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An atomic mean-field spin-orbit approach within exact two-component theory for a non-perturbative treatment of spin-orbit coupling

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An atomic mean-field (AMF) spin-orbit (SO) approach within exact two-component theory (X2C) is reported, thereby exploiting the exact decoupling scheme of X2C, the one-electron approximation for the scalar-relativistic contributions, the mean-field approximation for the treatment of the two-electron SO contribution, and the local nature of the SO interactions. The Hamiltonian of the proposed SOX2CAMF scheme comprises the one-electron X2C Hamiltonian, the instantaneous two-electron Coulomb interaction, and an AMF SO term derived from spherically averaged Dirac-Coulomb Hartree-Fock calculations of atoms; no molecular relativistic two-electron integrals are required. Benchmark calculations for bond lengths, harmonic frequencies, dipole moments, and electric-field gradients for a set of diatomic molecules containing elements across the periodic table show that the SOX2CAMF scheme offers a balanced treatment for SO and scalar-relativistic effects and appears to be a promising candidate for applications to heavy-element containing systems. SOX2CAMF coupled-cluster calculations of molecular properties for bismuth compounds (BiN, BiP, BiF, BiCl, and BiI) are also presented and compared with experimental results to further demonstrate the accuracy and applicability of the SOX2CAMF scheme. Published by AIP Publishing. https://doi.org/10.1063/1.5023750

I. INTRODUCTION

A central topic in the field of relativistic quantum chemistry is the development of the so-called “two-component methods” by means of decoupling the electronic and positronic degrees of freedom in the four-component Dirac-Coulomb(-Breit) approach in order to focus on the electronic states pertinent to chemistry and molecular physics. Among a variety of two-component methods reported in the literature, the exact two-component (X2C) theory using a one-step unitary transformation to block-diagonalize the four-component Hamiltonian in the matrix representation appears especially promising. Conceptually, a two-component method using an “electrons-only” Hamiltonian is a natural choice for the computational studies in the area of chemistry and molecular physics. In practice, the computational efficiency of a two-component method in comparison with the original parent four-component theory relies not only on the removal of the positronic degree of freedom but also on the reduction of the number of molecular two-electron integrals involved in the computation. The practical scalar-relativistic two-component methods perform the unitary transformation that decouples electronic and positronic states for the one-electron part of the spin-free (SF) Dirac Hamiltonian, hereby taking advantage of the fact that scalar-relativistic corrections are dominated by the one-electron contributions. The resulting electrons-only SF two-component Hamiltonian is then combined with the untransformed two-electron Coulomb interaction in the subsequent many-electron treatment. In this way, a SF relativistic method requires only the non-relativistic two-electron integrals and at the same time preserves the spatial and spin symmetry and thus is essentially as efficient as the corresponding non-relativistic method.

By contrast, the two-electron spin-orbit (SO) term makes significant contributions to the SO corrections to molecular energies and properties and thus has to be taken into account in accurate treatments of SO coupling. The two-electron SO term effectively screens the one-electron SO interaction. This screening may be efficiently taken into account by using parametrized screened nuclear charges in the evaluation of one-electron SO integrals or by using model densities derived from accurate atomic data within density-functional calculations. More rigorous treatments with explicit inclusion of two-electron SO integrals have been reported using the four-component Dirac-Coulomb approach or the Breit-Pauli Hamiltonian and are challenging due to the large number of molecular two-electron SO integrals required in the computation.

One possible underlying idea for obtaining a cost-effective treatment of two-electron SO contributions is the mean-field SO approach, which was first proposed by Heß et al. and has extensively been used in many applications. In general, a mean-field approximation of a genuine two-electron operator makes use of a predetermined mean-field wave function [a single determinant or a complete active space self-consistent-field (SCF) wave function] to generate an averaged effective one-electron operator. In molecular mean-field SO approaches using mean-field wave functions composed of non-relativistic...
or scalar-relativistic orbitals, the two-electron SO integrals are contracted with a spin-averaged self-consistent-field (SCF) density matrix to obtain effective one-electron SO integrals. Here the two-electron SO integrals need to be evaluated only once and processed in an on-the-fly fashion. The computational and storage requirements are thus greatly alleviated in comparison to those of fully relativistic methods. On the other hand, the use of orbitals optimized in the absence of SO coupling for the definition of the mean-field wave function may introduce noticeable errors for heavy-element containing systems. A molecular mean-field approach using a mean-field wave function composed of molecular spinors (instead of orbitals) has also been developed. In this approach, the four-component SCF equation is first solved and the four-component Fock matrix including both two-electron SF and SO contributions is block-diagonalized to obtain the two-component Hamiltonian matrix. Such a two-component approach is equivalent to the parent four-component method at the SCF level, while the integral-transformation step is greatly accelerated. The neglect of picture change effects for the fluctuation potential has been demonstrated to introduce rather small errors in the treatment of electron correlation.

Another central idea for enhancing the efficiency in the treatment of SO coupling is to exploit the local nature of the SO interactions. The one-electron SO integrals contain a local operator that scales as $1/|\vec{r} - \vec{R}_K|^2$, and thus they are “nearsighted.” The two-electron SO term serves as a screening of the one-electron SO interactions and is of a similar local nature. One-center approximations for the SO integrals have been successfully used within the molecular mean-field approaches. The so-called atomic mean-field (AMF) approach using atomic orbitals instead of molecular orbitals in the generation of mean-field SO integrals has been implemented and is widely used.

In this paper, we report an atomic mean-field (AMF) SO approach within exact two-component theory that combines the four main ideas in relativistic quantum chemistry mentioned above: the X2C decoupling scheme, the one-electron approximation for scalar-relativistic effects (i.e., the neglect of the scalar-two-electron picture-change effects), the mean-field SO approach, and the atomic approximation for the two-electron SO interactions. The Hamiltonian in the proposed SOX2CAMF scheme comprises the one-electron X2C Hamiltonian, the instantaneous electron-electron Coulomb interaction, and AMF SO integrals obtained using the solution of Dirac-Coulomb Hartree-Fock equations for spherically averaged atoms. The SOX2CAMF scheme requires no molecular relativistic two-electron integrals and is computationally appealing. The formulation of the SOX2CAMF scheme is introduced in Sec. II. Both Hartree-Fock calculations for diatomic molecules containing elements across the periodic table and coupled-cluster calculations for bismuth-containing diatomic molecules are presented in order to demonstrate the accuracy and applicability of the SOX2CAMF scheme. The computational details are given in Sec. III, while the computational results are presented and discussed in Sec. IV. Finally, a summary and a discussion of future developments are given in Sec. V.

II. THEORY

The two-component Hamiltonian of the proposed SOX2CAMF scheme is derived from the parent four-component theory by individually transforming three separate terms in the Dirac-Coulomb (DC) Hamiltonian into the two-component representation. The one-electron term in the DC Hamiltonian is block-diagonalized using the X2C decoupling scheme, giving rise to the one-electron term in the two-component Hamiltonian. The spin-free (SF) part of the two-electron term in the DC Hamiltonian reduces to the non-relativistic instantaneous Coulomb interaction, when the scalar two-electron picture change is neglected. The spin-dependent (SD) part of the two-electron term is approximated within an atomic mean-field approach using the solutions of the spherically averaged DC Hartree-Fock (HF) equations for individual atoms. As the three distinct terms in the DC Hamiltonian are separately treated, the present scheme is free of double counting of relativistic effects.

The four-component DC Hamiltonian in the occupation-number representation can be written as

$$H^{4c} = h^{4c,1e}_{pq} \epsilon_p \alpha_q + \frac{1}{2} \delta_{pq} C^{4c}_{\alpha \beta} \alpha_p \beta_q \alpha_q \beta_p.$$  

The summation over repeated indices is always assumed throughout the discussion. “No-pair” projection is imposed here with $p, q, \ldots$ representing positive energy state spinors. Unless otherwise stated, $p, q, \ldots$ are assumed to be eigenfunctions of the one-electron part of the DC Hamiltonian $h^{4c,1e}$. With the four-component spinors expanded in terms of a kinetically balanced basis set, the matrix elements of the one-electron Hamiltonian can be written as

$$h^{4c,1e}_{pq} = (C^{L} V C^{L} + C^{L^+} T C^{L^+} + C^{S^+} T C^{S^+})_{pq}.$$  

$V, T,$ and $W$ are the atomic-orbital (AO) integral matrices for the nuclear potential, the kinetic energy operator, and the relativistic one-electron operator,

$$V_{\mu\nu} = \langle f_\mu | V | f_\nu \rangle, \quad V = -\sum_{A} \frac{q_A}{|\vec{r} - \vec{R}_A|},$$  

$$T_{\mu\nu} = \langle f_\mu | T | f_\nu \rangle, \quad T = \frac{1}{2} \vec{p}^2,$$  

$$W_{\mu\nu} = \langle f_\mu | (\vec{\sigma} \cdot \vec{p}) V (\vec{\sigma} \cdot \vec{p}) | f_\nu \rangle,$$

in which $q_A$ represents the nuclear charge of nucleus $A$, $\vec{p}$ is the momentum operator, and $\vec{\sigma}$ is the vector of Pauli spin matrices. The transformation from the four-component to the two-component formulation is determined by two key relations, i.e., the relation between the large- and small-component wave functions and the relation between the large-component wave function and the two-component wave function. The corresponding essential quantities involved in
the X2C theory are the X matrix connecting the expansion coefficients for the large- and small-component wave functions,
\[ C^s = X C^l, \]
and the R matrix relating the large-component wave function and the two-component wave function,
\[ C^l = RC^s, \]
\[ R = (S^{-1} \tilde{S})^{-1/2}, \quad \tilde{S} = S + \frac{1}{2e^2} X^T TX. \]

Note that by definition the X2C matrix elements in terms of molecular spinors \( (h_{pq}^{2c,1e}) \) are identical to the corresponding matrix elements in the four-component theory \( (h_{pq}^{4c,1e}) \). By substituting Eqs. (7) and (8) into Eq. (3), the X2C one-electron Hamiltonian matrix elements \( ^{3,14,16,55} \) are readily obtained as
\[ h_{pq}^{2c,1e} = h_{pq}^{4c,1e} = C_{\mu \rho}^{2c} C_{\nu \lambda}^{1e} C_{\sigma \tau}^{2c}, \]
\[ h_{\mu \nu}^{2c,1e} = [R(V + X^T T + TX + X^T (\frac{1}{4e^2} W - T) X)]_{\mu \nu}. \]

The \( g_{\mu \nu}^{pq,rs} \)’s in Eq. (1) are the matrix elements for the instantaneous two-electron Coulomb interaction in terms of the four-component spinors,
\[ g_{\mu \nu}^{pq,rs} = C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{LLLL} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{LLSS} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL}, \]

with the AO integrals given by
\[ g_{\mu \nu}^{pq,rs} = (\mu | \nu \lambda), \]
\[ g_{\mu \nu}^{pq,rs} = \frac{1}{4e^2} (\mu | [\tilde{\sigma} \cdot \tilde{p} \nu] | \tilde{\sigma} \cdot \tilde{p} \lambda), \]
\[ g_{\mu \nu}^{pq,rs} = \frac{1}{4e^2} ([\tilde{\sigma} \cdot \tilde{p} \mu] | [\tilde{\sigma} \cdot \tilde{p} \nu] | [\tilde{\sigma} \cdot \tilde{p} \lambda]), \]
\[ g_{\mu \nu}^{pq,rs} = \frac{1}{16e^4} ([\tilde{\sigma} \cdot \tilde{p} \mu] | [\tilde{\sigma} \cdot \tilde{p} \nu] | [\tilde{\sigma} \cdot \tilde{p} \lambda]). \]

The Mulliken notation \( (\cdots | \cdots) \) is used here for the two-electron AO integrals, e.g.,
\[ (\mu | \nu \lambda) = \int \psi^\dagger (\mathbf{r}_1) \psi (\mathbf{r}_2) \frac{1}{r_{12}} f_{\mu} (\mathbf{r}_1) f_{\nu} (\mathbf{r}_2) f_{\lambda} (\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \]

Using the Dirac relation
\[ [\tilde{\sigma} \cdot \mathbf{A} | [\tilde{\sigma} \cdot \mathbf{B}] = \tilde{A} \cdot \tilde{B} + i \tilde{\sigma} \cdot [\tilde{A} \times \tilde{B}] = \tilde{A} \cdot \tilde{B} + i e_{uvw} A_u \sigma_u B_w, \]

in which \( e_{xyz} = 1 \) and \( e_{uvw} = -e_{u'vw} = -e_{uwv} = e_{uwv} \)
for \( u, v, w = x, y, z, \)
\( g_{pq,rs}^{2c,4c} \) can be partitioned into its SF and SD contributions,
\[ g_{pq,rs}^{2c,4c} = g_{pq,rs}^{2c,4c, SF} + g_{pq,rs}^{2c,4c, SD}, \]

The expression for the SF part \( g_{pq,rs}^{2c,4c, SF} \) can be written as
\[ g_{pq,rs}^{2c,4c, SF} = C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{LLLL} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{LLSS} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL}. \]

When the scalar-two-electron picture change is neglected, \( g_{pq,rs}^{2c,4c} \) reduces to the non-relativistic two-electron Coulomb integral, which is defined as the two-electron part of the present SOX2CAMF scheme,
\[ g_{pq,rs}^{2c,4c} = C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{LLLL}, \quad g_{pq,rs}^{2c,4c} = g_{pq,rs}^{2c,4c, SF}. \]

A detailed derivation is supplied in the Appendix and essentially follows ideas already sketched in Ref. 21. A subtle difference of the present derivation from that in Ref. 21 is that in Ref. 21 the total two-electron term \( g_{pq,rs}^{2c,4c} \) instead of the SF part is reduced to the non-relativistic two-electron Coulomb integrals in the two-component picture. We emphasize that the SD term in \( g_{pq,rs}^{2c,4c} \) is not required in obtaining the non-relativistic two-electron Coulomb integral in the derivation and thus can be treated separately, as proposed here.

Now we address the treatment of the two-electron SD term \( g_{pq,rs}^{2c,4c, SD} \) given by
\[ g_{pq,rs}^{2c,4c, SD} = C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{LLSS} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL} + C_{\mu \rho}^{pq} C_{\nu \lambda}^{rs} C_{\sigma \tau}^{SLLL}, \]

in which
\[ g_{pq,rs}^{2c,4c, SD} = \frac{1}{4e^2} ([\tilde{\sigma} \cdot \tilde{p} \mu] | [\tilde{\sigma} \cdot \tilde{p} \nu] | [\tilde{\sigma} \cdot \tilde{p} \lambda] + [\tilde{\sigma} \cdot \tilde{p} \nu] | [\tilde{\sigma} \cdot \tilde{p} \lambda] | [\tilde{\sigma} \cdot \tilde{p} \mu]), \]
\[ g_{pq,rs}^{2c,4c, SD} = \frac{1}{16e^4} ([\tilde{\sigma} \cdot \tilde{p} \mu] | [\tilde{\sigma} \cdot \tilde{p} \nu] | [\tilde{\sigma} \cdot \tilde{p} \lambda]). \]

Here \( u, v, w, u', v', w' \) are the Cartesian axes \( x, y, z \). We invoke a mean-field approximation for \( g_{pq,rs}^{2c,4c, SD} \)
\[ \sum_{\mu \nu}^{\dagger} \phi_{\mu,\nu}^{pq,rs} \phi_{\mu,\nu}^{pq,rs}, \]

in which \( \phi_{\mu,\nu}^{pq,rs} \) belong to a set of predetermined occupied spinors with \( n_{\mu,\nu}^{pq,rs} \) as the corresponding occupation numbers. Within the occupation-number representation, a mean-field approximation can be interpreted as re-writing the genuine two-electron interaction in normal order with respect to a chosen mean-field wave function as the vacuum and then discarding the normal-ordered two-electron part (the fluctuation potential of the two-electron interaction with respect to the chosen
A major computational advantage of the SOX2CAMF scheme over the one-electron term in Eq. (11), the two-electron density matrices in the construction of the atomic mean-field DC-HF density matrices instead of spin-averaged integrals, are defined to comprise these one-center mean-field SO integrals of the spherically averaged atom are solved, and the one-center SO integrals are evaluated using the CFOUR program. In future studies, it might be interesting to explore a model-density-based approach for the application in the Hartree-Fock method. In order to demonstrate the accuracy of the SOX2CAMF scheme for calculations of a variety of molecular properties. We mention that the model-potential techniques include a correction for both scalar and SO two-electron picture-change effects. In the example calculations presented in Secs. III and IV, the magnitude of these errors is analyzed to demonstrate the accuracy of the SOX2CAMF scheme for calculations of a variety of molecular properties. We mention that the model-potential techniques include a correction for both scalar and SO two-electron picture-change effects. On the other hand, such model-density-based approaches are most naturally formulated and implemented in the framework of density-functional theory, while a Hartree-only approximation has to be introduced for the application in the Hartree-Fock method.

In summary, the Hamiltonian of the SOX2CAMF scheme as given in Eq. (43) has been implemented within the CFOUR program. The implementation of the relativistic integrals has been verified by comparing Dirac-Coulomb Hartree-Fock results for closed-shell atoms with those obtained using the DIRAC program. In order to demonstrate the accuracy of the SOX2CAMF scheme, SOX2CAMF results obtained at the Hartree-Fock level for geometrical and electrical properties of selected diatomic molecules are reported and compared with the corresponding Dirac-Coulomb Hartree-Fock results. The test set for bond lengths and harmonic frequencies consists of the hydrogen halides (HX, X = F–At). For the benchmark calculations of the dipole moments and electric-field gradients, we adopt the test set introduced in Ref. 61 containing the hydrogen-halide series (HX, X = F–At). Uncontracted correlation-consistent triple-zeta basis sets have been used for H, F, and Cl, while uncontracted Dyall’s triple-zeta basis sets have been used for Br, I, and At. For the benchmark calculations of the dipole moments and electric-field gradients, we adopt the test set introduced in Ref. 61 containing the hydrogen-halide series (HX, X = F–At) and coinage-metal fluorides (CuF, AgF, and AuF) and further augment the test set with five bismuth compounds (BiN, BiP, BiF, BiCl, BiI). Spin-orbit effects are known to qualitatively affect calculated electric-field gradients at the position of the bismuth atom. Uncontracted ANO-RCC basis sets have been used for Br, I, and At. For the benchmark calculations of the dipole moments and electric-field gradients, we adopt the test set introduced in Ref. 61 containing the hydrogen-halide series (HX, X = F–At) and coinage-metal fluorides (CuF, AgF, and AuF) and further augment the test set with five bismuth compounds (BiN, BiP, BiF, BiCl, BiI). Spin-orbit effects are known to qualitatively affect calculated electric-field gradients at the position of the bismuth atom. A major computational advantage of the SOX2CAMF scheme in comparison with the parent four-component theory and the molecular mean-field approach based on the DC-HF density matrix is that the SOX2CAMF scheme does not require molecular relativistic two-electron integrals. In addition, analytic evaluation of nuclear forces within the SOX2CAMF scheme is convenient, as the AMF SO term is by definition geometrical independent. In Sec. IV, we will also show that the neglect of the response of the AMF SO term in the calculations of electrical properties such as dipole moments and electric-field gradients also produces accurate results. In contrast to the X2C mean-field SO approach for perturbative treatments of spin-orbit coupling and the sf-X2C+SO-DKHn methods, the present SOX2CAMF scheme does not involve an order-by-order expansion for the transformation of the SO operator and thus is specifically designed for use in non-perturbative treatments of spin-orbit coupling. The underlying approximations in the SOX2CAMF scheme, in comparison to the parent Dirac-Coulomb approach, are the neglect of the scalar two-electron picture-change correction and the AMF approximation for the two-electron SO term. In the example calculations presented in Secs. III and IV, the magnitude of these errors is analyzed to demonstrate the accuracy of the SOX2CAMF scheme for calculations of a variety of molecular properties. We mention that the model-potential techniques include a correction for both scalar and SO two-electron picture-change effects. On the other hand, such model-density-based approaches are most naturally formulated and implemented in the framework of density-functional theory, while a Hartree-only approximation has to be introduced for the application in the Hartree-Fock method.

In summary, the Hamiltonian of the SOX2CAMF scheme consists of the one-electron term in Eq. (11), the two-electron term in Eq. (26), and the AMF SO term in Eq. (42) and can be written as

\[ H_{\text{SOX2CAMF}} = h_{pq}^a C_{pq}^a C_{pq}^a + 1 \right \]

A major computational advantage of the SOX2CAMF scheme in comparison with the parent four-component theory and the molecular mean-field approach based on the DC-HF density matrix is that the SOX2CAMF scheme does not require molecular relativistic two-electron integrals. In addition, analytic evaluation of nuclear forces within the SOX2CAMF scheme is convenient, as the AMF SO term is by definition geometrical independent. In Sec. IV, we will also show that the neglect of the response of the AMF SO term in the calculations of electrical properties such as dipole moments and electric-field gradients also produces accurate results. In contrast to the X2C mean-field SO approach for perturbative treatments of spin-orbit coupling and the sf-X2C+SO-DKHn methods, the present SOX2CAMF scheme does not involve an order-by-order expansion for the transformation of the SO operator and thus is specifically designed for use in non-perturbative treatments of spin-orbit coupling. The underlying approximations in the SOX2CAMF scheme, in comparison to the parent Dirac-Coulomb approach, are the neglect of the scalar two-electron picture-change correction and the AMF approximation for the two-electron SO term. In the example calculations presented in Secs. III and IV, the magnitude of these errors is analyzed to demonstrate the accuracy of the SOX2CAMF scheme for calculations of a variety of molecular properties. We mention that the model-potential techniques include a correction for both scalar and SO two-electron picture-change effects. On the other hand, such model-density-based approaches are most naturally formulated and implemented in the framework of density-functional theory, while a Hartree-only approximation has to be introduced for the application in the Hartree-Fock method.
been used for the present benchmark calculations of electrical properties. All the SOX2CAMF results presented here as well as the results from calculations using the spin-free X2C in its one-electron variant (SFX2C-1e) scheme and spin-free Dirac-Coulomb (SFDC) approach for comparison have been obtained using the CFOUR program, while the benchmark Dirac-Coulomb results have been obtained using the DIRAC program.

In the calculations of the bond lengths and harmonic frequencies for each diatomic molecule, the energies for eleven points with an interval of 0.01 Å on the local potential curve close to the equilibrium structure have been calculated and fit to an eight-order polynomial. The equilibrium bond lengths and harmonic frequencies have been extracted using the coefficients of the polynomial. For the calculations of dipole moments and electric-field gradients at the Hartree-Fock level, analytic X2C-1e energy-derivative formulation as described in Ref. 66 has been used. Here we assume that &gamma;C, g2c, SD, AMF is fixed to the field-free values and is not included in the transformation of the property operators to the two-component representation.

Coupled-cluster singles and doubles (CCSD)\(^{67}\) with a perturbative treatment triple [CCSD(T)]\(^{68}\) excitations calculations using the SOX2CAMF Hamiltonian are also reported for the bond lengths, harmonic frequencies, and electric-field gradients of five bismuth compounds (BiN, BiP, BiF, BiCl, BiI). The SOX2CAMF-CCSD(T) calculations have used a recent implementation that features an atomic-orbital-based algorithm for the particle-particle ladder term.\(^{69}\) Here the computational results are compared with experimental values\(^{70-74}\) to demonstrate the accuracy and applicability of the SOX2CAMF-CCSD(T) method. Uncontracted ANO-RCC basis sets have been used for all CCSD(T) calculations. The 5p6s6p electrons of Bi, the 3s3p electrons of P and Cl, and the 2s2p electrons of N and F have been correlated together with all virtual spinors in the CCSD(T) calculations for BiN, BiF, BiP, and BiCl. The space of correlated spinors in the CCSD(T) calculations for BiI comprises the 5d6s6p electrons of Bi, the 4d5s5p electrons of I, and the virtual spinors with spinor energies lower than 1000 hartree. The CCSD(T) bond lengths and harmonic frequencies have been obtained using the same numerical procedure as described in the previous paragraph. The CCSD(T) electron-correlation contributions to the electric-field gradients at the position of the bismuth atom have been obtained by finite-difference calculations using a two-point formula and a field strength of 10\(^{-7}\) a.u., as suggested in Ref. 75.

### IV. RESULTS AND DISCUSSIONS

#### A. Benchmark calculations of molecular properties for representative diatomic molecules and comparison with Dirac-Coulomb results

Benchmark results for bond lengths, harmonic frequencies, dipole moments, and electric-field gradients (efgs) of selected diatomic molecules are reported in Tables I–IV. The SOX2CAMF results are given together with the SFX2C-1e results, with their difference ∆SO,X2C representing the SO corrections within the X2C scheme. Dirac-Coulomb (DC) results, spin-free Dirac-Coulomb (SFDC) results, and their difference ∆SO,4c are also reported for comparison. As shown in Table I and in line with previous benchmark studies,\(^{21,76,77}\) the SO corrections to the bond lengths are negligible (\(<0.0002\) Å) for molecules containing only first- and second-row elements but grow quickly when going down the periodic table. For HAt and At2, the SO corrections to bond lengths obtained in the four-component calculations amount to 0.0274 Å and 0.1272 Å, respectively. The SOX2CAMF scheme works well in recovering these SO corrections. The SO corrections in the X2C scheme amount to 0.0273 Å for HAt and 0.1274 Å for At2. The corresponding errors with respect to the four-component values are less than 0.0002 Å. Interestingly, the errors for the SO corrections in the SOX2CAMF scheme are of similar magnitude to the scalar two-electron

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*The ratio could not be determined accurately due to the small absolute value of the correction and the limited accuracy in the numerical procedure.*
picture-change errors (the difference between the SFDC and SFX2C-1e results). Therefore, the SOX2CAMF scheme seems to provide a balanced treatment of scalar-relativistic and SO effects.

Similar trends are observed in the calculations of harmonic frequencies. As shown in Table II, the SO corrections are negligible for first- and second-row elements but become important for compounds containing heavier elements, especially for the astatine compounds. The SOX2CAMF scheme provides excellent results here. For the SO corrections to the harmonic frequencies of the molecules in the present test set, the errors of the SOX2CAMF scheme with respect to four-component results are less than 0.3 cm\(^{-1}\). The SO corrections for HAt and At\(_2\) amount to \(-160.7\) cm\(^{-1}\) and \(-38.5\) cm\(^{-1}\), respectively, which compare favorably with the four-component values of \(-160.9\) cm\(^{-1}\) and \(-38.4\) cm\(^{-1}\).

As shown in Table III, the SOX2CAMF results for the SO corrections to the dipole moments are in excellent agreement with the four-component results for all molecules in the present test set, except for the HF molecule. The SO correction to the dipole moment of the HF molecule is insignificant and amounts to only \(-0.000\,006\,71\) a.u., but the SOX2CAMF result of \(0.000\,006\,52\) a.u. is qualitatively wrong. This observation agrees with the finding in a previous study dealing with perturbative treatments of SO corrections,\(^4\) namely, that the one-center approximation for the two-electron SO integrals leads to inaccurate results for this quantity. Another

<table>
<thead>
<tr>
<th>Four-component theory</th>
<th>Exact two-component theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFDC</td>
<td>SOX2CAMF</td>
</tr>
<tr>
<td>DC</td>
<td>(\Delta_{SO,4c})</td>
</tr>
<tr>
<td>HF 4477.4</td>
<td>4477.4</td>
</tr>
<tr>
<td>HCl 3134.3</td>
<td>3134.3</td>
</tr>
<tr>
<td>HBr 2785.8</td>
<td>2785.8</td>
</tr>
<tr>
<td>HI 2444.0</td>
<td>2444.0</td>
</tr>
<tr>
<td>HAt 2281.0</td>
<td>2281.0</td>
</tr>
<tr>
<td>F(_2) 1268.7</td>
<td>1268.7</td>
</tr>
<tr>
<td>Cl(_2) 613.6</td>
<td>613.6</td>
</tr>
<tr>
<td>Br(_2) 354.9</td>
<td>354.9</td>
</tr>
<tr>
<td>I(_2) 236.5</td>
<td>236.5</td>
</tr>
<tr>
<td>At(_2) 168.9</td>
<td>168.9</td>
</tr>
</tbody>
</table>

\(\Delta_{SO,4c}\) represents spin-orbit corrections in the four-component theory. The column \(\Delta_{SO,X2C}\) (the difference between SOX2CAMF and SFX2C-1e results) gives spin-orbit correction obtained from the proposed SOX2CAMF scheme.

### Table III. Dipole moments (in a.u.) computed at the HF-SCF level with uncontracted ANO-RCC basis sets.

<table>
<thead>
<tr>
<th>Four-Component Theory</th>
<th>Exact two-component theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFDC(^{61})</td>
<td>SFX2C-1(^{48})</td>
</tr>
<tr>
<td>DC(^{61})</td>
<td>SOX2CAMF</td>
</tr>
<tr>
<td>(\Delta_{SO,4c})</td>
<td>(\Delta_{SO,X2C})</td>
</tr>
<tr>
<td>HF 0.7548</td>
<td>0.7548</td>
</tr>
<tr>
<td>HCl 0.4599</td>
<td>0.4599</td>
</tr>
<tr>
<td>HBr 0.3546</td>
<td>0.3546</td>
</tr>
<tr>
<td>HI 0.2101</td>
<td>0.2101</td>
</tr>
<tr>
<td>HAt 0.0343</td>
<td>0.0343</td>
</tr>
<tr>
<td>CuF 2.4028</td>
<td>2.4028</td>
</tr>
<tr>
<td>AgF 2.6398</td>
<td>2.6398</td>
</tr>
<tr>
<td>AuF 2.1480</td>
<td>2.1480</td>
</tr>
<tr>
<td>BiN 1.9752</td>
<td>1.9752</td>
</tr>
<tr>
<td>BiP 1.9291</td>
<td>1.9291</td>
</tr>
<tr>
<td>BiF 1.4318</td>
<td>1.4318</td>
</tr>
<tr>
<td>BiCl 1.3425</td>
<td>1.3425</td>
</tr>
<tr>
<td>Bi 1.0951</td>
<td>1.0951</td>
</tr>
</tbody>
</table>

\(^{61}\) The ratio could not be determined accurately due to the small absolute value of the correction and the limited accuracy in the numerical procedure.
interesting observation is that the SO corrections obtained using the SOX2CAMF scheme tend to be more accurate for heavier elements. For example, the percentage of SO corrections recovered by the SOX2CAMF scheme is 90.8%, 97.0%, 98.1%, and 99.5% for HCl, HBr, HI, and HAt, respectively. A similar trend is observed for CuF, AgF, and AuF. The reason is that two-electron SO contributions in the case of heavier elements are dominated by the contributions from the core electrons, which are not perturbed significantly by the presence of other atoms in a molecule. Consequently, the atomic mean-field approach introduces smaller relative errors for heavier elements than for lighter elements. By contrast, the two-electron SO contributions to the dipole moment of the HF molecule are mainly due to the valence region and thus are inaccurately described by the atomic approximation. Therefore, if one is interested in faithfully reproducing the tiny SO corrections to dipole moments in systems containing only first-row elements, the molecular mean-field approaches instead of the AMF approach are recommended. Nevertheless, we conclude that the excellent performance of the SOX2CAMF scheme for heavy elements, especially for 6p-block elements with very large SO contributions, is promising.

The performance of the SOX2CAMF scheme for the calculation of efg’s is similar to that for dipole moments. The SOX2CAMF scheme works well for heavy elements, while the SO correction obtained from the SOX2CAMF calculation for the HF molecule is inaccurate (with a relative error of 209%). One exception is the CuF molecule, for which a large relative error in the SOX2CAMF calculation is observed. This can readily be attributed to a finding reported in a previous study, namely, that a partial cancellation among contributions from various SO integrals leads to the very small absolute magnitude for the SO correction to the Cu efg in CuF. The relative errors of the SOX2CAMF SO corrections for HAt and the five bismuth compounds are less than 3% in comparison to the corresponding four-component results. In particular, the SOX2CAMF scheme yields accurate SO corrections to the bismuth efg’s for all five bismuth compounds, for which the SO corrections are in the same magnitude as the total values. The errors of the SOX2CAMF scheme for the bismuth efg’s in comparison with the DC results are consistently at the order of several hundreds of atomic units, with the largest error appearing for BiP and amounting to 0.045 a.u. These errors are again of the same order of magnitude as the two-electron picture-change errors, which indicates a balanced treatment of scalar-relativistic and SO effects in the SOX2CAMF scheme. The good performance for efg’s demonstrates the accuracy of the SOX2CAMF scheme for the description of the core region.

### B. Spin-orbit coupled-cluster calculations of molecular properties for bismuth compounds

As example calculations for molecular properties of heavy-element containing compounds with accurate treatments of both relativistic and electron-correlation effects, the SOX2CAMF-CCSD(T) results for bond lengths, harmonic frequencies, and Bi electric-field gradients (efg’s) of the BiN, BiP, BiF, BiCl, and BiI molecules are given in Table V. For bond lengths and harmonic frequencies, the computational results are in general in good agreement with the experimental values. The discrepancies for the bond lengths are below 0.01 Å for BiN, BiP, BiF, and BiCl. The relatively large discrepancy for BiI (0.0101 Å) might tentatively be attributed to remaining basis-set effects that tend to shorten the bond. The computed harmonic vibrational frequencies agree very well with the available experimental values for BiP, BiF, BiCl, and BiI, with discrepancies smaller than 10 cm\(^{-1}\). On the other hand, the computed value of 755 cm\(^{-1}\) for BiN is around 20 cm\(^{-1}\) higher than the experimental value of 737 cm\(^{-1}\). Since remaining

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**TABLE IV.** Electric-field gradient (in a.u.) computed at the HF-SCF level with uncontracted ANO-RCC basis sets. The column \(\Delta_{SO,4c}\) (the difference between DC and SFDC results) represents spin-orbit corrections in the four-component theory. The column \(\Delta_{SO,X2C}\) (the difference between SOX2CAMF and SFXC-1e results) gives spin-orbit corrections obtained from the proposed SOX2CAMF scheme. The SFDC, SFXC-1e, and DC results are taken from Ref. 61 for all the molecules except the bismuth compounds, which have been calculated in the present work.

<table>
<thead>
<tr>
<th></th>
<th>SFDC</th>
<th>DC</th>
<th>(\Delta_{SO,4c})</th>
<th>SFXC-1e</th>
<th>SOX2CAMF</th>
<th>(\Delta_{SO,X2C})</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>2.8647</td>
<td>2.8647</td>
<td>(-1.10 \times 10^{-5})</td>
<td>2.8643</td>
<td>2.8644</td>
<td>2.29 \times 10^{-5}</td>
<td>(-209.3)</td>
</tr>
<tr>
<td>HCl</td>
<td>3.6370</td>
<td>3.6369</td>
<td>(-1.17 \times 10^{-4})</td>
<td>3.6361</td>
<td>3.6360</td>
<td>(-1.13 \times 10^{-4})</td>
<td>96.6</td>
</tr>
<tr>
<td>HBr</td>
<td>7.6033</td>
<td>7.6001</td>
<td>(-0.0032)</td>
<td>7.5981</td>
<td>7.5954</td>
<td>(-0.0028)</td>
<td>86.5</td>
</tr>
<tr>
<td>HI</td>
<td>11.6960</td>
<td>11.6703</td>
<td>(-0.0257)</td>
<td>11.6836</td>
<td>11.6599</td>
<td>(-0.0236)</td>
<td>91.8</td>
</tr>
<tr>
<td>HAt</td>
<td>26.7679</td>
<td>26.0721</td>
<td>(-0.6958)</td>
<td>26.7166</td>
<td>26.0387</td>
<td>(-0.6779)</td>
<td>97.4</td>
</tr>
<tr>
<td>CuF</td>
<td>(-1.2408)</td>
<td>(-1.2409)</td>
<td>(-0.0001)</td>
<td>(-1.2416)</td>
<td>(-1.2418)</td>
<td>(-0.0002)</td>
<td>286.4</td>
</tr>
<tr>
<td>AgF</td>
<td>(-2.5847)</td>
<td>(-2.5935)</td>
<td>(-0.0088)</td>
<td>(-2.5841)</td>
<td>(-2.5932)</td>
<td>(-0.0091)</td>
<td>103.8</td>
</tr>
<tr>
<td>AuF</td>
<td>(-4.3068)</td>
<td>(-4.6248)</td>
<td>(-0.3180)</td>
<td>(-4.3208)</td>
<td>(-4.6443)</td>
<td>(-0.3235)</td>
<td>101.7</td>
</tr>
<tr>
<td>BiN</td>
<td>(-12.8222)</td>
<td>(-5.7490)</td>
<td>(7.0732)</td>
<td>(-12.8096)</td>
<td>(-5.7404)</td>
<td>(7.0693)</td>
<td>99.9</td>
</tr>
<tr>
<td>BiP</td>
<td>(-13.2717)</td>
<td>(-9.7664)</td>
<td>(3.5054)</td>
<td>(-13.2584)</td>
<td>(-9.8080)</td>
<td>(3.4503)</td>
<td>98.4</td>
</tr>
<tr>
<td>BiF</td>
<td>11.3992</td>
<td>13.3855</td>
<td>(1.9863)</td>
<td>11.3741</td>
<td>13.3459</td>
<td>(1.9718)</td>
<td>99.3</td>
</tr>
<tr>
<td>BiCl</td>
<td>10.0254</td>
<td>11.9402</td>
<td>(1.9148)</td>
<td>10.0019</td>
<td>11.9233</td>
<td>(1.9213)</td>
<td>100.3</td>
</tr>
<tr>
<td>BiI</td>
<td>8.1105</td>
<td>10.6244</td>
<td>(2.5139)</td>
<td>8.0888</td>
<td>10.6038</td>
<td>(2.5151)</td>
<td>100.0</td>
</tr>
</tbody>
</table>
basis-set effects and contributions from correlation of inner-shell electrons are expected to further increase the computed value, it seems necessary to take into account higher-order correlation contributions to draw a firm conclusion for this discrepancy.

As reported in Table V, the computed efg’s at the position of the bismuth nucleus have been combined with the experimental values for $^{209}\text{Bi}$ quadrupole’s to obtain the value for the $^{209}\text{Bi}$ nuclear quadrupole moment using the standard formula

$$Q = \chi_{zz}/\kappa q_{zz}, \quad (45)$$

in which the $zz$ component of the efg $q_{zz}$ is given in atomic units, $\chi_{zz}$ is the $zz$ component of the nuclear quadrupole-coupling constant in MHz, $Q$ is the value of the nuclear quadrupole moment in millibarn (mb), and $\kappa$ is a conversion factor $\kappa = 1/0.234\,964\,7$. The experimental values of $\chi_{zz}$’s [894.5607(69) MHz for BiN, $^{70}$ 898.2172(46) MHz for BiP, $^{70}$ 1148.08(10) MHz for BiF, $^{71}$ 1027.0(120) MHz for BiCl, $^{72}$ and $909.5(20)$ MHz for BiI $^{73}$] have been adopted. The values for the $^{209}\text{Bi}$ nuclear quadrupole moment obtained from calculations of these five molecules are in the range of $-411$ to $-422$ mb. They appear to be consistent with the results from molecular studies in the literature $^{(-420}\text{mb})$ but deviate substantially from the value derived from atomic calculations $[-516(15)$ mb]. $^{79}$ While higher-order correlation contributions might be required to further improve the molecular calculations, it might also be worthwhile to revisit the atomic calculation in order to settle this controversy.

V. SUMMARY AND OUTLOOK

An atomic mean-field spin-orbit approach within the exact two-component theory (SOX2CAMF) is formulated and implemented for a non-perturbative treatment of spin-orbit coupling. The SOX2CAMF scheme does not require molecular relativistic integrals and is computationally efficient. The accuracy of the SOX2CAMF scheme for treating SO effects in heavy-element containing systems has been demonstrated by comparing SOX2CAMF results for a variety of molecular properties with results from the parent four-component theory. SOX2CAMF coupled-cluster calculations of selected bismuth-containing diatomic molecules and comparison with experimental results are also reported.

The next step forward is perhaps to extend the present formulation based on the Dirac-Coulomb Hamiltonian to include the Breit term. Analytic evaluation of nuclear forces is especially convenient within the SOX2CAMF scheme and will be useful for calculations of polyatomic molecules containing heavy atoms. While the response of the AMF SO term seems insignificant in the calculation of dipole moment and electric-field gradients, it might still be of interest to study the contribution from the response of the AMF SO term in the calculations of properties that potentially can strongly perturb the core region, e.g., magnetic hyperfine interaction. The SOX2CAMF Hamiltonian has been used together with CC methods in the present work but can also be combined with any other quantum-chemical methods including density-functional theory and multireference methodologies.

ACKNOWLEDGMENTS

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APPENDIX: SCALAR ONE- AND TWO-ELECTRON PICTURE CHANGE

The matrix elements for a one-electron four-component “even” operator

$$B^{4c} = \begin{pmatrix} B & 0 \\ 0 & B \end{pmatrix} \quad (A1)$$

in terms of four-component spinors can be written as

$$B^{4c}_{pq} = C_{\mu\nu}^{\star}C_{\mu\nu}^{\star}C_{\mu\nu}^{\star}C_{\mu\nu}^{\star} + \frac{1}{4\mu^{2}} e_{\mu\nu}^{\mu\nu}B_{\mu\nu}^{\mu\nu} + B_{\mu\nu}^{\mu\nu},$$

$$B^{4c}_{\mu\nu} = \langle \mu|\hat{B}|\nu \rangle, \quad B_{\mu\nu}^{\mu\nu} = B_{\mu\nu}^{\mu\nu},$$

$$B_{\mu\nu}^{\mu\nu} = \langle \mu|\hat{B}\cdot\hat{B}|\nu \rangle, \quad B_{\mu\nu}^{\mu\nu} = \langle \mu|\hat{B}|\nu \rangle.$$
The SF part $B_{pq}^{2c, SF} = C_{pq}^{c, SF}C_{pq}^{c, SF} + \frac{1}{4\xi} C_{pq}^{c, SF} B_{pq}^{2c, SF}$ can be transformed into the two-component representation and can be rewritten as

$$B_{pq}^{2c, SF} = B_{pq}^{c, SF} = C_{pq}^{c, SF}C_{pq}^{c, SF}$$

(A5)

$$B_{pq}^{c, SF} = \left[ R^I(B_{pq}^{LL} + \frac{1}{4\xi} X^I B_{pq}^{SS, SF} X) R^I \right]_{\mu\nu}.$$  

(A6)

Omitting the commutator between $\vec{p}$ and $B$, $B_{pq}^{SS, SF}$ can be approximated as

$$B_{pq}^{SS, SF} \approx \langle \mu | B \vec{p} \cdot \vec{p} | \nu \rangle = 2 \langle \mu | B T | \nu \rangle.$$  

(A7)

or

$$B_{pq}^{SS, SF} \approx \langle \mu | \vec{p} \cdot \vec{p} | \nu \rangle = 2 \langle \mu | T B | \nu \rangle.$$  

(A8)

By inserting the resolution of identity between $T$ and $B$, Eqs. (A7) and (A8) can further be approximated as

$$B_{pq}^{SS, SF} \approx 2(B^{LL} - T)^{1}_{\mu\nu}$$  

(A9)

and

$$B_{pq}^{SS, SF} \approx 2(TS - B^{LL})_{\mu\nu},$$  

(A10)

respectively. Using Eq. (A9) and further neglecting the commutator between $X^I$ and $B^{LL} - 1$, we obtain

$$B^{LL} + \frac{1}{4\xi} X^I B^{SS, SF} X \approx B^{LL} + \frac{1}{2\xi} X^I B^{LL} (B^{LL} - 1) X$$

(A11)

$$\approx B^{LL} (S + \frac{1}{2\xi} X^I TX)$$

(A12)

$$= B^{LL} S^{-1} S$$

(A13)

$$= B^{LL} R^{-2}.$$  

(A14)

Similarly, one can approximate Eq. (A10) as

$$B^{LL} + \frac{1}{4\xi} X^I B^{SS, SF} X \approx B^{LL} + \frac{1}{2\xi} X^I (B^{LL} - 1) X$$

(A15)

$$\approx (S + \frac{1}{2\xi} X^I TX) S^{-1} B^{LL}$$

(A16)

$$= S^{-1} S$$

(A17)

$$= [R^I]^2 B^{LL}.$$  

(A18)

The neglect of the commutator between $B^{LL}$ and $R$ and combining the results in Eqs. (A14) and (A18) give

$$B^{LL} + \frac{1}{4\xi} X^I B^{SS, SF} X \approx [R^I]^2 B^{LL} R^{-1}.$$  

(A19)

Substituting Eq. (A19) into Eq. (A6), we obtain

$$B_{pq}^{2c, SF} \approx B_{pq}^{c, SF}.$$  

(A20)

Among the approximations introduced above, the neglect of the commutator between the momentum operator and the property operator may lead to significant errors when the gradient of the property operator is large. This is, for example, why the “picture change” contribution is significant in the calculation of electric-field gradients.\(^{80,81}\)

It should be mentioned that the full $p_{pq}^{SS} = \langle \mu | [\vec{p} \cdot \vec{r}] B [\vec{r} \cdot \vec{p}] | \nu \rangle$ is also reduced to $2(\mu | B T | \nu)$ or $2(\mu | T B | \nu)$ when the commutator between $\vec{r} \cdot \vec{p}$ and $B$ is neglected since $\vec{r} \cdot \vec{p} \cdot \vec{p} = \vec{p} \cdot \vec{p} = 2T$. In other words, the neglect of the commutator between $\vec{r} \cdot \vec{p}$ and $B$ not only introduces the same approximation as the neglect of the commutator between $\vec{p}$ and $B$ but also omits all SD contributions. Therefore, although $B_{pq}^{2c}$ is reduced to $C_{pq}^{c, SF} B_{pq}^{c, SF}$ following essentially the same derivation given above, the SD term $p_{pq}^{SS}$ is not required in the derivation and can be treated separately.

The derivation for the two-electron Coulomb interaction follows essentially the same route. First take the contribution $C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF}$, SF as the example. This term may be rewritten as

$$C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF}$$

(A21)

with $(\xi^I_{\mu\nu})_{\mu\nu}$ and $(\xi^I_{\mu\nu})_{\mu\nu}$ defined as

$$(\xi^I_{\mu\nu})_{\mu\nu} = C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A22)

Following the same derivation as for the one-electron case, one obtains

$$C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} \approx C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A23)

Similarly, we have

$$C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} \approx C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A24)

and

$$C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} \approx C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A25)

Therefore, the SF part of two-electron Coulomb matrix elements $C_{pq}^{c, SF}$ can be reduced approximately to the nonrelativistic Coulomb matrix elements in terms of two-component wave function,

$$C_{pq, rs}^{c, SF} = C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF}$$

(A26)

$$\approx C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A27)

$$\approx C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A28)

$$\approx C_{pq}^{c, SF} C_{pq}^{c, SF} C_{pq}^{c, SF},$$

(A29)

11K. G. Dyall and K. Fegri, Introduction to Relativistic Quantum Chemistry (Oxford University Press, New York, 2007), part III.