Perturbation Theory Treatment of Spin–Orbit Coupling, Part I: Double Perturbation Theory Based on a Single-Reference Initial Approximation

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$$\begin{aligned}\hat{H}|\psi_I\rangle &= \left[\hat{H}^{(0,0)} + \lambda\hat{H}^{(1,0)} + \mu\hat{H}^{(0,1)}\right]\left[|\psi_I^{(0,0)}\rangle + \lambda|\psi_I^{(1,0)}\rangle + \mu|\psi_I^{(0,1)}\rangle + \lambda^2|\psi_I^{(2,0)}\rangle + \mu^2|\psi_I^{(0,2)}\rangle + \lambda\mu|\psi_I^{(1,1)}\rangle + \dots\right]\\ &= \left[E_I^{(0,0)} + \lambda E_I^{(1,0)} + \mu E_I^{(0,1)} + \lambda^2 E_I^{(2,0)} + \mu^2 E_I^{(0,2)} + \lambda\mu E_I^{(1,1)} + \dots\right]\\ &\times \left[|\psi_I^{(0,0)}\rangle + \lambda|\psi_I^{(1,0)}\rangle + \mu|\psi_I^{(0,1)}\rangle + \lambda^2|\psi_I^{(2,0)}\rangle + \mu^2|\psi_I^{(0,2)}\rangle + \lambda\mu|\psi_I^{(1,1)}\rangle + \dots\right]\end{aligned}$$

ABSTRACT: We develop a perturbation theory for solving the many-body Dirac equation within a given relativistic effective-core potential approximation. Starting from a scalar-relativistic unrestricted Hartree−Fock (SR UHF) solution, we carry out a double perturbation expansion in terms of spin−orbit coupling (SOC) and the electron fluctuation potential. Computationally convenient energy expressions are derived through fourth order in SOC, second order in the electron fluctuation potential, and a total of third order in the coupling between the two. Illustrative calculations on the halogen series of neutral and singly positive diatomic molecules show that the perturbation expansion is well-converged by taking into account only the leading (nonvanishing) term at each order of the electron fluctuation potential. Our perturbation theory approach provides a computationally attractive alternative to a two-component self-consistent field treatment of SOC. In addition, it includes coupling with the fluctuation potential through third order and can be extended (in principle) to multireference calculations, when necessary for both closed- and open-shell cases, using quasi-degenerate perturbation theory.

I. INTRODUCTION

The treatment of relativistic effects in solids and molecular systems is usually carried out, nowadays, starting from a self-consistent field (SCF) treatment. This can be achieved using two- or four-component representations of the Dirac equation. Some of the most popular two-component variational approaches include the zeroth (and higher)-order regular approximations (ZORAs),[1−5] the Douglas−Kroll−Hess family of methods,[6−17] and methods based on the eXact-2-component (X2C) approach.[18−28] Four-component variational treatments are also in use both for molecules[29,30] and solids.[31]

The computational bottleneck in performing variational relativistic calculations is the need to explicitly diagonalize the secular equations in a large two- or four-component spinor basis (2c-SCF or 4c-SCF). "Diagonalization-free" methods have also been discussed, but they usually necessitate a small number of diagonalizations.[32−34] Diagonalization cost can be greatly reduced by exploitation of the double-group symmetry if the corresponding irreducible representations (IRREPs) can be built. While algorithms exist for constructing the IRREPs of the double group, they are generally limited to the treatment of states that preserve time-reversal symmetry (the so-called Kramer's restricted, KR, variant of the theory) but could also be extended to Kramer's unrestricted theory.[29,35−37] KR theory is best suited to treat closed-shell electronic configurations although, even in this context, the symmetries are usually not exploited for diagonalization due, in part, to a lack of efficient algebraic routines. As for open-shell systems, a single-reference 2c-SCF or 4c-SCF is insufficient for treating those cases with a strong multireference character. Attempts for a multireference generalization of such self-consistent treatments lead to approaches that are either prohibitively expensive or lack the property of size extensivity.[30,38−45] Both cases represent important obstacles for the application of multireference approaches to extended systems.

Perturbation theory represents an alternative to the SCF treatment of relativistic effects. Some spin−orbit configuration-interaction (CI) algorithms include a part of the spin−orbit coupling (SOC) effects both in the CI diagonalization and by a perturbation theory treatment. As a matter of fact, the CIPSO algorithm of Teichteil, Pelissier, and Spiegelmann[46] is a part of a class of algorithms sometimes referred to as CI^{LS} + SO, in which SOC is partly included through perturbation theory in a target space determined from the correlated scalar-relativistic (SR) wave function and its quasi-degenerate complement. Double group CI methods are somewhat similar in spirit, with one important difference being that the diagonalization of the full Hamiltonian is achieved in a target space that may be enlarged by configurations, which are selected by a SOC criterion.[47,48]

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Some success in the perturbation theory treatment of relativistic effects has been achieved for methods based on the two-component Pauli or Breit−Pauli equations.[49−58] A possibly more accurate alternative, however, is to directly solve a suitable approximation for the four-component Dirac equation by a perturbation expansion, following the direct perturbation theory (DPT) developed independently by Rutkowski[59−61] and by Kutzelnigg and co-workers.[62] Most total energy DPT calculations reported thus far involve the perturbation theory treatment of both SR (generally more important for the total energy) and SOC effects. DPT has been applied in the context of density functional theory (DFT) calculations[63] and Hartree−Fock calculations[64−66] and with coupled-cluster wave functions.[67] The extension of DPT to open-shell systems by means of quasi-degenerate perturbation theory (QDPT) has also been discussed.[68−72] Coincidentally, QDPT also allows for some otherwise nondynamical electron correlation to be included in a size-extensive way.[73−76]

An alternative to the traditional two- or four-component representations of the Dirac equation is the use of relativistic effective-core potentials (RECPs).[77−80] In fact, the RECP approximation is probably the most popular approach to treat relativistic effects (albeit, only at the SR level) and is implemented in most first-principles programs.[77,81−97] The SR RECP approach represents a very convenient means to treat relativistic effects because it is no more expensive than a one-component nonrelativistic (NR) calculation. However, SOC effects are not included. If they were, the RECP approach could lead to a computational method that is more accurate than the costlier four-component Dirac−Coulomb approach.[77,98] The main drawback of the RECP methodology is the use of the frozen-core approximation, which can be inappropriate for calculating properties that directly involve core orbitals (e.g., nuclear magnetic resonance chemical shifts, Mössbauer isomer shifts, and X-ray spectroscopies).[77]

Given the widespread use of the SR RECP approach, it is desirable to develop a means of including SOC effects perturbatively. We intend to provide the necessary theory for such treatments in a series of papers. The first paper of this series (part I), presented here, provides an appropriate (noniterative) double perturbation theory for solving the many-body Dirac equation in a given RECP approximation, starting from the corresponding SR single-reference unrestricted Hartree−Fock (UHF) solution. Part II will present an iterative single-reference approach based on the coupled-perturbed Hartree−Fock/Kohn−Sham (CPHF/CPKS) spin−current density functional perturbation theory formalism.[99] Further additions to the series will consider multireference generalizations of the theory, based on QDPT, as well as the treatment of periodic systems. This series complements work by some of the present authors to provide a program for two-component spin−current DFT calculations on periodic systems within the CRYSTAL code.[100−105]

In this paper, we present a formalism for solving the many-body Dirac equation starting from the SR UHF solution. Our formalism is based on a double perturbation treatment of SOC and the electron fluctuation potential. Computational results are provided for the halogen series of diatomic molecules (F_2, Cl_2, Br_2, I_2, and At_2). Although the formalism could be used to calculate the density matrix and the related properties, as well as orbital energy levels, we limit our considerations in this first paper to the convergence of the perturbation series for the energy. The illustrative calculations show that the perturbation series in SOC, both zeroth order and first order in the electron fluctuation potential, converge rapidly to the expected values. Thus, our treatment provides a convenient starting point for the extension to include, for example, ordinary Møller−Plesset second-order correlation energy (second order in the electron fluctuation potential and zeroth order in SOC) and higher-order coupling between SOC and the electron fluctuation potential. Detailed formulas are provided through total order three for this purpose. Moreover, a brief discussion is included regarding cases where the application of QDPT may become necessary.

II. FORMALISM

II.I. Statement of the Problem. Our treatment is formulated within the RECP approximation. Thus, the many-electron problem is partitioned into one involving only the core electrons and one describing valence−valence and core−valence interactions. We assume that the core electron problem has already been solved within a sufficiently accurate approximation to the many-electron four-component Dirac equation (e.g., Dirac−Coulomb, Dirac−Coulomb−Breit, or generally any other variant, possibly including higher-order corrections from quantum electrodynamics) and that the parameters of the RECPs have been extracted. The reader is referred to excellent reviews of the RECP method for more explicit details on the procedure for extraction of the RECP operators.[77,78,97,106−109]

Our task is to solve the remaining problem involving the valence−valence and core−valence interactions. The starting point is the many-electron time-independent Dirac equation in the RECP approximation

$$\hat{H}|\psi_I\rangle = E_I|\psi_I\rangle \tag{1}$$

where E_I are the energies of the stationary states $|\psi_I\rangle$ labeled by the index I. Our approach could, in principle, be used to treat excited states, but here we limit our discussion to approximating the ground-state $|\psi\rangle$. In general, eq 1 can be written in terms of a two- or a four-component representation. Although some RECP calculations have been performed within an explicitly relativistic four-component representation of the valence Hamiltonian $\hat{H}$, these calculations have not found appreciable differences with respect to a computationally less demanding two-component ansatz.[77,110−114] We, therefore, write $\hat{H}$ in a two-component basis wherein all explicitly relativistic effects are accounted for by the SR $\hat{U}^{\mathrm{AREP}}$ (the averaged relativistic effective potential) plus the spin-dependent parts $\hat{h}_{\mathrm{SO}}$ of the effective-core potential

$$\hat{H} = \mathcal{I}_2 \odot [\hat{H}_{\mathrm{NR}} + \hat{U}^{\mathrm{AREP}}] + \hat{h}_{\mathrm{SO}} \tag{2}$$

Here, $\mathcal{I}_2$ is the 2×2 identity matrix and $\hat{H}_{\mathrm{NR}}$ is the many-electron NR valence Schrödinger Hamiltonian. The operator $\odot$ ensures that the direct product $\otimes$ with $\mathcal{I}_2$ is taken once for the one-electron part and twice for the two-electron part of the Hamiltonian. All spin-dependent relativistic effects (SOC, spin-other-orbit coupling, spin−spin coupling, etc.) are included in $\hat{h}_{\mathrm{SO}}$ (sometimes called the spin−orbit relativistic effective potential, SOREP). The two-electron scalar and spin-dependent relativistic effects are included in the core−valence interactions but are assumed to be negligible for the valence−valence interactions. $\hat{U}^{\mathrm{AREP}}$ and $\hat{h}_{\mathrm{SO}}$ can, in turn, be written as a sum of one-electron operators (labeled by the index i)

$$\hat{U}^{\mathrm{AREP}} = \sum_i^{\mathrm{val}} \hat{U}_i^{\mathrm{AREP}} \tag{3a}$$

$$\hat{h}_{\mathrm{SO}} = \sum_i^{\mathrm{val}} \hat{h}_{\mathrm{SO},i} \tag{3b}$$

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where val indicates that the index i runs over the set of valence electron coordinates including both space and spin. The operators $\hat{h}_{\mathrm{SO},i}$ may be expressed in terms of the components of the one-electron spin $\hat{S}_i$ and angular momentum $\hat{L}_i$ operators as follows[100]

$$\hat{h}_{\mathrm{SO},i} = \hat{\zeta}_i\left(\hat{L}_{z,i}\hat{S}_{z,i} + \frac{1}{2}\hat{L}_{+,i}\hat{S}_{-,i} + \frac{1}{2}\hat{L}_{-,i}\hat{S}_{+,i}\right) \tag{4}$$

where $\hat{\zeta}_i$ is a linear combination of radial and angular operators that depend on the parameters obtained from the RECP fitting, $\hat{S}_{z,i}$ and $\hat{L}_{z,i}$ are the z-components of the one-electron spin and angular momentum operators (the product $\hat{L}_{z,i}\,\hat{S}_{z,i}$ is purely imaginary), respectively, and $\hat{S}_{\pm,i}$ and $\hat{L}_{\pm,i}$ are the one-electron spin and angular momentum ladder operators, respectively.

Our choice for $\hat{H}^{(0,0)}$ is the analog of the usual Møller−Plesset sum of one-electron Fock operators[115,116]

$$\hat{H}^{(0,0)} = \sum_i^{\mathrm{val}} \hat{F}_i = \sum_i^{\mathrm{val}} [\hat{h}_i + \hat{U}_i^{\mathrm{AREP}} + (\hat{C}_i - \hat{K}_i)] \tag{5}$$

where $\hat{h}_i$ contains the NR electronic kinetic energy and electron−nuclear attraction terms, while $\hat{C}_i$ and $\hat{K}_i$ are the usual Coulomb and exchange operators, respectively. Practically, $\hat{F}_i$ is determined by the self-consistent solution of the one-component SR unrestricted Hartree−Fock−Roothaan equations

$$\hat{F}_m|m\rangle = \epsilon_m|m\rangle \tag{6}$$

where $|m\rangle$ are singly occupied orbitals. In eq 6, the spin index is implicit; when desirable to make it explicit, we write

$$\hat{F}_m^{\sigma}|m,\sigma\rangle = \epsilon_m^{\sigma}|m,\sigma\rangle \tag{7}$$

where $\sigma = \alpha$ or β. We note that $|m,\sigma\rangle$ can be expanded in the atomic orbital (AO) $|\nu\rangle$ basis (here a set of atom-centered Gaussian functions) as follows

$$|m,\sigma\rangle = \sum_{\nu} c_{\nu m}^{\sigma}|\nu\rangle \otimes |\sigma\rangle \tag{8}$$

With the above definition of $\hat{H}^{(0,0)}$, the first-order Hamiltonians associated with SOC and the electron fluctuation potential, i.e., $\hat{H}^{(1,0)}$ and $\hat{H}^{(0,1)}$, become

$$\hat{H}^{(1,0)} = \hat{h}_{\mathrm{SO}} \tag{9a}$$

$$\hat{H}^{(0,1)} = \frac{1}{2}\sum_{j\neq i}^{\mathrm{val}}\frac{1}{r_{ij}} - \sum_i^{\mathrm{val}}(\hat{C}_i - \hat{K}_i)$$

$$= \hat{V}_{\mathrm{ee}} - (\hat{C} - \hat{K}) \tag{9b}$$

We solve eq 1 with $\hat{H}$ given by the sum of Hamiltonians in eqs 5, 9a, and 9b by expanding the valence energy and wave function, including core−valence interactions, in a conventional Dalgarno double perturbation series[117]

$$\begin{aligned}\hat{H}|\psi_I\rangle &= [\hat{H}^{(0,0)} + \lambda\hat{H}^{(1,0)} + \mu\hat{H}^{(0,1)}][|\psi_I^{(0,0)}\rangle \\ &\quad + \lambda|\psi_I^{(1,0)}\rangle + \mu|\psi_I^{(0,1)}\rangle + \lambda^2|\psi_I^{(2,0)}\rangle \\ &\quad + \mu^2|\psi_I^{(0,2)}\rangle + \lambda\mu|\psi_I^{(1,1)}\rangle + \cdots] \\ &= [E_I^{(0,0)} + \lambda E_I^{(1,0)} + \mu E_I^{(0,1)} + \lambda^2 E_I^{(2,0)} \\ &\quad + \mu^2 E_I^{(0,2)} + \lambda\mu E_I^{(1,1)} + \cdots] \\ &\quad \times[|\psi_I^{(0,0)}\rangle + \lambda|\psi_I^{(1,0)}\rangle + \mu|\psi_I^{(0,1)}\rangle + \lambda^2|\psi_I^{(2,0)}\rangle \\ &\quad + \mu^2|\psi_I^{(0,2)}\rangle + \lambda\mu|\psi_I^{(1,1)}\rangle + \cdots]\end{aligned} \tag{10}$$

The energy terms of zeroth order in SOC and arbitrary order $M = 0, 1, 2, \ldots$ in the electron fluctuation potential, $E^{(0,M)}$, are elements of the well-known SR MP series. The energy terms of arbitrary order $N = 0, 1, 2, \ldots$ in SOC and zeroth order in the electron fluctuation potential, $E^{(N,0)}$, represent pure SOC contributions to the energy. All other terms couple SOC with the electron fluctuation potential. A key issue, of course, is the convergence properties of the various energy subseries.

II.II. Energy Contributions. In accordance with the standard MP theory, the sum of the terms $E^{(0,0)}$ and $E^{(0,1)}$ give us the SR UHF energy

$$E_{\mathrm{UHF}} = E^{(0,0)} + E^{(0,1)} \tag{11a}$$

with

$$E^{(0,0)} = \langle\psi^{(0,0)}|\hat{H}^{(0,0)}|\psi^{(0,0)}\rangle = \sum_m^{\mathrm{occ}}\epsilon_m \tag{11b}$$

where occ denotes the set of occupied SR UHF valence orbitals; similarly, virt later denotes the set of virtual (or unoccupied) orbitals. For the MP1 term, we have

$$\begin{aligned}E^{(0,1)} &= \langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle \\ &= -\frac{1}{2}\sum_{mn}^{\mathrm{occ}}[(mm|nn) - (mn|nm)]\end{aligned} \tag{11c}$$

wherein the bielectronic integrals are written in Mulliken notation.

II.II.I. Terms of Order Zero in the Electron Fluctuation Potential. Expressions for the contributions $E^{(N,0)}$ $(N = 1-4)$ in terms of the many-electron wave functions $|\psi_I^{(0,0)}\rangle$ of eq 10 are readily obtained from ordinary nondegenerate (see further below) Rayleigh−Schrödinger perturbation theory (RSPT). In first order

$$E^{(1,0)} = \langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle \tag{12}$$

and in second order

$$E^{(2,0)} = \langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}\hat{R}^{(0,0)}\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle \tag{13}$$

where the nondegenerate RSPT resolvant operator $\hat{R}^{(0,0)}$ is written as

$$\hat{R}^{(0,0)} = \sum_I{}' |\psi_I^{(0,0)}\rangle(E^{(0,0)} - E_I^{(0,0)})^{-1}\langle\psi_I^{(0,0)}| \tag{14}$$

where the sum is over all configurations spanned by the SR UHF valence orbitals of the (0, 0) problem and the prime over the summation indicates that the ground state is excluded. The occurrence of the energy denominators $E^{(0,0)} - E_I^{(0,0)}$ in eq 13, and in higher-order terms of the series, implies that the perturbation theory expansion may not converge if degenerate and/or quasi-degenerate configurations interact with the ground state, as is the case, for example, in many open-shell systems. An adequate treatment of such cases would require, in general, a QDPT approach, which is postponed until later papers of this series. The corresponding third- and fourth-order expressions can be found in Appendix A, along with a demonstration of how these expressions can be reduced to a computationally manageable form in terms of one-electron SR UHF orbitals.

Here, we simply quote the final orbital formulas from Appendix A. In first order

$$E^{(1,0)} = \sum_m^{\mathrm{occ}}\langle m|\hat{h}_{\mathrm{SO}}|m\rangle = 0 \tag{15}$$

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An explanation for why $E^{(1,0)}$ vanishes is provided in the discussion associated with eq A1 of Appendix A. To write the energy contributions of higher order, it is convenient to introduce the following complex-Hermitian matrix

$$G_{mp}^{\sigma\sigma'(1,0)} = \langle m,\ \sigma|\hat{h}_{SO}|p,\ \sigma'\rangle \tag{16a}$$

and the following complex-anti-Hermitian matrix

$$U_{mp}^{\sigma\sigma'(1,0)} = \frac{G_{mp}^{\sigma\sigma'(1,0)}}{\epsilon_p^{\sigma'} - \epsilon_m^{\sigma}} \tag{16b}$$

In terms of these matrices, we obtain, in second order

$$E^{(2,0)} = \sum_{\sigma,\sigma'}\sum_{m}^{occ}\sum_{p}^{virt} G_{mp}^{\sigma\sigma'(1,0)}U_{pm}^{\sigma'\sigma(1,0)} \tag{17}$$

in third order

$$E^{(3,0)} = \sum_{\sigma,\sigma',\sigma''}\Bigg[\sum_{mn}^{occ}\sum_{p}^{virt} U_{mp}^{\sigma\sigma'(1,0)}U_{pn}^{\sigma'\sigma''(1,0)}G_{nm}^{\sigma''\sigma(1,0)} - \sum_{m}^{occ}\sum_{pq}^{virt} U_{mp}^{\sigma\sigma'(1,0)}G_{pq}^{\sigma'\sigma''(1,0)}U_{qm}^{\sigma''\sigma(1,0)}\Bigg] \tag{18}$$

and in fourth order

$$E^{(4,0)} = \sum_{\sigma,\sigma',\sigma'',\sigma'''}\Bigg[2\sum_{mn}^{occ}\sum_{pq}^{virt}\frac{U_{mp}^{\sigma\sigma'(1,0)}G_{pq}^{\sigma'\sigma''(1,0)}G_{nm}^{\sigma'''\sigma'(1,0)}U_{qn}^{\sigma''\sigma'''(1,0)}}{\epsilon_m^{\sigma} - \epsilon_q^{\sigma''}} - \sum_{m}^{occ}\sum_{pqr}^{virt}\frac{U_{mp}^{\sigma\sigma'(1,0)}G_{pq}^{\sigma'\sigma''(1,0)}G_{qr}^{\sigma''\sigma'''(1,0)}U_{rm}^{\sigma'''\sigma(1,0)}}{\epsilon_m^{\sigma} - \epsilon_q^{\sigma''}} - \sum_{mno}^{occ}\sum_{p}^{virt}\frac{U_{mp}^{\sigma\sigma'(1,0)}G_{nm}^{\sigma''\sigma(1,0)}G_{on}^{\sigma'''\sigma''(1,0)}U_{po}^{\sigma'\sigma'''(1,0)}}{\epsilon_n^{\sigma''} - \epsilon_p^{\sigma'}} + \sum_{mn}^{occ}\sum_{pq}^{virt}\frac{U_{mp}^{\sigma\sigma'(1,0)}G_{pn}^{\sigma'\sigma''(1,0)}U_{qm}^{\sigma'''\sigma(1,0)}G_{nq}^{\sigma''\sigma'''(1,0)}}{\epsilon_n^{\sigma''} - \epsilon_p^{\sigma'}}\Bigg] \tag{19}$$

The energy denominators in eqs 17−19 make explicit the possibility, discussed above, that near degeneracies due, for example, to a small highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gap may occasion the need for a QDPT treatment.

II.II.II. Terms of Order One in the Electron Fluctuation Potential. We now proceed to the energy contributions $E^{(N,1)}$ through third order in SOC. Detailed derivations can be found in Appendix B. For the case $N = 1$

$$E^{(1,1)} = 2\mathcal{R}[\langle\psi^{(0,0)}|\hat{h}_{SO}|\psi^{(0,1)}\rangle] = 0 \tag{20}$$

where $\mathcal{R}$ denotes the real part of the argument. Here, $E^{(1,1)}$ vanishes since, according to Brillouin's theorem, $|\psi^{(0,1)}\rangle$ consists only of doubly excited configurations, whereas $\hat{h}_{SO}$, given by eq 3a, consists only of monoelectronic operators. For $N = 2$

$$E^{(2,1)} = 2\mathcal{R}[\langle\psi^{(0,0)}|\hat{H}^{(0,1)}\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle] + \langle\psi^{(0,0)}|\hat{h}_{SO}\hat{R}^{(0,0)}(\hat{H}^{(0,1)} - E^{(0,1)})\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle \tag{21}$$

and for $N = 3$

$$E^{(3,1)} = 2\mathcal{R}[\langle\psi^{(0,0)}|\hat{h}_{SO}\hat{R}^{(0,0)}(H^{(0,1)} - E^{(0,1)}) \times\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle] + 2\mathcal{R}[\langle\psi^{(0,0)}|\hat{H}^{(0,1)}\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)} \times\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle] \tag{22}$$

The terms $E^{(2,1)}$ and $E^{(3,1)}$ can be conveniently re-expressed in the AO basis (see the discussion associated with eqs B10−BB22b of Appendix B). For $E^{(2,1)}$, we obtain

$$E^{(2,1)} = \sum_{\sigma,\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}[P_{\omega\nu}^{\sigma\sigma(1,0)}]^*\sum_{\tau\gamma}M_{\gamma\tau}^{\sigma'\sigma'(1,0)}(\omega\nu|\tau\gamma)\Bigg] - \sum_{\sigma,\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}[P_{\omega\nu}^{\sigma\sigma'(1,0)}]^*\sum_{\tau\gamma}M_{\gamma\tau}^{\sigma\sigma'(1,0)}(\omega\gamma|\tau\nu)\Bigg] \tag{23}$$

where $P_{\omega\nu}^{\sigma\sigma'(1,0)}$ are elements of the complex-Hermitian first-order perturbed-density matrix and $M_{\gamma\tau}^{\sigma\sigma'(1,0)}$ are elements of a complex non-Hermitian matrix (for definition, see eqs B15 and B17 in Appendix B). Both these matrices are defined in terms of the orbital coefficients $c_{\nu m}^{\sigma}$ of eq 8 and the matrix of first-order orbital rotations $\mathbf{U}^{\sigma\sigma'(1,0)}$, whose elements are defined in eq 16b.

For $E^{(3,1)}$, we obtain

$$E^{(3,1)} = 2\sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}[P_{\omega\nu}^{\sigma\sigma(1,0)}]^*\sum_{\tau\gamma}M_{\gamma\tau}^{\sigma'\sigma'(2,0)}(\omega\nu|\tau\gamma)\Bigg] - 2\sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}[P_{\omega\nu}^{\sigma\sigma'(1,0)}]^*\sum_{\tau\gamma}M_{\gamma\tau}^{\sigma\sigma'(2,0)}(\omega\gamma|\tau\nu)\Bigg] + 4\sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}M_{\nu\omega}^{\sigma\sigma(1,0)}\sum_{\tau\gamma}[O_{\gamma\tau}^{\sigma'\sigma'(2,0)} - V_{\gamma\tau}^{\sigma'\sigma'(2,0)}](\omega\nu|\tau\gamma)\Bigg] - 4\sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}M_{\nu\omega}^{\sigma'\sigma(1,0)}\sum_{\tau\gamma}[O_{\gamma\tau}^{\sigma\sigma'(2,0)} - V_{\gamma\tau}^{\sigma\sigma'(2,0)}](\omega\gamma|\tau\nu)\Bigg] \tag{24}$$

where $M_{\gamma\tau}^{\sigma\sigma'(2,0)}$, $O_{\gamma\tau}^{\sigma\sigma'(2,0)}$, and $V_{\gamma\tau}^{\sigma\sigma'(2,0)}$ are elements of non-Hermitian matrices that are defined in terms of the occupied−virtual, occupied−occupied, and virtual−virtual blocks, respectively, of the second-order matrix of orbital rotations $\mathbf{U}^{\sigma\sigma'(2,0)}$ (see eqs BB21a−BB22b of Appendix B).

II.II.III. Terms of Order Two in the Electron Fluctuation Potential. Finally, we consider terms that are second order in the fluctuation potential and through first order in SOC. Although these terms are not calculated here, it is of interest to establish that they can both be obtained without a significant increase in computational effort.

For $E^{(0,2)}$, we have the usual sum-over-state expression obtained, as before, from ordinary nondegenerate RSPT

$$E^{(0,2)} = \langle\psi^{(0,0)}|\hat{H}^{(0,1)}\hat{R}^{(0,0)}\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle \tag{25}$$

On the other hand, for the $E^{(1,2)}$ term, a derivation is provided in the discussion associated with eq C1 of Appendix C, which yields

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$$E^{(1,2)} = 2\mathcal{R}[\langle\psi^{(0,0)}|\hat{h}_{SO}\hat{R}^{(0,0)} \times(\hat{H}^{(0,1)} - E^{(0,1)})\hat{R}^{(0,0)}\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle] + \langle\psi^{(0,0)}|\hat{H}^{(0,1)}\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)}\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle \quad (26)$$

Writing the configurations $|\psi_I^{(0,0)}\rangle$ in eq 25 as doubly excited Slater determinants $|\psi_{mn}^{pq}\rangle$ and evaluating matrix elements using the Slater−Condon rules, we obtain the well-known SR MP2 energy formula[115]

$$E^{(0,2)} = \frac{1}{4}\sum_{mn}^{occ}\sum_{pq}^{virt}\frac{|(mp|nq) - (mq|np)|^2}{\epsilon_m + \epsilon_n - \epsilon_q - \epsilon_p} \quad (27)$$

The corresponding expression for $E^{(1,2)}$ in eq 26 is derived in the discussion associated with eqs C2−C6 of Appendix C. To write our working expression for $E^{(1,2)}$ in a compact way, it is expedient to introduce the following four-index tensors

$$A_{m,n,p,q} = \frac{[(mp|nq) - (mq|np)]}{(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q)} \quad (28a)$$

$$B_{m,n,q,r} = \sum_{p}^{virt} A_{m,n,p,q}\langle p|\hat{h}_{SO}|r\rangle \quad (28b)$$

$$D_{n,o,p,q} = \sum_{m}^{occ} A_{m,n,p,q}\langle o|\hat{h}_{SO}|m\rangle \quad (28c)$$

$$I_{n,p,q,r} = -\sum_{m}^{occ} A_{m,n,p,q}U_{mr}^{(1,0)} \quad (28d)$$

$$J_{m,n,o,q} = -\sum_{p}^{virt} A_{m,n,p,q}U_{op}^{(1,0)} \quad (28e)$$

$$K_{n,p,q,r} = (rp|nq) - (rq|np) \quad (28f)$$

and

$$L_{m,n,o,q} = (no|mq) - (nq|mo) \quad (28g)$$

With these tensors, we obtain

$$E^{(1,2)} = \sum_{n}^{occ}\sum_{pqr}^{virt}\mathcal{R}[I_{n,p,q,r}\,K_{n,p,q,r}] + \sum_{mno}^{occ}\sum_{q}^{virt}\mathcal{R}[J_{m,n,o,q}\,L_{m,n,o,q}] + \frac{1}{2}\sum_{mn}^{occ}\sum_{qr}^{virt}B_{m,n,q,r}A_{m,n,r,q} - \frac{1}{2}\sum_{no}^{occ}\sum_{pq}^{virt}D_{n,o,p,q}A_{o,n,p,q} \quad (29)$$

II.III. Computational Cost for Calculation of $E^{(1,2)}$. From eq 27, a determination of $E^{(0,2)}$ involves calculating $N_{occ}^2 \times N_{virt}^2$ four-index bielectronic integrals, where there are N_{occ} occupied orbitals and N_{virt} virtual orbitals. If the bielectronic integrals are calculated and stored in an AO basis, it is well-known that they can be transformed to molecular orbitals (MOs) one index at a time for a cost approximately proportional to $N_{occ}N_{AO}^4$. The integrals in the molecular orbital basis (including those involving three virtual orbital indices) can also be used to calculate $E^{(1,2)}$ from eq 29 for a modest additional cost, as shown below.

The tensor **A** of eq 28a is constructed, using the bielectronic integrals in the MO basis, for a cost that is proportional to $N_{occ}^2 \times N_{virt}^2$. Then, to include SOC in the third line of eq 29, for example, we need to calculate the tensor **B** of eq 28b, which involves a computational cost proportional to $N_{occ}^2 \times N_{virt}^3$. Similarly, for the fourth line of eq 29, we require the tensor **D** of eq 28c, which may be obtained at a lesser cost proportional to $N_{occ}^3 \times N_{virt}^2$. Then, the above tensors can be used to calculate both energy contributions as

$$\frac{1}{2}\sum_{mn}^{occ}\sum_{qr}^{virt}B_{m,n,q,r}A_{m,n,r,q} \quad (30)$$

for the term in the third line of eq 29 and

$$-\frac{1}{2}\sum_{no}^{occ}\sum_{pq}^{virt}D_{n,o,p,q}A_{o,n,p,q} \quad (31)$$

for the term in the fourth line of eq 29. Once the energy contributions in the third and fourth lines of eq 29 are calculated, we can concentrate on the energy contributions in the first and second lines. At this point, the tensors **B** and **D** can be deallocated. Then, to include the first line of eq 29, we can calculate the tensor **I** of eq 28d, which is an $N_{occ}^2 \times N_{virt}^3$ step. Similarly, for the second line of eq 29, we require the tensor **J** of eq 28e, an $N_{occ}^3 \times N_{virt}^2$ step. At this point, the tensor **A** may be deallocated to free up space for the tensors **K** and **L** of eqs 28f and 28g. Finally, the above tensors can be used to calculate both remaining energy contributions as

$$\sum_{n}^{occ}\sum_{pqr}^{virt}\mathcal{R}[I_{n,p,q,r}\,K_{n,p,q,r}] \quad (32)$$

for the term in the first line of eq 29 and

$$\sum_{mno}^{occ}\sum_{q}^{virt}\mathcal{R}[J_{m,n,o,q}\,L_{m,n,o,q}] \quad (33)$$

for the term in the second line of eq 29. In summary, the total computational cost of calculating both $E^{(0,2)}$ and $E^{(1,2)}$ involves only a modest increase over that of an SR MP2 calculation. As in the case of the latter, the computational bottleneck is the time needed for transforming the bielectronic integrals from the AO to the molecular orbital basis, a cost that is approximately proportional to $N_{occ}N_{AO}^4$.

III. COMPUTATIONAL DETAILS

The zeroth-order SR UHF calculations were carried out with a developer's version of the CRYSTAL17 code.[101] These were performed with the RECPs and associated basis sets from the libraries available in refs 118 and119. The experimental bond lengths of 1.42, 2.00, 2.28, 2.67, and 3.00 Å were used for the molecules F_2, Cl_2, Br_2, and I_2, respectively, whereas for At_2, the bond length was estimated from the trend along the series.[120] All SCF procedures were converged to a total energy difference of less than 1×10^{-12} hartree atomic units (E_h). After the last SCF cycle, the SR UHF eigenvectors and eigenvalues were used to calculate the various perturbation theory energy contributions of section II. These were compared with reference energies determined from our previously existing two-component SCF

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Table I. SOC Perturbation Theory Contributions to the SV Energy (in E_h) Calculated for the Diatomic Molecules of the Halogen Series[a]

	F_2	Cl_2	Br_2	I_2
$E^{(2,0)}$	-4.09×10^{-05}	-1.60×10^{-04}	-3.60×10^{-03}	-2.07×10^{-02}
$E^{(3,0)}$	-6.98×10^{-08}	-2.16×10^{-07}	-2.08×10^{-05}	-7.19×10^{-04}
$E^{(4,0)}$	-3.02×10^{-10}	$+1.59 \times 10^{-09}$	$+1.47 \times 10^{-06}$	-6.10×10^{-05}
$E^{(2,1)}$	-1.19×10^{-05}	-6.08×10^{-05}	-1.57×10^{-03}	-7.91×10^{-03}
$E^{(3,1)}$	-2.82×10^{-08}	-6.38×10^{-08}	$+7.41 \times 10^{-08}$	-2.09×10^{-04}
PT∞	-4.10×10^{-05}	-1.61×10^{-04}	-3.62×10^{-03}	-2.15×10^{-02}
PT∞1	-5.30×10^{-05}	-2.22×10^{-04}	-5.19×10^{-03}	-2.96×10^{-02}
SV	-5.30×10^{-05}	-2.21×10^{-04}	-5.18×10^{-03}	-2.95×10^{-02}
Δ_{21}	$+9.55 \times 10^{-08}$	$+1.98 \times 10^{-07}$	$+5.65 \times 10^{-06}$	$+8.24 \times 10^{-04}$
$\Delta_{\infty 1}$	-2.81×10^{-09}	-2.96×10^{-07}	-1.36×10^{-05}	-1.64×10^{-04}

[a]Our results were obtained with the fully relativistic shape-consistent RECPs and associated basis sets of the Columbus group available at ref 119, with seven electrons included in the valence space. See the text for definition of individual entries.

(2c-SCF) implementation in the CRYSTAL code as described in section IV.

IV. COMPUTATIONAL RESULTS FOR THE HALOGEN SERIES DIATOMIC MOLECULES

We investigated the convergence of the perturbation series by calculating the terms $E^{(N,M)}$ for values up to order four in SOC and order one in the electron fluctuation potential ($N = 0-4$ and $M = 0, 1$). In analogy to eq 11a, we may partition the HF energy obtained after one iteration of the SCF procedure E_{SV} into terms of zeroth and first order in the fluctuation potential (i.e., $M = 0, 1$)

$$E_{SV} = E^{(0)} + E^{(1)} \tag{34a}$$

Expanding both the MP0 $E^{(0)}$ and MP1 $E^{(1)}$ terms of eq 34a in orders of SOC, we obtain a double perturbation series for E_{SV}

$$E_{SV} = E^{(0,0)} + E^{(1,0)} + E^{(2,0)} + E^{(3,0)} + \cdots + E^{(0,1)} + E^{(1,1)} + E^{(2,1)} + E^{(3,1)} + \cdots \tag{34b}$$

Thus, according to eq 34b, a calculation of all terms $E^{(N,M)}$ ($N = 0, 1, 2, 3, 4, \ldots$ and $M = 0, 1$) up to order one in the fluctuation potential corresponds to a perturbation theory expansion of the second-variational (SV) approach to SOC in solid-state physics.[122−124] The reference SV energy E_{SV} is simply calculated using the zeroth-order SR UHF density matrix as a starting guess for performing one iteration of the 2c-SCF.

A comparison of the perturbation theory approach with an SV calculation, performed with our 2c-SCF implementation, also in the CRYSTAL code,[100,101,103−105] is given in Table I for the members F_2, Cl_2, Br_2, and I_2 of the halogen diatomic molecule series. This set of molecules was chosen because of the availability of many sets of RECPs and the large contribution of SOC to their energy. The results in Table I were obtained from large-core shape-consistent RECPs,[125−129] with seven electrons in the valence space for each atom. The pure SOC contribution to the energy is reported for $E^{(2,0)}$, $E^{(3,0)}$, and $E^{(4,0)}$, as well as for the sum $E^{(2,0)} + E^{(3,0)} + E^{(4,0)} + \cdots$ extrapolated to infinite order, using an extrapolation formula from ref 130 (PT∞). The addition of $E^{(2,1)}$ and $E^{(3,1)}$ to PT∞ is denoted in the table as PT∞1. The quantities Δ_{21} and $\Delta_{\infty 1}$ in the last two rows represent the difference between $E^{(2,0)} + E^{(2,1)}$ and SV ($=E_{SV} - E_{UHF}$) and between PT∞ + $E^{(2,1)} + E^{(3,1)}$ and SV, respectively.

It is clear from the first three rows of the table that the individual perturbation theory energy contributions, $E^{(2,0)}$, $E^{(3,0)}$, $E^{(4,0)}$, ..., monotonically decrease (in absolute value), such that the pure SOC perturbation series is rapidly convergent for all systems. Moreover, the reported differences in the last row of the table are very small (about 2−4 orders of magnitude smaller than the energy of the SV approach). We note also that $E^{(3,1)}$ is always much smaller than $E^{(2,1)}$. In fact, a simple calculation through $E^{(2,0)}$ and $E^{(2,1)}$ is sufficient to adequately reproduce the SV energy. Thus, the coupling between SOC and the fluctuation potential is well described using only the leading (nonvanishing) term for order $M = 0, 1$ of the fluctuation potential. We speculate that this is likely to extend to $M = 2$ so that a first-order treatment in SOC would satisfactorily describe the coupling with correlation through MP2.

In Table II, we report similar calculations (again with large-core potentials, including seven electrons in the valence space of each atom), this time using RECPs and associated basis sets generated by the energy-consistent method from ref 118. These RECPs are available for the systems Br_2, I_2, and At_2. We see that the difference reported in the last row of Table II is now 2−3 orders of magnitude smaller than the SV energy for the systems Br_2 and I_2. For the most challenging system, At_2, the difference is -7.24×10^{-04} E_h, which represents an error of 1.4% in approximating the SV energy. The difference Δ_{21} is -9.04×10^{-04} E_h; it represents an error of 1.7%. The energy contributions $E^{(2,0)}$, $E^{(3,0)}$, $E^{(4,0)}$, ..., as well as $E^{(2,1)}$, $E^{(3,1)}$, ..., again monotonically (and rapidly) decrease. Thus, the perturbation series through order 2 in SOC and order 1 in the electron fluctuation potential again provides an excellent approximation for the SV energy.

Table III gives results for the systems Br_2, I_2, and At_2, now using a smaller core shape-consistent potential, with 17 electrons included in the valence space of each atom. Again, the differences between perturbation theory and the SV approach are 2−3 orders of magnitude smaller than the SV energy for Br_2 and I_2. Once more, At_2 shows a larger discrepancy (about 3.8% for $\Delta_{\infty 1}$ or 1.8% for Δ_{21}). Thus, the small-core RECPs behave in the same way as the large-core potentials.

Table IV provides results for systems that are identical to those reported in Table I, except that now one electron has been removed from the highest occupied molecular orbital, such that they represent open-shell electronic configurations. The reported energy differences between perturbation theory and the SV value remain small as in the case of the closed-shell configurations in Table I. In the worst case (I_2^+), the perturbation theory approach overestimates the SV energy by 1.7% (for $\Delta_{\infty 1}$). This difference is reduced to 0.1% for Δ_{21}. As for the closed-shell systems, the perturbation series $E^{(2,0)}$, $E^{(3,0)}$, $E^{(4,0)}$, ... and $E^{(2,1)}$, $E^{(3,1)}$, ... converge

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Table II. Same as Table I but Using Instead the Energy-Consistent RECPs and Associated Basis Sets of the Stuttgart Group, Available in Ref 118, with Seven Electrons in the Valence Space[a]

	Br_2	I_2	I_2^*	At_2
$E^{(2,0)}$	-2.86×10^{-03}	-3.86×10^{-03}	-3.59×10^{-03}	-3.70×10^{-02}
$E^{(3,0)}$	$+4.17 \times 10^{-05}$	-2.32×10^{-05}	-1.68×10^{-05}	-5.59×10^{-04}
$E^{(4,0)}$	-4.39×10^{-06}	$+1.72 \times 10^{-06}$	$+1.90 \times 10^{-06}$	$+1.91 \times 10^{-04}$
$E^{(2,1)}$	-2.98×10^{-04}	-1.63×10^{-03}	-1.58×10^{-03}	-1.74×10^{-02}
$E^{(3,1)}$	-6.14×10^{-06}	$+6.41 \times 10^{-06}$	$+7.72 \times 10^{-06}$	$+5.49 \times 10^{-04}$
PT∞	-2.82×10^{-03}	-3.88×10^{-03}	-3.61×10^{-03}	-3.74×10^{-02}
PT∞1	-3.12×10^{-03}	-5.50×10^{-03}	-5.18×10^{-03}	-5.42×10^{-02}
SV	-3.12×10^{-03}	-5.49×10^{-03}	-5.17×10^{-03}	-5.35×10^{-02}
Δ_{21}	-3.29×10^{-05}	$+1.28 \times 10^{-07}$	-8.31×10^{-06}	-9.04×10^{-04}
$\Delta_{\infty 1}$	-1.68×10^{-06}	-1.49×10^{-05}	-1.55×10^{-05}	-7.24×10^{-04}

[a]The asterisk denotes a calculation on the I_2 molecule using the larger valence basis set of ref 121.

Table III. Same as Tables I and III Above but This Time Using a Smaller Core Shape-Consistent RECP from the Columbus Group, in which 17 Electrons Are Treated Explicitly in the Valence Space

	Br_2	I_2	At_2
$E^{(2,0)}$	-5.73×10^{-03}	-2.83×10^{-02}	-2.40×10^{-01}
$E^{(3,0)}$	-2.78×10^{-05}	-9.04×10^{-04}	-1.69×10^{-02}
$E^{(4,0)}$	$+1.45 \times 10^{-06}$	-8.28×10^{-05}	$+2.03 \times 10^{-03}$
$E^{(2,1)}$	-1.83×10^{-03}	-8.80×10^{-03}	-8.62×10^{-02}
$E^{(3,1)}$	-2.54×10^{-06}	-2.48×10^{-04}	-3.53×10^{-03}
PT∞	-5.75×10^{-03}	-2.93×10^{-02}	-2.54×10^{-01}
PT∞1	-7.59×10^{-03}	-3.83×10^{-02}	-3.44×10^{-01}
SV	-7.57×10^{-03}	-3.82×10^{-02}	-3.32×10^{-01}
Δ_{21}	$+1.40 \times 10^{-05}$	$+1.09 \times 10^{-03}$	$+5.84 \times 10^{-03}$
$\Delta_{\infty 1}$	-1.49×10^{-05}	-1.49×10^{-04}	-1.25×10^{-02}

rapidly. A more-than-adequate treatment is obtained, again, simply by calculating $E^{(2,0)}$ and $E^{(2,1)}$, since the terms $E^{(3,0)}$, $E^{(4,0)}$, and $E^{(3,1)}$ are around 2−3 orders of magnitude smaller than the SV energy.

To provide results on other challenging cases for perturbation theory, in Table S1 of the Supporting Information (SI), we report on calculations for selenium oxide (SeO)[131] (using the experimental bond length of 2.648 Å from ref 132) and the positively charged homonuclear diatomic tennessine Ts_2^+ molecule (bond length of 3.00 Å). The ECP10MDF and ECP92MDFQ Stuttgart potentials were used for Se and Ts, respectively, along with the associated double-ζ valence basis sets,[118] while the basis set of ref 133 was used for O. Excellent agreement between the double perturbation and SV methods is obtained in both cases (see Table S1), as the reported Δ_{21} and $\Delta_{\infty 1}$ values are smaller than the SV energy by around 1 order of magnitude for Ts_2^+ and 4 orders of magnitude for SeO. In the case of Ts_2^+, monotonicity of the $E^{(2,0)}$, $E^{(3,0)}$, $E^{(4,0)}$, ... series breaks down in fourth order because $E^{(4,0)}$ (=0.0504) is slightly larger in absolute value than $E^{(3,0)}$ (=−0.0459). For Ts_2^+, monotonicity is restored by scaling down the SOC operator (scaling factor ≤0.90) to ensure that the ratio of $|E^{(2,0)}|$ and the HOMO−LUMO gap E_{gap} is less than 3.9. Coincidentally, this criterion on $|E^{(2,0)}|/E_{gap} < 3.9$ also ensures monotonicity for the whole positively charged homonuclear diatomic halogen series through fourth order, as shown in Figure S1, as well as Table S2.

V. CONCLUSIONS

We have presented a double perturbation theory approach to the solution of the many-body Dirac equation in a given relativistic effective-core potential (RECP) approximation. The zeroth-order approximation is the corresponding scalar relativistic unrestricted Hartree−Fock (SR UHF) solution. This is followed by a double perturbation theory expansion in terms of the spin−orbit coupling (SOC) and electron fluctuation potential. Practical perturbation energy expressions are provided up to a total order of three with most higher-order terms included.

Tests on the neutral halogen diatomic molecules F_2, Cl_2, Br_2, I_2, and At_2, as well as their single positive open-shell ions, show that the proposed approach is well-converged to the second-variational (SV) value through second order in SOC and first order in the fluctuation potential. Since the double perturbation treatment is no more difficult to carry out than the SV procedure, it is a computationally attractive alternative to performing a 2c-SCF for treatment of SOC and, in addition, represents a convenient starting point for further improvements.

Table IV. Same as Table I but Now for the Open-Shell Radicals, in which One Electron from the Highest Occupied Molecular Orbital Has Been Removed

	F_2^+	Cl_2^+	Br_2^+	I_2^+
$E^{(2,0)}$	-4.45×10^{-05}	-1.90×10^{-04}	-4.35×10^{-03}	-2.43×10^{-02}
$E^{(3,0)}$	-7.99×10^{-08}	-3.27×10^{-07}	-3.13×10^{-05}	-8.98×10^{-04}
$E^{(4,0)}$	-3.09×10^{-10}	$+4.66 \times 10^{-09}$	$+3.62 \times 10^{-06}$	-1.82×10^{-05}
$E^{(2,1)}$	-1.93×10^{-05}	-1.05×10^{-04}	-2.68×10^{-03}	-1.33×10^{-02}
$E^{(3,1)}$	-2.49×10^{-08}	$+2.75 \times 10^{-07}$	$+5.30 \times 10^{-05}$	$+3.20 \times 10^{-04}$
PT∞	-4.45×10^{-05}	-1.90×10^{-04}	-4.38×10^{-03}	-2.52×10^{-02}
PT∞1	-6.38×10^{-05}	-2.95×10^{-04}	-7.00×10^{-03}	-3.81×10^{-02}
SV	-6.38×10^{-05}	-2.94×10^{-04}	-6.94×10^{-03}	-3.75×10^{-02}
Δ_{21}	$+5.58 \times 10^{-08}$	-7.10×10^{-07}	-8.36×10^{-05}	-4.28×10^{-05}
$\Delta_{\infty 1}$	-4.93×10^{-08}	-7.57×10^{-07}	-5.84×10^{-05}	-6.39×10^{-04}

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A calculation of $E^{(0,2)}$, that is to say, the familiar SR MP2 energy, a procedure that represents an $O(N_{occ}N_{AO}^4)$ computational problem for a calculation with N_{AO} atomic and N_{occ} occupied orbitals, would provide a computationally tractable, relativistic correlated approach. A further calculation of $E^{(1,2)}$ involves only a modest additional cost and allows for a full treatment of the coupling between SOC and the fluctuation potential through total order three. Furthermore, the present approach gives rise to the possibility of a multireference treatment through quasi-degenerate perturbation theory (QDPT) that could be used in those cases where it is necessary (i.e., open-shell or closed-shell systems of a strong multireference character).

APPENDIX A: ENERGY CONTRIBUTIONS OF ZEROTH ORDER IN THE ELECTRON FLUCTUATION POTENTIAL IN TERMS OF SR UHF ORBITALS

Since $\hat{L}_{z,i}\hat{S}_{z,i}$ is purely imaginary, it follows from eq 4 that the real part of the matrix elements of $\hat{h}_{SO}$ involving orbitals of like spin (the real part of diagonal spin-block matrix elements of $\hat{h}_{SO}$) vanishes

$$\mathcal{R}[\langle m,\alpha|\hat{h}_{SO}|n,\alpha\rangle] = 0 \tag{A1}$$

On the other hand, the off-diagonal spin-block matrix elements of $\hat{h}_{SO}$ are complex. It follows that $E^{(1,0)}$ in eq 15 vanishes because $\hat{h}_{SO}$ is Hermitian, which means that diagonal matrix elements must be real.

In second order, ordinary nondegenerate RSPT reduces to eq 17 since $\hat{h}_{SO}$ is a sum of one-electron operators and only single excitation configurations contribute to the sum-over-states. Our choice for the (0, 0) problem ensures that the $E^{(0,0)} - E_I^{(0,0)}$ denominators of eq 13 become only a difference of SR UHF eigenvalues.

Ordinary nondegenerate RSPT, in third order, gives

$$E^{(3,0)} = \langle\psi^{(0,0)}|\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle \tag{A2}$$

and in fourth order (using intermediated normalization)

$$\begin{aligned}E^{(4,0)} = {} & \langle\psi^{(0,0)}|\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle \\ & - \langle\psi^{(0,0)}|\hat{h}_{SO}\hat{R}^{(0,0)}E^{(2,0)}\hat{R}^{(0,0)}\hat{h}_{SO}|\psi^{(0,0)}\rangle\end{aligned} \tag{A3}$$

To simplify eq A2, we denote singly excited configurations by $|\psi_m^p\rangle$ where virtual orbital $|p\rangle$ is substituted for occupied orbital $|m\rangle$; and the associated energy is E_m^p. Doubly excited configurations are denoted as $|\psi_{mn}^{pq}\rangle$. On expanding eq A2 in singly excited Slater determinants, we find

$$\begin{aligned}E^{(3,0)} = {} & \sum_{m}^{occ}\sum_{pq}^{virt}\frac{\langle\psi^{(0,0)}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi^{(0,0)}\rangle}{(E^{(0,0)} - E_m^p)(E^{(0,0)} - E_m^q)} \\ & + \sum_{mn}^{occ}\sum_{p}^{virt}\frac{\langle\psi^{(0,0)}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi^{(0,0)}\rangle}{(E^{(0,0)} - E_m^p)(E^{(0,0)} - E_n^p)}\end{aligned} \tag{A4}$$

which can be written in terms of one-electron orbitals as

$$\begin{aligned}E^{(3,0)} = {} & \sum_{m}^{occ}\sum_{pq}^{virt}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{(\epsilon_m-\epsilon_p)(\epsilon_m-\epsilon_q)} \\ & - \sum_{mn}^{occ}\sum_{p}^{virt}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{(\epsilon_m-\epsilon_p)(\epsilon_n-\epsilon_p)}\end{aligned} \tag{A5}$$

Expressing eq A5 in terms of the matrices reported in eq 16a, we obtain eq 18.

A similar demonstration can be carried out in fourth order, starting from eq A3 to obtain eq 19. The full derivation is reported in the SI.

APPENDIX B: ENERGY CONTRIBUTIONS OF FIRST ORDER IN THE ELECTRON FLUCTUATION POTENTIAL IN TERMS OF SR UHF ORBITALS

Equation 20 is obtained by combining the (1,1), (1,0), and (0,1) RSPT equations. We use intermediate normalization here and throughout this paper

$$\langle\psi^{(0,0)}|\psi^{(N,M)}\rangle = \delta_{N,0}\,\delta_{M,0} \tag{B1}$$

The (1,1) RSPT equation

$$\begin{aligned}&[\hat{H}^{(0,0)} - E^{(0,0)}]|\psi^{(1,1)}\rangle + [\hat{h}_{SO} - E^{(1,0)}]|\psi^{(0,1)}\rangle + [\hat{H}^{(0,1)} - E^{(0,1)}]|\psi^{(1,0)}\rangle \\ &\quad - E^{(1,1)}|\psi^{(0,0)}\rangle = 0\end{aligned} \tag{B2}$$

may be multiplied on the left by $\langle\psi^{(0,0)}|$ to yield

$$E^{(1,1)} = \langle\psi^{(0,0)}|\hat{h}_{SO}|\psi^{(0,1)}\rangle + \langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(1,0)}\rangle \tag{B3}$$

Similarly, for the (1,0) RSPT equation

$$[\hat{H}^{(0,0)} - E^{(0,0)}]|\psi^{(1,0)}\rangle + [\hat{h}_{SO} - E^{(1,0)}]|\psi^{(0,0)}\rangle = 0 \tag{B4}$$

we multiply on the left by $\langle\psi^{(0,1)}|$, which gives

$$\langle\psi^{(0,1)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(1,0)}\rangle + \langle\psi^{(0,1)}|\hat{h}_{SO}|\psi^{(0,0)}\rangle = 0 \tag{B5}$$

Finally, the (0,1) RSPT equation leads to

$$\langle\psi^{(1,0)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(1,0)}|\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle = 0 \tag{B6}$$

after multiplication on the left by $\langle\psi^{(1,0)}|$. The sum of eq B3 minus the complex conjugate-transpose of eq B6 plus eq B5 leads directly to eq 20.

Below, we provide an outline of the derivation that allows us to obtain expressions for $E^{(2,1)}$ and $E^{(3,1)}$. More details on the derivation can be found in Section H.6 of ref 134. A procedure analogous to that developed in eqs B2−B6 can be used for $E^{(2,1)}$ by combining the (1,0), (0,1), (1,1), (2,0), and (2,1) RSPT equations to obtain

$$\begin{aligned}E^{(2,1)} = {} & 2\mathcal{R}[\langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(2,0)}\rangle] \\ & + \langle\psi^{(1,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi^{(1,0)}\rangle\end{aligned} \tag{B7}$$

For $E^{(3,1)}$, we combine the (1,0), (0,1), (1,1), (2,0), (2,1), (3,0), and (3,1) RSPT equations

$$\begin{aligned}E^{(3,1)} = {} & 2\mathcal{R}[\langle\psi^{(1,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi^{(2,0)}\rangle] \\ & + 2\mathcal{R}[\langle\psi^{(0,1)}|\hat{h}_{SO}|\psi^{(2,0)}\rangle] - 2E^{(2,0)}\mathcal{R}[\langle\psi^{(1,0)}|\psi^{(0,1)}\rangle]\end{aligned} \tag{B8}$$

The last term in eq B8 vanishes since, from Brillouin's theorem, $|\psi^{(0,1)}\rangle$ consists only of doubly excited configurations, while $|\psi^{(1,0)}\rangle$ consists only of singly excited configurations because the SOC operator is a sum of monoelectronic operators. Thus, eq B8 reduces to

$$\begin{aligned}E^{(3,1)} = {} & 2\mathcal{R}[\langle\psi^{(1,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi^{(2,0)}\rangle] \\ & + 2\mathcal{R}[\langle\psi^{(0,1)}|\hat{h}_{SO}|\psi^{(2,0)}\rangle]\end{aligned} \tag{B9}$$

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Then, expanding $|\psi^{(2,0)}\rangle$, $|\psi^{(1,0)}\rangle$, and $|\psi^{(0,1)}\rangle$ in eqs B7 and B9 in eigenfunctions of the (0,0) problem, we obtain eqs 21 and 22. Taking into account the form of the perturbation operators from eq 9a for the case of $E^{(2,1)}$ leads to

$$
\begin{aligned}
E^{(2,1)} = {} & 2\sum_{n<m}^{\mathrm{occ}}\sum_{q<p}^{\mathrm{virt}}\mathcal{R}\Bigg[\langle\psi^{(0,0)}|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{p}\rangle\langle\psi_{m}^{p}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{mn}^{pq})(E^{(0,0)}-E_{m}^{p})} \\
& + \frac{\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{n}^{p}\rangle\langle\psi_{n}^{p}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{mn}^{pq})(E^{(0,0)}-E_{n}^{p})} \\
& + \frac{\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{q}\rangle\langle\psi_{m}^{q}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{\{E^{(0,0)}-E_{mn}^{pq}\}(E^{(0,0)}-E_{m}^{q})} + \frac{\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{n}^{q}\rangle\langle\psi_{n}^{q}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{mn}^{pq})(E^{(0,0)}-E_{n}^{q})}\Bigg\}\Bigg] \\
& + \sum_{n\neq m}^{\mathrm{occ}}\sum_{q\neq p}^{\mathrm{virt}}\langle\psi_{m}^{p}|\hat{V}_{\mathrm{ee}}|\psi_{n}^{q}\rangle\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{p}\rangle\langle\psi_{n}^{q}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{m}^{p})(E^{(0,0)}-E_{n}^{q})} \\
& + \sum_{m}^{\mathrm{occ}}\sum_{q\neq p}^{\mathrm{virt}}\langle\psi_{m}^{p}|\hat{V}_{\mathrm{ee}}-(\hat{C}-\hat{K})|\psi_{m}^{q}\rangle\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{p}\rangle\langle\psi_{m}^{q}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{m}^{p})(E^{(0,0)}-E_{m}^{q})} \\
& + \sum_{n\neq m}^{\mathrm{occ}}\sum_{p}^{\mathrm{virt}}\langle\psi_{m}^{p}|\hat{V}_{\mathrm{ee}}-(\hat{C}-\hat{K})|\psi_{n}^{p}\rangle\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{p}\rangle\langle\psi_{n}^{p}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{m}^{p})(E^{(0,0)}-E_{n}^{p})} \\
& - E^{(0,1)}\sum_{m}^{\mathrm{occ}}\sum_{p}^{\mathrm{virt}}\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{p}\rangle\langle\psi_{m}^{p}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{m}^{p})(E^{(0,0)}-E_{m}^{p})} \\
& + \sum_{m}^{\mathrm{occ}}\sum_{p}^{\mathrm{virt}}\langle\psi_{m}^{p}|\hat{V}_{\mathrm{ee}}-(\hat{C}-\hat{K})|\psi_{m}^{p}\rangle\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_{m}^{p}\rangle\langle\psi_{m}^{p}|\hat{h}_{\mathrm{SO}}|\psi^{(0,0)}\rangle}{(E^{(0,0)}-E_{m}^{p})(E^{(0,0)}-E_{m}^{p})}
\end{aligned}
\tag{B10}
$$

Based on the Slater−Condon rules, we can evaluate all of the integrals in eq B10 and express $E^{(2,1)}$ as a sum of two terms $E_{\mathrm{S}}^{(2,1)}$ and $E_{\mathrm{D}}^{(2,1)}$, arising, respectively, from singly excited and doubly (as well as singly) excited configurations

$$
E^{(2,1)} = E_{\mathrm{S}}^{(2,1)} + E_{\mathrm{D}}^{(2,1)} \tag{B11}
$$

where

$$
\begin{aligned}
E_{\mathrm{S}}^{(2,1)} = {} & \sum_{mn}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\{(pm|nq) - (pq|nm)\} \\
& \times \frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle\langle q|\hat{h}_{\mathrm{SO}}|n\rangle}{(\epsilon_m-\epsilon_p)(\epsilon_n-\epsilon_q)}
\end{aligned}
\tag{B12}
$$

and

$$
\begin{aligned}
E_{\mathrm{D}}^{(2,1)} = {} & 2\sum_{n<m}^{\mathrm{occ}}\sum_{q<p}^{\mathrm{virt}}\mathcal{R}\Bigg[\frac{(mp|nq) - (mq|np)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q} \\
& \times\Bigg\{\frac{\langle q|\hat{h}_{\mathrm{SO}}|n\rangle\langle p|\hat{h}_{\mathrm{SO}}|m\rangle}{\epsilon_m-\epsilon_p} - \frac{\langle q|\hat{h}_{\mathrm{SO}}|m\rangle\langle p|\hat{h}_{\mathrm{SO}}|n\rangle}{\epsilon_n-\epsilon_p} \\
& - \frac{\langle p|\hat{h}_{\mathrm{SO}}|n\rangle\langle q|\hat{h}_{\mathrm{SO}}|m\rangle}{\epsilon_m-\epsilon_q} + \frac{\langle p|\hat{h}_{\mathrm{SO}}|m\rangle\langle q|\hat{h}_{\mathrm{SO}}|n\rangle}{\epsilon_n-\epsilon_q}\Bigg\}\Bigg]
\end{aligned}
\tag{B13}
$$

Since the contribution to $E_{\mathrm{D}}^{(2,1)}$ in eq B13 from the terms $m = n$ and $p = q$ vanish, we can extend the summations over orbital indices to all values of the occupied and virtual sets occ and virt. Then, using the fact that $(mp|nq) - (mq|np) = -\{(np|mq) - (nq|mp)\}$, eq B13 can be simplified to

$$
\begin{aligned}
E_{\mathrm{D}}^{(2,1)} = {} & \sum_{mn}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\mathcal{R}\Bigg[\{(mp|nq) - (mq|np)\} \\
& \times \frac{\langle q|\hat{h}_{\mathrm{SO}}|n\rangle\langle p|\hat{h}_{\mathrm{SO}}|m\rangle}{(\epsilon_n-\epsilon_q)(\epsilon_m-\epsilon_p)}\Bigg]
\end{aligned}
\tag{B14}
$$

Equations B11, B12, and B14 can be combined to write a computationally convenient expression for $E^{(2,1)}$ by introducing the complex non-Hermitian matrix

$$
M_{\omega\nu}^{\sigma\sigma'(N,0)} = \sum_{m}^{\mathrm{occ}}\sum_{p}^{\mathrm{virt}} c_{\omega p}^{\sigma}[c_{\nu m}^{\sigma'}]^{*}U_{pm}^{\sigma\sigma'(N,0)} \tag{B15}
$$

where the orbital coefficients $c_{\omega p}^{\sigma}$ are defined through eq 8 and the elements of the matrix of orbital rotations $\mathbf{U}^{\sigma\sigma'(N,0)}$ are defined for the case $N = 1$ in eq 16b. Combining eqs B11, B12, B14, and B15, we obtain

$$
\begin{aligned}
E^{(2,1)} = {} & \sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}\{[M_{\omega\nu}^{\sigma\sigma(1,0)}]^{*} + M_{\nu\omega}^{\sigma\sigma(1,0)}\}\sum_{\tau\gamma}M_{\gamma\tau}^{\sigma'\sigma'(1,0)}(\omega\nu|\tau\gamma)\Bigg] \\
& - \sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{\omega\nu}\{[M_{\omega\nu}^{\sigma\sigma'(1,0)}]^{*} + M_{\nu\omega}^{\sigma'\sigma(1,0)}\}\sum_{\tau\gamma}M_{\gamma\tau}^{\sigma\sigma'(1,0)}(\omega\gamma|\tau\nu)\Bigg]
\end{aligned}
\tag{B16}
$$

Finally, to write eq B16 in a more compact way, it proves useful to define the elements of the first-order perturbed-density matrix

$$
P_{\omega\nu}^{\sigma\sigma'(1,0)} = M_{\omega\nu}^{\sigma\sigma'(1,0)} + [M_{\nu\omega}^{\sigma'\sigma(1,0)}]^{*} \tag{B17}
$$

Substituting eq B17 in eq B16, we obtain eq 23.

A similar demonstration to that provided in eqs B10−B13 can be developed for $E^{(3,1)}$ starting from eq 22. The full derivation is provided in the SI. We write $E^{(3,1)}$ as a sum of two terms $E_{\mathrm{S}}^{(3,1)}$ and $E_{\mathrm{D}}^{(3,1)}$, arising, respectively, from singly excited and doubly (as well as singly) excited configurations

$$
E^{(3,1)} = E_{\mathrm{S}}^{(3,1)} + E_{\mathrm{D}}^{(3,1)} \tag{B18}
$$

After evaluation of all of the integrals employing the Slater−Condon rules, the corresponding expressions for $E_{\mathrm{S}}^{(3,1)}$ and $E_{\mathrm{D}}^{(3,1)}$ in eq B18 are

$$
\begin{aligned}
E_{\mathrm{S}}^{(3,1)} = {} & 2\sum_{mn}^{\mathrm{occ}}\sum_{pqr}^{\mathrm{virt}}\mathcal{R}[\{(pm|nq) - (pq|nm)\} \\
& \times\frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle\langle q|\hat{h}_{\mathrm{SO}}|r\rangle\langle r|\hat{h}_{\mathrm{SO}}|n\rangle}{(\epsilon_m-\epsilon_p)(\epsilon_n-\epsilon_q)(\epsilon_n-\epsilon_r)}] \\
& -2\sum_{mno}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\mathcal{R}[\{(pm|nq) - (pq|nm)\} \\
& \times\frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle\langle o|\hat{h}_{\mathrm{SO}}|n\rangle\langle q|\hat{h}_{\mathrm{SO}}|o\rangle}{(\epsilon_m-\epsilon_p)(\epsilon_n-\epsilon_q)(\epsilon_o-\epsilon_q)}]
\end{aligned}
\tag{B19}
$$

and

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$$E_{\mathrm{D}}^{(3,1)} = 2\sum_{mn}^{\mathrm{occ}}\sum_{pqr}^{\mathrm{virt}} \mathcal{R}[\{(rp|nq) - (rq|np)\} \times \frac{\langle m|\hat{h}_{\mathrm{SO}}|r\rangle\langle q|\hat{h}_{\mathrm{SO}}|n\rangle\langle p|\hat{h}_{\mathrm{SO}}|m\rangle}{(\epsilon_m - \epsilon_r)(\epsilon_n - \epsilon_q)(\epsilon_m - \epsilon_p)}] + 2\sum_{mno}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}} \mathcal{R}[\{(mq|no) - (mo|nq)\} \times \frac{\langle o|\hat{h}_{\mathrm{SO}}|p\rangle\langle q|\hat{h}_{\mathrm{SO}}|n\rangle\langle p|\hat{h}_{\mathrm{SO}}|m\rangle}{(\epsilon_o - \epsilon_p)(\epsilon_n - \epsilon_q)(\epsilon_m - \epsilon_p)}] + 2\sum_{mn}^{\mathrm{occ}}\sum_{pqr}^{\mathrm{virt}} \mathcal{R}[\{(mp|nq) - (mq|np)\} \times \frac{\langle q|\hat{h}_{\mathrm{SO}}|n\rangle\langle p|\hat{h}_{\mathrm{SO}}|r\rangle\langle r|\hat{h}_{\mathrm{SO}}|m\rangle}{(\epsilon_n - \epsilon_q)(\epsilon_m - \epsilon_p)(\epsilon_m - \epsilon_r)}] - 2\sum_{mno}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}} \mathcal{R}[\{(mp|nq) - (mq|np)\} \times \frac{\langle q|\hat{h}_{\mathrm{SO}}|n\rangle\langle o|\hat{h}_{\mathrm{SO}}|m\rangle\langle p|\hat{h}_{\mathrm{SO}}|o\rangle}{(\epsilon_n-\epsilon_q)(\epsilon_m-\epsilon_p)(\epsilon_o-\epsilon_p)}] \tag{B20}$$

We can represent $E^{(3,1)}$ in the AO basis by introducing the elements of the matrix of second-order orbital rotations $\mathbf{U}^{(2,0)}$, which reads as follows for the occupied−virtual block

$$U_{pm}^{\sigma'\sigma(2,0)} = \frac{1}{\epsilon_p^{\sigma'} - \epsilon_m^{\sigma}}\sum_{\sigma''}\left(\sum_{n}^{\mathrm{occ}} U_{pn}^{\sigma'\sigma''(1,0)} G_{nm}^{\sigma''\sigma(1,0)} - \sum_{q}^{\mathrm{virt}} G_{pq}^{\sigma'\sigma''(1,0)} U_{qm}^{\sigma''\sigma(1,0)}\right) \tag{B21a}$$

For the virtual−virtual blocks

$$U_{qr}^{\sigma\sigma'(2,0)} = -\frac{1}{2}\sum_{\sigma''}\sum_{n}^{\mathrm{occ}} [U_{nq}^{\sigma''\sigma(1,0)}]^* U_{nr}^{\sigma''\sigma'(1,0)} \tag{B21b}$$

and for the occupied−occupied blocks

$$U_{on}^{\sigma\sigma'(2,0)} = -\frac{1}{2}\sum_{\sigma''}\sum_{q}^{\mathrm{virt}} [U_{qo}^{\sigma''\sigma(1,0)}]^* U_{qn}^{\sigma''\sigma'(1,0)} \tag{B21c}$$

$U_{qr}^{\sigma\sigma\prime(2,0)}$ and $U_{on}^{\sigma\sigma\prime(2,0)}$ are used to represent $E^{(3,1)}$ in the basis of AOs through the following matrices

$$O_{\omega\nu}^{\sigma\sigma'(2,0)} = \sum_{on}^{\mathrm{occ}} c_{\omega o}^{\sigma}[c_{\nu n}^{\sigma'}]^* U_{on}^{\sigma\sigma'(2,0)} \tag{B22a}$$

and

$$V_{\omega\nu}^{\sigma\sigma'(2,0)} = \sum_{qr}^{\mathrm{virt}} c_{\omega q}^{\sigma}[c_{\nu r}^{\sigma'}]^* U_{qr}^{\sigma\sigma'(2,0)} \tag{B22b}$$

Substituting eqs BB21a−BB22b and B15 into eqs B19 and B20, we obtain eq 24 (see the SI for more details).

APPENDIX C: $E^{(1,2)}$ CONTRIBUTION IN TERMS OF SR UHF ORBITALS

For eq 26, we proceed in a manner similar to that outlined in eqs B2−B6 and combine the (0,1), (1,0), (1,1), (0,2), and (1,2) RSPT equations to find

$$E^{(1,2)} = 2\mathcal{R}[\langle\psi^{(1,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi^{(0,1)}\rangle] + \langle\psi^{(0,1)}|\hat{h}_{\mathrm{SO}}|\psi^{(0,1)}\rangle \tag{C1}$$

Then, expanding $|\psi^{(0,1)}\rangle$ and $|\psi^{(1,0)}\rangle$ in the basis of configurations of the (0,0) problem, we obtain eq 26. Only singly- and doubly excited configurations contribute to the double sum, which leads to

$$\begin{aligned}
E^{(1,2)} = {} & 2\sum_{n<m}^{\mathrm{occ}}\sum_{q<p}^{\mathrm{virt}} \mathcal{R}\left[\frac{\langle\psi_{mn}^{pq}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{E^{(0,0)} - E_{mn}^{pq}}\left\{\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_m^p\rangle\langle\psi_m^p|\hat{V}_{\mathrm{ee}} - (\hat{C}-\hat{K})|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_m^p} + \frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_n^p\rangle\langle\psi_n^p|\hat{V}_{\mathrm{ee}} - (\hat{C}-\hat{K})|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_n^p} + \frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_m^q\rangle\langle\psi_m^q|\hat{V}_{\mathrm{ee}} - (\hat{C}-\hat{K})|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_m^q} + \frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_n^q\rangle\langle\psi_n^q|\hat{V}_{\mathrm{ee}} - (\hat{C}-\hat{K})|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_n^q}\right\}\right] \\
& + 2\sum_{n<m}^{\mathrm{occ}}\sum_{q<p}^{\mathrm{virt}}\sum_{r}^{\mathrm{virt}}{}'' \mathcal{R}\left[\frac{\langle\psi_{mn}^{pq}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{E^{(0,0)} - E_{mn}^{pq}}\left\{\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_m^r\rangle\langle\psi_m^r|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_m^r} + \frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_n^r\rangle\langle\psi_n^r|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_n^r}\right\}\right] \\
& + 2\sum_{n<m}^{\mathrm{occ}}\sum_{o}^{\mathrm{occ}}{}''\sum_{q<p}^{\mathrm{virt}} \mathcal{R}\left[\frac{\langle\psi_{mn}^{pq}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{E^{(0,0)} - E_{mn}^{pq}}\left\{\frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_o^p\rangle\langle\psi_o^p|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_o^p} + \frac{\langle\psi^{(0,0)}|\hat{h}_{\mathrm{SO}}|\psi_o^q\rangle\langle\psi_o^q|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle}{E^{(0,0)} - E_o^q}\right\}\right] \\
& + \sum_{n<m}^{\mathrm{occ}}\sum_{q<p}^{\mathrm{virt}}\sum_{r}^{\mathrm{virt}}{}'' \frac{\langle\psi^{(0,0)}|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{mn}^{rq}\rangle\langle\psi_{mn}^{rq}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{(E^{(0,0)} - E_{mn}^{pq})(E^{(0,0)} - E_{mn}^{rq})} \\
& + \sum_{n<m}^{\mathrm{occ}}\sum_{r<p<q}^{\mathrm{virt}} \frac{\langle\psi^{(0,0)}|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{mn}^{pr}\rangle\langle\psi_{mn}^{pr}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{(E^{(0,0)} - E_{mn}^{pq})(E^{(0,0)} - E_{mn}^{pr})} \\
& + \sum_{n<m}^{\mathrm{occ}}\sum_{o}^{\mathrm{occ}}{}''\sum_{q<p}^{\mathrm{virt}} \frac{\langle\psi^{(0,0)}|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{on}^{pq}\rangle\langle\psi_{on}^{pq}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{(E^{(0,0)} - E_{mn}^{pq})(E^{(0,0)} - E_{on}^{pq})} \\
& + \sum_{o<n<m}^{\mathrm{occ}}\sum_{q<p}^{\mathrm{virt}} \frac{\langle\psi^{(0,0)}|\hat{V}_{\mathrm{ee}}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{\mathrm{SO}}|\psi_{mo}^{pq}\rangle\langle\psi_{mo}^{pq}|\hat{V}_{\mathrm{ee}}|\psi^{(0,0)}\rangle}{(E^{(0,0)} - E_{mn}^{pq})(E^{(0,0)} - E_{mo}^{pq})}
\end{aligned} \tag{C2}$$

where the symbol $''$ on the sum over r, for example, indicates that it extends to all r that satisfy $r \neq p, q$. Evaluating all of the integrals in eq C2 gives

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$$
\begin{aligned}
E^{(1,2)} = \frac{1}{2}\sum_{m\neq n}^{\mathrm{occ}}\sum_{p\neq q}^{\mathrm{virt}}\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\\
&\Bigg\{\frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle([(nq|pp)-(np|pq)]-[(nq|mm)-(nm|mq)])}{\epsilon_m-\epsilon_p}\\
&+\frac{\langle n|\hat{h}_{\mathrm{SO}}|p\rangle([(mq|nn)-(mn|nq)]-[(mq|pp)-(mp|pq)])}{\epsilon_n-\epsilon_p}\\
&+\frac{\langle m|\hat{h}_{\mathrm{SO}}|q\rangle([(np|mm)-(nm|mp)]-[(np|qq)-(nq|qp)])}{\epsilon_m-\epsilon_q}\\
&+\frac{\langle n|\hat{h}_{\mathrm{SO}}|q\rangle([(mp|qq)-(mq|qp)]-[(mp|nn)-(mn|np)])}{\epsilon_n-\epsilon_q}\Bigg\}\Bigg]\\
+\frac{1}{2}\sum_{m\neq n}^{\mathrm{occ}}\sum_{p\neq q}^{\mathrm{virt}}\sum_{r}^{\mathrm{virt}}{}''\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\Bigg\{\frac{\langle m|\hat{h}_{\mathrm{SO}}|r\rangle[(rp|nq)-(rq|np)]}{\epsilon_m-\epsilon_r}\\
&+\frac{\langle n|\hat{h}_{\mathrm{SO}}|r\rangle[(mp|rq)-(mq|rp)]}{\epsilon_n-\epsilon_r}\Bigg\}\Bigg]\\
+\frac{1}{2}\sum_{m\neq n}^{\mathrm{occ}}\sum_{o}^{\mathrm{occ}}{}''\sum_{p\neq q}^{\mathrm{virt}}\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\Bigg\{\frac{\langle o|\hat{h}_{\mathrm{SO}}|p\rangle[(no|mq)-(nq|mo)]}{\epsilon_o-\epsilon_p}\\
&+\frac{\langle o|\hat{h}_{\mathrm{SO}}|q\rangle[(mo|np)-(mp|no)]}{\epsilon_o-\epsilon_q}\Bigg\}\Bigg]\\
+\frac{1}{4}\sum_{m\neq n}^{\mathrm{occ}}\sum_{p\neq r\neq q}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle p|\hat{h}_{\mathrm{SO}}|r\rangle[(rm|qn)-(qm|rn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_n-\epsilon_r-\epsilon_q)}\\
+\frac{1}{4}\sum_{m\neq n}^{\mathrm{occ}}\sum_{p\neq q\neq r}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle q|\hat{h}_{\mathrm{SO}}|r\rangle[(pm|rn)-(rm|pn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_r)}\\
-\frac{1}{4}\sum_{m\neq o\neq n}^{\mathrm{occ}}\sum_{p\neq q}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle o|\hat{h}_{\mathrm{SO}}|m\rangle[(po|qn)-(qo|pn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_o+\epsilon_n-\epsilon_p-\epsilon_q)}\\
-\frac{1}{4}\sum_{m\neq n\neq o}^{\mathrm{occ}}\sum_{p\neq q}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle o|\hat{h}_{\mathrm{SO}}|n\rangle[(pm|qo)-(qm|po)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_o-\epsilon_p-\epsilon_q)}
\end{aligned}
\tag{C3}
$$

The double and triple sums in eq C3 can now be extended to all values by realizing that the cases $m = n$, $p = q$, $o = m$, $o = n$, $r = p$, and $r = q$ have vanishing contributions to $E^{(1,2)}$

$$
\begin{aligned}
E^{(1,2)} = \frac{1}{2}\sum_{mn}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\\
&\Bigg\{\frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle([(nq|pp)-(np|pq)]-[(nq|mm)-(nm|mq)])}{\epsilon_m-\epsilon_p}\\
&+\frac{\langle n|\hat{h}_{\mathrm{SO}}|p\rangle([(mq|nn)-(mn|nq)]-[(mq|pp)-(mp|pq)])}{\epsilon_n-\epsilon_p}\\
&+\frac{\langle m|\hat{h}_{\mathrm{SO}}|q\rangle([(np|mm)-(nm|mp)]-[(np|qq)-(nq|qp)])}{\epsilon_m-\epsilon_q}\\
&+\frac{\langle n|\hat{h}_{\mathrm{SO}}|q\rangle([(mp|qq)-(mq|qp)\}-[(mp|nn)-(mn|np)])}{\epsilon_n-\epsilon_q}\Bigg\}\Bigg]\\
+\frac{1}{2}\sum_{mn}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\sum_{r}^{\mathrm{virt}}{}''\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\Bigg\{\frac{\langle m|\hat{h}_{\mathrm{SO}}|r\rangle[(rp|nq)-(rq|np)]}{\epsilon_m-\epsilon_r}\\
&+\frac{\langle n|\hat{h}_{\mathrm{SO}}|r\rangle[(mp|rq)-(mq|rp)]}{\epsilon_n-\epsilon_r}\Bigg\}\Bigg]\\
+\frac{1}{2}\sum_{mn}^{\mathrm{occ}}\sum_{o}^{\mathrm{occ}}{}''\sum_{pq}^{\mathrm{virt}}\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\Bigg\{\frac{\langle o|\hat{h}_{\mathrm{SO}}|p\rangle[(no|mq)-(nq|mo)]}{\epsilon_o-\epsilon_p}\\
&+\frac{\langle o|\hat{h}_{\mathrm{SO}}|q\rangle[(mo|np)-(mp|no)]}{\epsilon_o-\epsilon_q}\Bigg\}\Bigg]\\
+\frac{1}{4}\sum_{mn}^{\mathrm{occ}}\sum_{prq}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle p|\hat{h}_{\mathrm{SO}}|r\rangle[(rm|qn)-(qm|rn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_n-\epsilon_r-\epsilon_q)}\\
+\frac{1}{4}\sum_{mn}^{\mathrm{occ}}\sum_{pqr}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle q|\hat{h}_{\mathrm{SO}}|r\rangle[(pm|rn)-(rm|pn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_r)}\\
-\frac{1}{4}\sum_{mon}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle o|\hat{h}_{\mathrm{SO}}|m\rangle[(po|qn)-(qo|pn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_o+\epsilon_n-\epsilon_p-\epsilon_q)}\\
-\frac{1}{4}\sum_{mno}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle o|\hat{h}_{\mathrm{SO}}|n\rangle[(pm|qo)-(qm|po)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_o-\epsilon_p-\epsilon_q)}
\end{aligned}
\tag{C4}
$$

Then, we use $(pm|qn)-(qm|pn) = -[(pn|qm)-(qn|pm)]$ and interchange the indices m and n in (i) the second line, (ii) the second term in the third line, (iii) the second term in the fourth line, and (iv) the last line of eq C4, which yields

$$
\begin{aligned}
E^{(1,2)} = \sum_{mn}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\\
&\Bigg\{\frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle([(nq|pp)-(np|pq)]-[(nq|mm)-(nm|mq)])}{\epsilon_m-\epsilon_p}\\
&+\frac{\langle m|\hat{h}_{\mathrm{SO}}|q\rangle([(np|mm)-(nm|mp)]-[(np|qq)-(nq|qp)])}{\epsilon_m-\epsilon_q}\Bigg\}\Bigg]\\
+\sum_{mn}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}\sum_{r}^{\mathrm{virt}}{}''\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\Bigg\{\frac{\langle m|\hat{h}_{\mathrm{SO}}|r\rangle[(rp|nq)-(rq|np)]}{\epsilon_m-\epsilon_r}\Bigg\}\Bigg]\\
+\frac{1}{2}\sum_{mn}^{\mathrm{occ}}\sum_{o}^{\mathrm{occ}}{}''\sum_{pq}^{\mathrm{virt}}\mathcal{R}\Bigg[&\frac{(pm|qn)-(qm|pn)}{\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q}\Bigg\{\frac{\langle o|\hat{h}_{\mathrm{SO}}|p\rangle[(no|mq)-(nq|mo)]}{\epsilon_o-\epsilon_p}\\
&+\frac{\langle o|\hat{h}_{\mathrm{SO}}|q\rangle[(mo|np)-(mp|no)]}{\epsilon_o-\epsilon_q}\Bigg\}\Bigg]\\
+\frac{1}{4}\sum_{mn}^{\mathrm{occ}}\sum_{prq}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle p|\hat{h}_{\mathrm{SO}}|r\rangle[(rm|qn)-(qm|rn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_n-\epsilon_r-\epsilon_q)}\\
+\frac{1}{4}\sum_{mn}^{\mathrm{occ}}\sum_{pqr}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle q|\hat{h}_{\mathrm{SO}}|r\rangle[(pm|rn)-(rm|pn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_r)}\\
-\frac{1}{2}\sum_{mno}^{\mathrm{occ}}\sum_{pq}^{\mathrm{virt}}&\frac{[(mp|nq)-(mq|np)]\langle o|\hat{h}_{\mathrm{SO}}|m\rangle[(po|qn)-(qo|pn)]}{(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q)(\epsilon_o+\epsilon_n-\epsilon_p-\epsilon_q)}
\end{aligned}
\tag{C5}
$$

Similarly, in eq C5, we interchange the indices p and q in (i) line 2, (ii) the second term in line 4, and (iii) the next-to-last line to obtain

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$$
\begin{aligned}
E^{(1,2)} = 2 \sum_{mn}^{\mathrm{occ}} \sum_{pq}^{\mathrm{virt}} \mathcal{R}\Bigg[& \frac{(pm|qn) - (qm|pn)}{\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q} \\
& \left\{ \frac{\langle m|\hat{h}_{\mathrm{SO}}|p\rangle([(nq|pp) - (np|pq)] - [(nq|mm) - (nm|mq)])}{\epsilon_m - \epsilon_p} \right\} \Bigg] \\
+ \sum_{mn}^{\mathrm{occ}} \sum_{pq}^{\mathrm{virt}} \sum_{r}^{\mathrm{virt}}{}'' \mathcal{R}\Bigg[& \frac{(pm|qn) - (qm|pn)}{\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q} \left\{ \frac{\langle m|\hat{h}_{\mathrm{SO}}|r\rangle[(rp|nq) - (rq|np)]}{\epsilon_m - \epsilon_r} \right\} \Bigg] \\
+ \sum_{mn}^{\mathrm{occ}} \sum_{o}^{\mathrm{occ}}{}'' \sum_{pq}^{\mathrm{virt}} \mathcal{R}\Bigg[& \frac{(pm|qn) - (qm|pn)}{\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q} \left\{ \frac{\langle o|\hat{h}_{\mathrm{SO}}|p\rangle[(no|mq) - (nq|mo)]}{\epsilon_o - \epsilon_p} \right\} \Bigg] \\
+ \frac{1}{2} \sum_{mn}^{\mathrm{occ}} \sum_{pqr}^{\mathrm{virt}} & \frac{[(mp|nq) - (mq|np)]\langle p|\hat{h}_{\mathrm{SO}}|r\rangle[(rm|qn) - (qm|rn)]}{(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q)(\epsilon_m + \epsilon_n - \epsilon_r - \epsilon_q)} \\
- \frac{1}{2} \sum_{mno}^{\mathrm{occ}} \sum_{pq}^{\mathrm{virt}} & \frac{[(mp|nq) - (mq|np)]\langle o|\hat{h}_{\mathrm{SO}}|m\rangle[(po|qn) - (qo|pn)]}{(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q)(\epsilon_o + \epsilon_n - \epsilon_p - \epsilon_q)}
\end{aligned}
\tag{C6}
$$

Finally, we recognize that the first line of eq C6 is equivalent to a combination of the cases $r = p$ and $r = q$ in the second line, as well as the cases $o = m$ and $o = n$ in the third line, so that eq C6 reduces to eq 29.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.1c00343.

Derivation of eqs 19, 24, B19, and B20 of the main text of the manuscript and for additional calculations on the systems SeO and $Ts_2^+$and a discussion on a necessary criterion to ensure monotonic convergence of the $E^{(2,0)}$, $E^{(3,0)}$, $E^{(4,0)}$, ... series through fourth order (PDF)

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Notes

The authors declare no competing financial interest.

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