lambda(\partial_n\nu)\rangle P_{\lambda\kappa}^{LS}] \\ &= \mathbb{i}\varepsilon_{lmn}\sigma_{\mu\nu}^l \sum_{\kappa\lambda} \{-2[\mu(\partial_m\nu)|\kappa(\partial_n\lambda)] P_{\lambda\kappa}^{SL} - 2[\mu(\partial_n\nu)|(\partial_m\kappa)\lambda] P_{\lambda\kappa}^{LS} - [\mu\lambda|(\partial_m\kappa)(\partial_n\nu)] P_{\lambda\kappa}^{LS}\} \\ &= \mathbb{i}\sigma_{\mu\nu}^l \left(\varepsilon_{lmn} \sum_{\kappa\lambda} \{-2[\mu(\partial_m\nu)|\kappa(\partial_n\lambda)] P_{\lambda\kappa}^{SL} + 2[\mu(\partial_m\nu)|(\partial_n\kappa)\lambda] P_{\lambda\kappa}^{LS} - [\mu\lambda|(\partial_m\kappa)(\partial_n\nu)] P_{\lambda\kappa}^{LS}\} \right),\end{aligned} \tag{B5}$$

$$\begin{aligned}
\left[\mathbf{G}_{SO}^{SL}\right]_{\mu\nu} &= \mathbb{i}\sum_i \left[-\langle\mu\bar{i}|\vec{\sigma}_1 - \vec{\sigma}_2|\nu i\rangle \cdot \langle\mu\bar{i}|(\vec{p}_1\times\vec{p}_2)\frac{1}{r_{12}}|\nu i\rangle + \langle\mu\bar{i}|\vec{\sigma}_1 - \vec{\sigma}_2|i\nu\rangle \cdot \langle\mu\bar{i}|(\vec{p}_1\times\vec{p}_2)\frac{1}{r_{12}}|i\nu\rangle\right] \\
&+ \mathbb{i}\sum_i \left[-\langle\mu i|\vec{\sigma}_1 + \vec{\sigma}_2|\nu\bar{i}\rangle \cdot \langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_2|\nu\bar{i}\rangle - \langle\mu i|\vec{\sigma}_1|\bar{i}\nu\rangle \cdot \langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle\right] \\
&= \mathbb{i}\vec{\sigma}_{\mu\nu}\cdot\sum_i \left[-2\langle\mu\bar{i}|(\vec{p}_1\times\vec{p}_2)\frac{1}{r_{12}}|\nu i\rangle - 2\langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_2|\nu\bar{i}\rangle - \langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_1|\bar{i}\nu\rangle\right] \\
&= \mathbb{i}\varepsilon_{lmn}\sigma^l_{\mu\nu}\sum_{\kappa\lambda}[2\langle(\partial_m\mu)(\partial_n\bar{i})|\nu i\rangle - 2\langle(\partial_m\mu)i|\nu(\partial_n\bar{i})\rangle - \langle(\partial_m\mu)i|(\partial_n\bar{i})\nu\rangle] \\
&= \mathbb{i}\varepsilon_{lmn}\sigma^l_{\mu\nu}\sum_{\kappa\lambda}[2\langle(\partial_m\mu)(\partial_n\kappa)|\nu\lambda\rangle P^{LS}_{\lambda\kappa} - 2\langle(\partial_m\mu)\kappa|\nu(\partial_n\lambda)\rangle P^{SL}_{\lambda\kappa} - \langle(\partial_m\mu)\kappa|(\partial_n\lambda)\nu\rangle P^{SL}_{\lambda\kappa}] \\
&= \mathbb{i}\sigma^l_{\mu\nu}\left(\varepsilon_{lmn}\sum_{\kappa\lambda}\{2[(\partial_m\mu)\nu|(\partial_n\kappa)\lambda]P^{LS}_{\lambda\kappa} - 2[(\partial_m\mu)\nu|\kappa(\partial_n\lambda)]P^{SL}_{\lambda\kappa} - [(\partial_m\mu)(\partial_n\lambda)|\kappa\nu]P^{SL}_{\lambda\kappa}\}\right), \qquad \text{(B6)}
\end{aligned}$$

$$\begin{aligned}
\left[\mathbf{G}_{SO}^{SS}\right]_{\mu\nu} &= \mathbb{i}\sum_i \left[\langle\mu i|\vec{\sigma}_1|\nu i\rangle \cdot \langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_1|\nu i\rangle + \langle\mu i|\vec{\sigma}_1 + \vec{\sigma}_2|i\nu\rangle \cdot \langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_2|i\nu\rangle\right] \\
&= \mathbb{i}\vec{\sigma}_{\mu\nu}\cdot\sum_i \left[2\langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_1|\nu i\rangle + 2\langle\mu i|\vec{p}_1\times\frac{1}{r_{12}}\vec{p}_2|i\nu\rangle\right] \\
&= \mathbb{i}\varepsilon_{lmn}\sigma^l_{\mu\nu}\sum_{\kappa\lambda}[2\langle(\partial_m\mu)\kappa|(\partial_n\nu)\lambda\rangle + 2\langle(\partial_m\mu)\kappa|\lambda(\partial_n\nu)\rangle]P^{LL}_{\lambda\kappa} \\
&= \mathbb{i}\sigma^l_{\mu\nu}\left(\varepsilon_{lmn}\sum_{\kappa\lambda}\{2[(\partial_m\mu)(\partial_n\nu)|\kappa\lambda] + 2[(\partial_m\mu)\lambda|\kappa(\partial_n\nu)]\}P^{LL}_{\lambda\kappa}\right). \qquad \text{(B7)}
\end{aligned}$$

To express the above results in terms of $K^l_{\mu\nu,\kappa\lambda}$ (252), the translation symmetry of the integrals

$$[\partial_m(AB)|CD] + [AB|\partial_m(CD)] = 0, \qquad \text{(B8)}$$

as well as the following relation:

$$J^l_{\mu\nu,\kappa\lambda} = \varepsilon_{lmn}[(\partial_m\mu)(\partial_n\nu)|\kappa\lambda] = -(K^l_{\mu\nu,\kappa\lambda} + K^l_{\mu\nu,\lambda\kappa}) \qquad \text{(B9)}$$

between J^l and K^l can be used. Without going further into details, the simplified results can be reorganized into Eq. (247).

[1] W. Liu, Phys. Rep. **537**, 59 (2014).
[2] W. Liu, Int. J. Quantum Chem. **114**, 983 (2014).
[3] W. Liu and I. Lindgren, J. Chem. Phys. **139**, 014108 (2013).
[4] V. M. Shabaev, I. I. Tupitsyn, and V. A. Yerokhin, Phys. Rev. A **88**, 012513 (2013).
[5] W. Kutzelnigg, "Generalization of Kato's cusp conditions to the relativistic case," in *Aspects of Many-Body Effects in Molecules and Extended Systems*, Lecture Notes in Chemistry Vol. 50, edited by D. Mukherjee (Springer, Berlin, 1989), pp. 353–366.
[6] Z. Li, S. Shao, and W. Liu, J. Chem. Phys. **136**, 144117 (2012).
[7] W. Kutzelnigg, Int. J. Quantum Chem. **108**, 2280 (2008).
[8] S. Ten-no and D. Yamaki, J. Chem. Phys. **137**, 131101 (2012).
[9] W. Liu, Phys. Chem. Chem. Phys. **14**, 35 (2012).
[10] K. Dyall, J. Chem. Phys. **106**, 9618 (1997).
[11] W. Kutzelnigg and W. Liu, J. Chem. Phys. **123**, 241102 (2005).
[12] W. Liu and W. Kutzelnigg, J. Chem. Phys. **126**, 114107 (2007).
[13] W. Liu and D. Peng, J. Chem. Phys. **131**, 031104 (2009).
[14] M. Iliaš and T. Saue, J. Chem. Phys. **126**, 064102 (2007).
[15] W. Liu, Mol. Phys. **108**, 1679 (2010).
[16] T. Saue, ChemPhysChem **12**, 3077 (2011).
[17] D. Peng and M. Reiher, Theor. Chem. Acc. **131**, 1081 (2012).
[18] W. Liu and D. Peng, J. Chem. Phys. **125**, 044102 (2006); **125**, 149901 (2006) (Erratum).
[19] D. Peng, W. Liu, Y. Xiao, and L. Cheng, J. Chem. Phys. **127**, 104106 (2007).
[20] J. Seino and H. Nakai, J. Chem. Phys. **136**, 244102 (2012).
[21] D. Peng and M. Reiher, J. Chem. Phys. **136**, 244108 (2012).
[22] D. Peng, N. Middendorf, F. Weigend, and M. Reiher, J. Chem. Phys. **138**, 184105 (2013).
[23] B. A. Hess, Phys. Rev. A **33**, 3742 (1986).
[24] G. Jansen and B. A. Hess, Phys. Rev. A **39**, 6016 (1989).
[25] Ch. Chang, M. Pelissier, and Ph. Durand, Phys. Scr. **34**, 394 (1986).
[26] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
[27] Q. Sun, W. Liu, Y. Xiao, and L. Cheng, J. Chem. Phys. **131**, 081101 (2009).
[28] Q. Sun, Y. Xiao, and W. Liu, J. Chem. Phys. **137**, 174105 (2012).
[29] L. Cheng, J. Gauss, and J. F. Stanton, J. Chem. Phys. **139**, 054105 (2013).
[30] Z. Li, Y. Xiao, and W. Liu, J. Chem. Phys. **137**, 154114 (2012).
[31] M. Douglas and N. M. Kroll, Ann. Phys. **82**, 89 (1974).
[32] T. Nakajima and K. Hirao, J. Chem. Phys. **113**, 7786 (2000).
[33] C. van Wüllen, J. Chem. Phys. **120**, 7307 (2004).
[34] A. Wolf, M. Reiher, and B. A. Hess, J. Chem. Phys. **117**, 9215 (2002).
[35] M. Reiher and A. Wolf, J. Chem. Phys. **121**, 2037 (2004).
[36] M. Reiher and A. Wolf, J. Chem. Phys. **121**, 10945 (2004).
[37] D. Peng and K. Hirao, J. Chem. Phys. **130**, 044102 (2009).
[38] M. Barysz, A. J. Sadlej, and J. G. Snijders, Int. J. Quantum Chem. **65**, 225 (1997).
[39] M. Barysz and A. J. Sadlej, J. Mol. Struct. (THEOCHEM) **573**, 181 (2001).
[40] M. Barysz and A. J. Sadlej, J. Chem. Phys. **116**, 2696 (2002).
[41] D. Kędziera and M. Barysz, Chem. Phys. Lett. **446**, 176 (2007).
[42] H. J. Aa. Jensen, in Proceedings of the International Conference on Relativistic Effects in Heavy Element Chemistry and Physics, Mülheim/Ruhr, 6–10 April 2005.
[43] M. Iliaš, H. J. Aa. Jensen, V. Kellö, B. O. Roos, and M. Urban, Chem. Phys. Lett. **408**, 210 (2005).

[44]W. Kutzelnigg, in *Relativistic Electronic Structure Theory. Part 1. Fundamentals*, edited by P. Schwerdtfeger (Elsevier, Amsterdam, 2002).
[45]J. D. Goddard, Y. Osamura, and H. F. Schaefer III, *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in ab initio Molecular Electronic Structure Theory* (Oxford University Press, New York, 1994).
[46]W. Kutzelnigg, Int. J. Quantum Chem. **25**, 107 (1984).
[47]K. G. Dyall, J. Chem. Phys. **100**, 2118 (1994).
[48]R. E. Stanton and S. Havriliak, J. Chem. Phys. **81**, 1910 (1984).
[49]Q. Sun, W. Liu, and W. Kutzelnigg, Theor. Chem. Acc. **129**, 423 (2011).
[50]V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. Lett. **93**, 130405 (2004).
[51]G. A. Aucar, T. Saue, L. Visscher, and H. J. Aa. Jensen, J. Chem. Phys. **110**, 6208 (1999).
[52]W. Kutzelnigg, J. Comput. Chem. **20**, 1199 (1999).
[53]S. Komorovsky, M. Repisky, O. L. Malkina, V. G. Malkin, I. Malkin Ondík, and M. Kaupp, J. Chem. Phys. **128**, 104101 (2008).
[54]Y. Xiao, Q. Sun, and W. Liu, Theor. Chem. Acc. **131**, 1080 (2012).
[55]Y. Xiao, D. Peng, and W. Liu, J. Chem. Phys. **126**, 081101 (2007).
[56]W. Kutzelnigg, Phys. Rev. A **67**, 032109 (2003).
[57]Y. Xiao, W. Liu, L. Cheng, and D. Peng, J. Chem. Phys. **126**, 214101 (2007).
[58]L. Visscher and E. van Lenthe, Chem. Phys. Lett. **306**, 357 (1999).
[59]T. Saue, Adv. Quantum Chem. **48**, 383 (2005).
[60]L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).
[61]A. Wolf and M. Reiher, J. Chem. Phys. **124**, 064102 (2006).
[62]K. G. Dyall, Theor. Chem. Acc. **115**, 441 (2006).
[63]K. Dyall, Int. J. Quantum Chem. **78**, 412 (2000).
[64]H. Fukui, T. Baba, and H. Inomata, J. Chem. Phys. **105**, 3175 (1996).
[65]J. Vaara, P. Manninen, and P. Lantto, in *Calculation of NMR and EPR Parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley-VCH, Weinheim, 2004), p. 209.
[66]K. Dyall and K. Fægri, Jr., *Introduction to Relativistic Quantum Chemistry* (Oxford University Press, 2007).
[67]L. Cheng and J. Gauss, J. Chem. Phys. **135**, 084114 (2011).
[68]Z. Li, B. Suo, Y. Zhang, Y. Xiao, and W. Liu, Mol. Phys. **111**, 3741 (2013).
[69]P. Tamukong, M. Hoffmann, Z. Li, and W. Liu, J. Phys. Chem. **118**, 1489 (2014).
[70]B. A. Hess, C. M. Marian, and S. D. Peyerimhoff, in *Advanced Series in Physical Chemistry: Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), p. 168.
[71]B. A. Hess, C. M. Marian, U. Wahlgren, and O. Groppen, Chem. Phys. Lett. **251**, 365 (1996).
[72]B. Schimmelpfennig, *Atomic Spin-Orbit Mean-Field Integral Program* (University of Stockholm, Sweden, 1996).
[73]G. Schreckenbach and T. Ziegler, J. Phys. Chem. A **101**, 3388 (1997).
[74]M. R. Pederson and S. N. Khanna, Phys. Rev. B **60**, 9566 (1999).
[75]F. Neese, J. Chem. Phys. **122**, 034107 (2005).