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A new approach for relativistic correlated electron structure calculations is proposed by which a transformation to a two-spinor basis is carried out after solving the four-component relativistic Hartree–Fock equations. The method is shown to be more accurate than approaches that apply an *a priori* transformation to a two-spinor basis. We also demonstrate how the two-component relativistic calculations with properly transformed two-electron interaction can be simulated at the four-component level by projection techniques, thus allowing an assessment of errors introduced by more approximate schemes. © *2009 American Institute of Physics.* [doi:10.1063/1.3239505]

I. INTRODUCTION

It is well known that inclusion of relativistic effects is necessary to reach spectroscopic accuracy in electronic structure calculations. Since relativistic effects on the energy scale roughly as $Z^2\alpha^2$ (with Z as the nuclear charge and α as the fine-structure constant), these effects are often included by means of first-order (degenerate) perturbation theory. A more rigorous approach incorporates at least scalar relativistic effects in the standard nuclear attraction plus kinetic energy terms of the one-electron part of the Hamiltonian, whereas the spin-orbit (SO) coupling is typically treated via perturbation theory. This procedure requires a variationally stable Hamiltonian. Widely used examples are the second-order Douglas–Kroll Hamiltonian (DKH) as implemented by Douglas and Kroll[1] and Hess,[2,3] as well as the zeroth order regular approximation[4–6] (ZORA) Hamiltonian, but high-order transformations[7–9] are also gaining popularity. While these approaches deliver an accuracy that is sufficient for most applications, it was realized some years ago[10–15] that matrix algebra techniques, commonly employed in quantum chemistry, can also be used to improve upon the treatment of relativity in quantum chemical calculations. The key idea behind these methods, that now go under the name eXact 2-Component (X2C) methods,[16] is that it is easy to construct and diagonalize a matrix representation of a one-electron Dirac Hamiltonian. The resulting eigenvectors can be used to define a transformation that exactly decouples the equations for the positive-energy (pe) and negative-energy (ne) branches of the Dirac equation. The upper two components of this matrix equation constitute a Hamiltonian "for elec-

trons only"[12,17,39] that can be used in existing quantum chemistry codes in much the same way as the more approximate DKH or ZORA Hamiltonians.

The X2C methods and the older methods then often make the assumption that the two-electron interactions are well represented by an untransformed Coulomb operator; in other words, that two-electron picture change errors[18–20] are small. More elaborate schemes have been reported, most of them in the framework of density functional theory (DFT).[21–25] Samzow *et al.*[26] found negligible differences between using the free-particle Foldy–Wouthuysen transformation and no transformation of the Coulomb term in atomic Hartree–Fock (HF) calculations. Park and Almlöf,[27] on the other hand, reported errors on the order of tenths of eV's at the MP2 level for the dissociation energies of Pt_2 and Au_2. The calculations in Refs. 26 and 27 were, however, based on spin-free forms of these Hamiltonians. For a proper treatment of SO coupling the untransformed Coulomb term is clearly insufficient since the two-electron SO terms are completely neglected. Nakajima and Hirao[28] reported HF and DFT calculations in which the third-order DKH transformation was applied to both the one- and two-electron operators. More recently Seino and Hada[29] reported HF calculations employing the infinite-order (DKH) transformation in the same manner although with higher-order spin-dependent terms of the Coulomb term neglected. The latter two studies indicate that the free-particle Foldy–Wouthuysen transformation for the Coulomb term ($2e$-FP) is insufficient only for very heavy atoms. However, the formal costs of these calculations are at best equivalent to that of four-component (4C) calculations. A more cost-efficient approach is afforded by the Atomic Mean-Field approach (AMFI)[30] in which the two-electron SO contributions at the 2e-FP level are constructed in a mean-field fashion separately for each constituent atom of a molecule and then added to the matrix representation of the (effective) one-electron molecular Hamiltonian.[31]

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It is the purpose of the current paper to assess the spectroscopic errors that different realizations of the X2C approach introduce relative to a reference 4C calculation. In particular we demonstrate that the effect of the two-component (2C) two-electron interaction, properly transformed from the corresponding 4C one, can be simulated at the 4C level, thus avoiding programming of new two-electron integrals. We thereby study the net effect of these approximations on the fine-structure splitting of the open-shell halogen monoxides and the platinum monohydride molecule. In addition we define an efficient procedure to further reduce the error made in the X2C approach by limiting the two-electron picture change error to valence two-electron interactions. Due to the significant reduction in computational time, while hardly affecting accuracy, this approach is well suited for correlated relativistic calculations.

II. THEORY

A. Four-component relativistic theory

We consider the molecular Dirac equation of an electron moving in the electromagnetic field of a set of nuclei. We invoke the clamped-nuclei approximation and choose the inertial frame of the fixed nuclei as our reference frame.[32] This makes it possible to write the Dirac wave function as a product of time and spatial functions and subsequently remove the time dependence (on the relative time in this particular reference frame). The resulting equation in atomic units ($m_e=1$, $\hbar=1$, and $e=1$) can be written as

$$h_D\begin{pmatrix} L \\ S \end{pmatrix} = \begin{pmatrix} V_{\text{ext}} + c^2 & c(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}) \\ c(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}) & V_{\text{ext}} - c^2 \end{pmatrix}\begin{pmatrix} L \\ S \end{pmatrix} = \begin{pmatrix} L \\ S \end{pmatrix}E,\tag{1}$$

with mechanical momentum $\boldsymbol{\pi}=\mathbf{p}+\mathbf{A}$. The potential energy term $V_{\text{ext}}=-\phi_{\text{ext}}$ describes the interaction of the electron with the electrostatic potential ϕ_{ext} of the nuclei. In the following we ignore nuclear spins and thus set their contribution $\mathbf{A}_{\text{ext}}$ to the total vector potential $\mathbf{A}$ to zero. We furthermore subtract the constant rest mass energy c^2 of the electron to align the relativistic energy scale with the nonrelativistic one. The above equation has pe, E^+, and ne, E^-, solutions, where the former includes the bound electronic states that we are interested in.

Many-electron systems are treated by leaving the fully relativistic framework since a relativistic two-electron interaction is not readily available in closed form. We choose the Coulomb–Gaunt interaction operator[33] that describes both the charge-charge and the current-current instantaneous interactions between the electrons in the chosen reference frame[34] to give the Dirac–Coulomb–Gaunt (DCG) Hamiltonian

$$H_{\text{DCG}} = \sum_{i=1}^{n_{e^-}} h_D(i) + \frac{1}{2}\sum_{i\neq j}^{n_{e^-}} \left\{ \frac{1}{r_{ij}} - \frac{c\boldsymbol{\alpha}_i\cdot c\boldsymbol{\alpha}_j}{c^2 r_{ij}} \right\}.\tag{2}$$

As it stands, this Hamiltonian has no normalizable eigenstates since the bound states couple to continuum states, leading to the so-called Brown–Ravenhall disease.[35] Pestka *et al.*[36] demonstrated how bound states can be recovered by a complex-coordinate rotation technique. Alternatively, the Hamiltonian may be restricted to operate only on a space

with as basis functions the Slater determinants constructed from pe solutions only,

$$H_{\text{DCG}} \rightarrow P^+ H_{\text{DCG}} P^+.\tag{3}$$

This corresponds to embedding the many-electron Hamiltonian, Eq. (2), by operators projecting out the (occupied) ne solutions of the Dirac sea. At this point it is important to note that the separation of the spaces spanned by pe and ne solutions depends on the external potential. This means that such projection operators must always be defined with respect to the potential. At the 4C-HF level, as proposed by Mittleman,[37] the projection operators can be updated in each iteration of the self consistent field (SCF) procedure to correspond to the current mean-field potential, thus allowing full relaxation of the electronic wave function. In practice such projection operators are realized by choosing the occupied orbitals in each iteration by an *Aufbau* principle, but leaving solutions with eigenvalues below $-2c^2$ unoccupied. Orbital optimization thus corresponds to a min-max procedure in which the energy that is sought should be a minimum with respect to pe-pe rotations and a maximum with respect to pe-ne rotations.[34,38,39] At the correlated configuration interaction (CI) and Coupled-Cluster (CC) level it is no longer possible to update the projection operators since they refer to the now fixed one-particle basis. Complete relaxation of the electronic wave function is possible with a multiconfiguration SCF approach with the CI expansion limited to determinants built from pe orbitals only. In the limit of a complete CI expansion the pe-pe rotations, but not the pe-ne ones, then become redundant. The reader may consult Refs. 34 and 40 for a more extensive discussion of the 4C variational methods and the connection to the theory of quantum electrodynamics.

Returning to 4C-HF theory, we expand the spinors in a basis with components χ^L and χ^S for the large and small parts of the wave function, respectively,

$$\begin{pmatrix} L \\ S \end{pmatrix} = \boldsymbol{\chi}\mathbf{c} = \begin{pmatrix} \chi^L \\ 0 \end{pmatrix}\mathbf{c}^L + \begin{pmatrix} 0 \\ \chi^S \end{pmatrix}\mathbf{c}^S.\tag{4}$$

Various choices of basis are possible,[41,42] but it is important to satisfy the kinetic balance relation $\{\chi_i^S\}\subseteq\{\boldsymbol{\sigma}\cdot\mathbf{p}\chi_i^L\}$. One may, for instance, choose a generally nonorthogonal set of scalar Gaussian-type orbitals and evaluate matrix elements of the Hamiltonian and overlap by the standard techniques and implementations of nonrelativistic quantum chemistry. Any such expansion in separate basis sets for the large and small components results in the matrix equation

$$\mathbf{F}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i\varepsilon_i; \quad \mathbf{S} = \begin{pmatrix} \mathbf{S}^{LL} & 0 \\ 0 & \mathbf{S}^{SS} \end{pmatrix},\tag{5}$$

where the overlap matrix $\mathbf{S}$ appears, as well as the Fock matrix $\mathbf{F}$,

$$\mathbf{F} = \begin{pmatrix} \mathbf{V}^{LL} - \mathbf{K}^{LL} & \boldsymbol{\Pi}^{LS} - \mathbf{K}^{LS} \\ \boldsymbol{\Pi}^{SL} - \mathbf{K}^{SL} & \mathbf{V}^{SS} - \mathbf{K}^{SS} - 2c^2\mathbf{S}^{SS} \end{pmatrix}.\tag{6}$$

The latter contains small component overlaps S^{SS}, integrals $\Pi^{XY}(X,Y\in\{L,S\})$ over the kinetic energy operator $c(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})$, as well as integrals V^{XX} over the effective scalar potential,

$$V(\mathbf{r}_i) = V_{\text{ext}}(\mathbf{r}_i) + \int \frac{\rho^{\text{HF}}(\mathbf{r}_j)}{r_{ij}} d\mathbf{r}_j, \tag{7}$$

with ρ^{HF} as the HF density. The effective vector potential $\mathbf{A}$ contains a screening contribution from the Gaunt part of the two-electron interaction

$$\mathbf{A}(\mathbf{r}_i) = \mathbf{A}_{\text{ext}}(\mathbf{r}_i) + \frac{1}{c^2} \int \frac{\mathbf{j}^{\text{HF}}(\mathbf{r}_j)}{r_{ij}} d\mathbf{r}_j. \tag{8}$$

The Coulomb and the Gaunt terms both contribute to the exchange matrix $\mathbf{K}$. In the case of the Gaunt interaction this is the only nonzero contribution for closed-shell systems as the HF current density $\mathbf{j}^{\text{HF}} = \mathbf{0}$.

The matrix Fock equations can be simplified by transformation to orthonormal basis, which eliminates the overlap matrix. Different orthonormalization procedures are possible and the transformation is typically also used to eliminate near-linear dependencies and those combinations of small component basis functions that are not necessary for kinetic balance.[43] In the following we will assume that a transformation to orthonormal basis has been applied.

B. X2C transformations

Building a matrix representation of the Fock operator requires evaluation of two-electron integrals due to the presence of the small component basis. In addition to the "nonrelativistic" $\langle LL|LL \rangle$ class, the diagonal Coulomb operator gives rise to the integral classes $\langle LS|LS \rangle$ and $\langle SS|SS \rangle$, while the Gaunt operator demands the evaluation of the $\langle SS|LL \rangle$ class of integrals. Here and in the following we use Dirac notation, e.g.,

$$\langle \chi_p^L \chi_r^S | \chi_q^L \chi_s^S \rangle = \int \int \chi_p^{L\dagger}(1) \chi_q^L(1) \frac{1}{r_{12}} \chi_r^{S\dagger}(2) \chi_s^S(2) d\mathbf{r}_1 d\mathbf{r}_2. \tag{9}$$

The evaluation of these additional integrals is the main reason that 4C-HF calculations are much more expensive than 2C or nonrelativistic calculations. A secondary problem is the diagonalization of the larger 4C Fock matrix that has twice the dimension of a 2C matrix.

Both problems are addressed by defining a transformation that decouples the equations for the pe and ne solutions and yields an equation for the pe solutions only. We follow the procedure outlined by Iliaš and Saue.[15] The starting point is a matrix representation of the Dirac equation or alternatively, an effective one-electron equation, such as the corresponding HF or Kohn–Sham (KS) equation, in an orthonormal basis, Eq. (4). The generic equation is then given by

$$\mathbf{h}\mathbf{c}_i = \begin{pmatrix} \mathbf{h}^{LL} & \mathbf{h}^{LS} \\ \mathbf{h}^{SL} & \mathbf{h}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{c}_i^L \\ \mathbf{c}_i^S \end{pmatrix} = \begin{pmatrix} \mathbf{c}_i^L \\ \mathbf{c}_i^S \end{pmatrix} \varepsilon_i \tag{10}$$

and we can define a unitary transformation matrix $\mathbf{U}$ that brings the matrix representation of the Hamiltonian h to a block-diagonal[44,45] form,

$$\mathbf{U}^\dagger \mathbf{h} \mathbf{U} = \widetilde{\mathbf{h}} = \begin{pmatrix} \mathbf{h}^{++} & \mathbf{0} \\ \mathbf{0} & \mathbf{h}^{--} \end{pmatrix}. \tag{11}$$

It is convenient[46,47] to decompose the transformation matrix in a decoupling $\mathbf{W}_1$ and a renormalization matrix $\mathbf{W}_2$,

$$\mathbf{U} = \mathbf{W}_1 \mathbf{W}_2, \quad \mathbf{W}_1 = \begin{pmatrix} \mathbf{I} & -\mathbf{R}^\dagger \\ \mathbf{R} & \mathbf{I} \end{pmatrix},$$

$$\mathbf{W}_2 = \begin{pmatrix} (\mathbf{I} + \mathbf{R}^\dagger \mathbf{R})^{-1/2} & \mathbf{0} \\ \mathbf{0} & (\mathbf{I} + \mathbf{R}\mathbf{R}^\dagger)^{-1/2} \end{pmatrix} = \begin{pmatrix} \mathbf{W}^{++} & \mathbf{0} \\ \mathbf{0} & \mathbf{W}^{--} \end{pmatrix}. \tag{12}$$

The optimal choice for $\mathbf{U}$ is a transformation that minimizes the picture change and alters the spinor basis as little as possible. This constraint is usually fulfilled by fixing the diagonal blocks of $\mathbf{W}_1$ to be the unit matrices, solving only for the off-diagonal blocks $\mathbf{R}$.

The resulting X2C Hamiltonian is given by the $\mathbf{h}^{++}$ block of the transformed Hamiltonian, while the expansion coefficients for the X2C wave function are related to those of the 4C wave function by the inverse transformation,

$$\widetilde{\mathbf{c}}_i = \begin{pmatrix} \mathbf{c}_i^+ \\ \mathbf{c}_i^- \end{pmatrix} = \mathbf{U}^\dagger \mathbf{c}_i = \begin{pmatrix} \mathbf{W}^{++}(\mathbf{c}_i^L + \mathbf{R}^\dagger \mathbf{c}_i^S) \\ \mathbf{W}^{--}(\mathbf{c}_i^S - \mathbf{R}\mathbf{c}_i^L) \end{pmatrix}. \tag{13}$$

For pe solutions one would like the coefficients $\mathbf{c}_i^-$ to be zero, which leads to the condition

$$\mathbf{c}_i^S = \mathbf{R}\mathbf{c}_i^L \tag{14}$$

and the identification of $\mathbf{R}$ as the matrix representation of the coupling between the large and small components. Due to the decoupling, one can take the size of the matrices $\widetilde{\mathbf{h}}$ and $\widetilde{\mathbf{C}}$ to be only half that of the original basis, as the equations for the ne solutions can now be discarded. The final equation for the pe solutions reads

$$\mathbf{h}_{\text{X2C}}\mathbf{c}_i^+ = \mathbf{W}^{\dagger++}[\mathbf{h}^{LL} + \mathbf{h}^{LS}\mathbf{R} + \mathbf{R}^\dagger \mathbf{h}^{SL} + \mathbf{R}^\dagger \mathbf{h}^{SS}\mathbf{R}]\mathbf{W}^{++}\mathbf{c}_i^+ = \mathbf{c}_i^+ \varepsilon_i. \tag{15}$$

Apart from the representation in a finite basis and the restriction to positive energy solutions, no approximations are introduced at this stage: The spectrum of the X2C matrix equation, Eq. (15), is identical to the positive energy branch of the 4C Dirac matrix equation. Molecular properties can be calculated from the X2C wave function by using the (++)-block of transformed property operators $\mathbf{U}^\dagger \mathbf{P} \mathbf{U}$ (with $\mathbf{P}$ as the operator in the original 4C basis). For valence properties such as the electric dipole operator, one may use the approximation $\mathbf{U}^\dagger \mathbf{P} \mathbf{U} \approx \mathbf{P}$ since the transformation affects mainly the region close to the nuclei. However, making the same approximation to "core properties" such as nuclear electric quadrupole coupling constants leads to very large "picture change errors."[19,48,49]

At this point it will be useful to compare to other 2C relativistic equations in literature. From the relation Eq. (14) one can easily deduce $\mathbf{c}_i^+ = \widetilde{\mathbf{S}}^{1/2}\mathbf{c}^L$, where $\widetilde{\mathbf{S}} = \mathbf{I} + \mathbf{R}^\dagger \mathbf{R}$ suggesting that $\mathbf{h}_{\text{X2C}}$ can be constructed from the large component basis only. Inserting this relation into the X2C equation, Eq. (15), and premultiplication with $\widetilde{\mathbf{S}}^{1/2}$ then gives

$$[\mathbf{h}^{LL} + \mathbf{h}^{LS}\mathbf{R} + \mathbf{R}^{\dagger}\mathbf{h}^{SL} + \mathbf{R}^{\dagger}\mathbf{h}^{SS}\mathbf{R}]\mathbf{c}_i^L = \widetilde{\mathbf{S}}\mathbf{c}_i^L\varepsilon_i, \quad (16)$$

which can be identified as the equation for the normalized elimination of the small components (NESCs).[10] *Exact* decoupling implies the relation

$$\mathbf{R}(\mathbf{h}^{LL} + \mathbf{h}^{LS}\mathbf{R}) = \mathbf{h}^{SL} + \mathbf{h}^{SS}\mathbf{R}, \quad (17)$$

which can be used to simplify the NESC equation to

$$\mathbf{L}\mathbf{c}_i^L\varepsilon_i = \mathbf{c}_i^L\varepsilon_i, \quad \mathbf{L} = \mathbf{h}^{LL} + \mathbf{h}^{LS}\mathbf{R}, \quad (18)$$

which in turn is identified as the equation for the unnormalized elimination of the small components (UESC).[10] This is, however, a non-Hermitian eigenvalue problem, which need not have sufficient solutions to diagonalize H. Premultiplication with $\widetilde{\mathbf{S}}$ and symmetrization leads to the Hermitian eigenvalue problem

$$\tfrac{1}{2}[\widetilde{\mathbf{S}}\mathbf{L} + \mathbf{L}^{\dagger}\widetilde{\mathbf{S}}] = \widetilde{\mathbf{S}}\mathbf{c}_i^L\varepsilon_i \quad (19)$$

which can be identified as equation for the symmetrized elimination of the small components (SESCs).[25,39] It should be pointed out that these variants of ESC are normally presented in terms of the modified Dirac equation,[50,51] which corresponds to the matrix representation of the standard Dirac equation in a restricted kinetic balance basis.[12]

Note that the equivalence of X2C and NESC on the one hand and UESC and SESC on the other hand hinges on using the exact coupling $\mathbf{R}$, that is the validity of Eq. (17). For approximate couplings X2C/NESC and UESC/SESC introduce errors of $O(c^{-2})$ and $O(c^{-4})$, respectively.[10] If the decoupling starts from the 4C-HF or KS matrix, Eq. (6), then the corresponding UESC/SESC matrix, Eqs. (18) and (19) can be constructed without the $\langle SS|SS \rangle$ class of two-electron integrals, in contrast to the X2C/NESC matrices. However, this integral class is needed in order to extract the exact coupling $\mathbf{R}$, in part needed for exact equivalence between X2C/NESC and UESC/SESC.

C. The two-electron interaction in a two-component relativistic framework

Approximations necessarily enter in the treatment of the two-electron interaction. The exact decoupling of a many-electron relativistic Hamiltonian such as Eq. (2) is as difficult as finding its exact eigenfunctions, so we will rather consider the transformation of the two-electron interaction in terms of unitary transformations defined in a one-electron framework. We write the electronic Hamiltonian in the second-quantization formalism as

$$\hat{H} = \int \psi^{\dagger}(1)\hat{h}(1)\psi(1)d1$$
$$+ \frac{1}{2}\int \psi^{\dagger}(1)\psi^{\dagger}(2)\hat{g}(1,2)\psi(2)\psi(1)d1d2, \quad (20)$$

where the field operator $\psi(1)$ is projected onto a basis $\{\phi_P\}$,

$$\psi(1) = \sum_P \phi_P(1)a_P, \quad (21)$$

giving

$$\hat{H} = \sum_{PQ} h_P^Q(1)a_P^{\dagger}a_Q + \frac{1}{2}\sum_{PQRS} G_{PR}^{QS}a_P^{\dagger}a_R^{\dagger}a_S a_Q. \quad (22)$$

If separate orthonormal bases are chosen for the large and small components, as in Eq. (4), the one-electron integrals h_P^Q correspond to elements of the matrix representation of the Dirac equation given in Eq. (10). Application of a decoupling transformation $\mathbf{U}$, Eq. (12), splits the one-electron term of Eq. (22) into positive (h^{++}) and negative (h^{--}) energy parts. If a decoupling transformation generated from a *different* 4C one-electron Hamiltonian $\hat{h}$ is employed, coupling terms h^{+-} and h^{-+} will appear. Retaining only the h^{++} part is strictly equivalent to restricting the summation of Eq. (21) to 4C pe solutions of the generating (effective) one-electron Hamiltonian.

Applying the picture-change transformation, Eq. (12) for both electrons in the corresponding two-electron integrals G_{PR}^{QS} yields

$$(\mathbf{U}(1) \otimes \mathbf{U}(2))^{\dagger}\mathbf{G}(1,2)(\mathbf{U}(1) \otimes \mathbf{U}(2))$$

$$= \begin{pmatrix} \widetilde{\mathbf{G}}_{++}^{++} & \widetilde{\mathbf{G}}_{++}^{+-} & \widetilde{\mathbf{G}}_{++}^{-+} & \widetilde{\mathbf{G}}_{++}^{--} \\ \widetilde{\mathbf{G}}_{+-}^{++} & \widetilde{\mathbf{G}}_{+-}^{+-} & \widetilde{\mathbf{G}}_{+-}^{-+} & \widetilde{\mathbf{G}}_{+-}^{--} \\ \widetilde{\mathbf{G}}_{-+}^{++} & \widetilde{\mathbf{G}}_{-+}^{+-} & \widetilde{\mathbf{G}}_{-+}^{-+} & \widetilde{\mathbf{G}}_{-+}^{--} \\ \widetilde{\mathbf{G}}_{--}^{++} & \widetilde{\mathbf{G}}_{--}^{+-} & \widetilde{\mathbf{G}}_{--}^{-+} & \widetilde{\mathbf{G}}_{--}^{--} \end{pmatrix}, \quad (23)$$

where the subscript (superscript) refers to the bra (ket) of the two-electron integrals in the Dirac notation, Eq. (9). If the basis is restricted to the positive energy solutions (the no-pair approximation) only the matrix elements of the upper-left block $\widetilde{\mathbf{G}}_{++}^{++}$ remain. These transformed integrals are given by the expression

$$\widetilde{\mathbf{G}}_{++}^{++} = \mathbf{W}^{\dagger++}(1)\mathbf{W}^{\dagger++}(2)(\mathbf{G}_{++;UC}^{++} + \mathbf{G}_{++;UG}^{++})\mathbf{W}^{++}(2)\mathbf{W}^{++}(1), \quad (24)$$

in which we define the un-normalized Coulomb (UC) as

$$\mathbf{G}_{++;UC}^{++} = \mathbf{G}_{LL}^{LL} + \mathbf{R}^{\dagger+S}(2)\mathbf{G}_{LS}^{LS}\mathbf{R}^{S+}(2) + \mathbf{R}^{\dagger+S}(1)\mathbf{G}_{SL}^{SL}\mathbf{R}^{S+}(1)$$
$$+ \mathbf{R}^{\dagger+S}(1)\mathbf{R}^{\dagger+S}(2)\mathbf{G}_{SS}^{SS}\mathbf{R}^{S+}(1)\mathbf{R}^{S+}(2) \quad (25)$$

and un-normalized Gaunt (UG) integrals

$$\widetilde{\mathbf{G}}_{++;UG}^{++} = \mathbf{G}_{LL}^{SS}\mathbf{R}^{S+}(1)\mathbf{R}^{S+}(2) + \mathbf{R}^{\dagger+S}(2)\mathbf{G}_{LS}^{SL}\mathbf{R}^{S+}(1)$$
$$+ \mathbf{R}^{\dagger+S}(1)\mathbf{G}_{SL}^{LS}\mathbf{R}^{S+}(2) + \mathbf{R}^{\dagger+S}(1)\mathbf{R}^{\dagger+S}(2)\mathbf{G}_{SS}^{LL}. \quad (26)$$

As is evident from the expressions, the exact evaluation of the transformed integrals requires evaluation of all original integrals, making the calculations more, rather than less, expensive. This observation is evidently also true when transformations based on an approximate coupling $\hat{R}$ between the large and the small components are used.

Cost reductions should come from approximate expressions that eliminate the need to evaluate the contribution the integrals involving the small component basis as much as possible. The simplest of such approximations is to neglect the contribution of the $\mathbf{G}_{SS}^{SS}$ integrals, or even all integrals other than $\mathbf{G}_{LL}^{LL}$. This approximation is readily carried out in 4C calculations and leads to a non-negligible effect on the

total electronic energy. This is easily interpreted as an underestimation of electron repulsion energy due to the neglect of the small-small and small-large repulsions.[52–54] The effect is largest for the core electrons, where up to a few percent of the density is contained in the small component. In a 2C picture this approximation takes the form

$$\widetilde{\mathbf{G}}^{++}_{++} \approx \mathbf{W}^{\dagger++}(1)\mathbf{W}^{\dagger++}(2)\mathbf{G}^{LL}_{LL}\mathbf{W}^{++}(2)\mathbf{W}^{++}(1) \qquad (27)$$

and reduction in two-electron repulsion is apparent due to the fact that we have $\mathbf{W}^{++}=(1+\mathbf{R}^{\dagger}\mathbf{R})^{-1/2}<1$. Realizing this problem one may also consider the approximation

$$\widetilde{\mathbf{G}}^{++}_{++} \approx \mathbf{G}^{LL}_{LL}, \qquad (28)$$

which corresponds to the complete neglect of two-electron picture change.

At the SCF level the error due to this neglect of two-electron picture change can be reduced by constructing corrections to the untransformed two-electron term from atomic contributions. One example is the AMFI approach[30,31] in which the spin same-orbit and spin other-orbit contributions at the free-particle ($2e$-FP) level, arising from the Coulomb and Gaunt terms, respectively,[55] are constructed in a mean-field fashion based on spin-free second-order DKH atomic calculations. A straightforward improvement of this procedure, which also allows the inclusion of scalar relativistic corrections, is to rather construct these atomic contributions from an exact picture change transformation of the corresponding converged atomic HF or KS matrices. A molecular correction term is then computed using the integrals of the untransformed two-electron operator. In this way one treats core-core interactions, for which the molecular corrections are small, almost exactly. A procedure along these lines was reported in the framework of DFT by Liu and Peng.[56]

The same idea can be used at the correlated level (CC and CI). We assume a closed shell reference and write the Hamiltonian for the valence electrons on normal-ordered form

$$H = \sum_{PQ} F^{Q}_{P}\{a^{\dagger}_{P}a_{Q}\} + \frac{1}{4}\sum_{PQRS} V^{QS}_{PR}\{a^{\dagger}_{P}a^{\dagger}_{R}a_{S}a_{Q}\}, \qquad (29)$$

where brackets indicate normal ordering with respect to occupied (hole) and virtual (particle) orbitals. Here F^{Q}_{P} are elements of the Fock matrix and $V^{QS}_{PR}=G^{QS}_{PR}-G^{SQ}_{PR}$ are antisymmetrized two-electron integrals. The summation is formally restricted to pe orbitals but in practice, it is even further reduced due to truncations of the occupied and virtual space commonly employed in correlated calculations. The matrix elements F^{Q}_{P} can be obtained from exact decoupling of the corresponding converged 4C *molecular* Fock matrix. If the basis chosen for the correlation calculation is taken to be the canonical HF orbitals, the list of nonzero matrix elements reduces to the orbital energies $\varepsilon : F^{Q}_{P}=\varepsilon_{P}\delta_{PQ}$.

At this point it is important to realize that the computational cost of 2C and 4C correlated (CC or CI) calculations is strictly identical since both approaches employ pe orbitals only. However, the approaches proposed above can reduce the effort spent in the four-index transformation needed to construct the two-particle matrix $\mathbf{G}$ in the molecular basis.

TABLE I. Overview of the approximate Hamiltonians used in this work.

Acronym	Description
^{4}DC	DC Hamiltonian
^{4}DC(P_{nuc})	DC Hamiltonian, projected on pe solutions of the bare nuclei Hamiltonian
^{4}DC(P_{free})	DC Hamiltonian, projected on pe solutions of the free particle Hamiltonian
^{2}DC(U_{nuc})	DC Hamiltonian, bare nuclei Hamiltonian defines transformation to 2C basis
^{2}DC^A(U_{nuc})	DC Hamiltonian, bare nuclei Hamiltonian defines transformation to 2C basis
	Atomic mean-field approximation for Coulomb interaction
^{4}DCG	DCG Hamiltonian
^{4}DCG*	DCG Hamiltonian
	Gaunt contribution to valence $2e$-interactions neglected
^{4}DCG**	DCG Hamiltonian
	Only G^{LL}_{LL} contribution to valence $2e$-interactions included
^{2}DCG^M(U_{mol})	DCG Hamiltonian, converged Fock operator defines transformation to 2C basis
	Molecular mean-field approximation for valence $2e$-interactions
^{2}DCG^A(U_{nuc})	DCG Hamiltonian, bare nuclei Hamiltonian defines transformation to 2C basis
	Atomic mean-field approximation for $2e$-interactions
^{2}DCG^0(U_{nuc})	DCG Hamiltonian, bare nuclei Hamiltonian defines transformation to 2C basis
	Relativistic corrections to $2e$-interactions neglected

As indicated above the properly transformed effective one-electron part $\mathbf{F}$ can be obtained at no additional costs once the converged 4C-HF solution is available. One may then employ an approximation by replacing the complete two-electron interaction $\widetilde{\mathbf{G}}^{++}_{++}$ by the nonpicture transformed operator $\mathbf{G}^{LL}_{LL}$ in the index transformation algorithm that is used to provide the matrix elements G^{QS}_{PR}. Specifically, in the following we will explore using the full Coulomb–Gaunt operator only in the construction of a 4C Fock matrix. This matrix will then be reduced to 2C form and employed together with the untransformed Coulomb operator in correlated calculations.

D. Summary of computational protocols

The considerations given above give rise to a large number of possible combinations of approximations. In this section we will identify the most promising approaches and define a limited number of models that are worthwhile to investigate. These are given in Table I in which we distinguish between models based on the Dirac–Coulomb (DC) and the more complete DCG Hamiltonian. The former allows for full analysis of the various approximations as various correlation methods are implemented for this Hamiltonian. We use this approach to study the effect of a replacement of the iterative (implicit) projection on the pe HF solutions by employing predefined projection operators based on either the free particle solutions or the solutions from the bare nuclei Hamiltonian (electrostatic potential given by the unscreened nuclear attraction). The latter ap-

TABLE II. Total HF energy (a.u.) of noble gas atoms calculated with different 4C and 2C Hamiltonians, see Table I for explanation of acronyms.

	^{4}DC	^{4}DC(P_{nuc})	^{4}DC(P_{free})	^{2}DC(U_{nuc})[a]	^{2}DC^A(U_{nuc})
Ne	−128.6912	−128.6912	−128.7115	−128.6912	−128.6841
Ar	−528.6832	−528.6832	−529.0199	−528.6831	−528.6328
Kr	−2788.8791	−2788.8795	−2797.1538	−2788.8770	−2788.3863
Xe	−7447.1271	−7447.1302	−7500.7640	−7447.1071	−7445.1901
Rn	−23 610.2163	−23 610.2463	−24 149.5150	−23 610.0370	−23 599.5567
Uuo	−55 023.8205	−55 023.9995	−59 465.2958	−55 023.3280	−54 974.0921

[a]Reference 29.

proach, ^{4}DC(P_{nuc}), should yield identical results to a full X2C treatment in which picture change corrections of the two-electron interaction are calculated, ^{2}DC(U_{nuc}). A more common and more efficient procedure is to approximate such picture change effects by the atomic mean field approximation, yielding the method ^{2}DC^A(U_{nuc}). The same set of protocols is possible for the DCG Hamiltonian but since the effect of fixing the projection operators will not depend much on the choice of two-electron operator, we will not explicitly investigate this point. The methods labeled ^{4}DCG and ^{2}DCG^A(U_{nuc}) are the reference method (no approximations) and the most commonly employed realization of the X2C approach, respectively. To illustrate the need to include SO screening corrections we will also list some results in which the atomic mean field correction is omitted, ^{2}DCG^0(U_{nuc}), but it is obvious that this approach should not be used in actual applications.

As discussed above, it may be beneficial for high-level correlated calculations to define methods that are less expensive than the ^{4}DCG treatment and less approximate than the ^{2}DCG^A(U_{nuc}) approach. The first of these is the ^{4}DCG* method in which only the set of two-electron integrals needed for the electron correlation treatment is calculated without including the Gaunt interaction. These approximate two-electron integrals are to combined with a set of exact effective one-electron matrix elements [conveniently available in molecular orbital (MO) basis as the set of converged orbital energies], yielding a molecular mean field approximation of just the Gaunt interaction. This approximation can be extended to neglect of all integrals that include small component basis functions, giving the method labeled ^{4}DCG** and corresponding to the approximation given in Eq. (27). As indicated by the first superscript, both methods are still formulated in terms of 4C wave functions. An alternative, which provides a proper normalization of the two-electron interaction, is to use the converged HF solutions to transform to a 2C basis. We can then use Eq. (28) yielding the method labeled ^{2}DCG^M(U_{mol}).

III. COMPUTATIONAL DETAILS

All calculations were done with a development version of the DIRAC package,[57] employing a value of 137.035 999 8 a.u. for the speed of light. To facilitate direct comparison with the results reported in Ref. 29, a point nucleus was employed in the calculations of noble gas atoms. For the other systems we used an isotropic Gaussian model for the nuclei.[58]

In the DIRAC program the four-index transformation of the Gaunt integrals is not yet implemented, which implies that for correlation calculations this part of the two-electron interaction can only be included in the Fock matrix elements. The most accurate method available is thus the ^{4}DCG* approach.

For the noble gases we used the same basis sets as in Ref. 29. In the other calculations Dunnings augmented correlation consistent quadruple zeta basis[59–61] sets were used for the elements from H to Br, while the Dyall augmented triple zeta correlation consistent basis[62] were employed for the heavier elements (Pt and I). Basis sets are uncontracted to allow for sufficient flexibility in the description of the core region.[63,64] All correlated calculations started with a HF calculation on a molecule with one additional electron followed by a Fock space CC calculation of the ionization energies thereof to obtain the SO splitting of the neutral molecule. This is necessary as the Fock space method needs a single reference state from which the active space is constructed. The X2C implementation by Saue and Iliaš was described in Ref. 15, while the Fock Space Coupled Cluster (FSCC) implementation by Visscher *et al.* was discussed in Ref. 65. Principles of the inclusion of the AMFI Hamiltonian in a 2C variational approach are given in Ref. 66 while the current implementation of AMFI (Ref. 67) in the DIRAC program suite shall be described in a future publication.

The number of electrons correlated was 14 for FO and ClO, 24 for BrO and IO, and 34 for PtH. The cutoff value for virtual orbitals to be taken into account in the correlation calculations was set at 20.0 a.u. The active space used in the Fock space calculations on the halogen monoxides consisted of the two π^* orbitals, while the active space used in PtH consisted of the five Pt 5d orbitals. Bond distances were taken from experimental data, specifically 1.354 Å [FO (Ref. 68)], 1.569 Å [ClO (Ref. 69)], 1.721 Å [BrO (Ref. 70)], 1.868 Å [IO (Ref. 71)], and 1.529 Å [PtH (Ref. 72)].

IV. RESULTS AND DISCUSSION

In Table II we report total HF energies of the noble gas atoms calculated with different 4C and 2C Hamiltonians. Embedding the DC Hamiltonian by the projection operator P_{nuc}^+ onto the pe solutions of the Dirac equation in the electrostatic potential of the bare nucleus introduces slight, but for most purposes acceptable errors, whereas sizable errors

TABLE III. Effect of projection operators on the SO splitting (cm^{-1}) for the $^2\Pi$ ground state of the XO (X=F,Cl,Br,I) molecules, see Table I for explanation of acronyms.

	Molecule			
Method	FO	ClO	BrO	IO
^{4}DC	221.151	345.411	1024.108	2215.662
^{4}DC(P_{nuc})	221.152	345.410	1024.113	2215.675
Error	0.001	0.001	0.005	0.013

TABLE IV. SO splittings in cm^{-1} for the XO (X, F, Cl, Br, I) molecules computed at equilibrium distances using the FSCC method in an aug-cc-pVQZ basis. The first line gives the 4C reference result based on the DCG Hamiltonian, the other lines concern results from approximate methods, see Table I for explanation of acronyms.

	FO	ClO	BrO	IO
^{4}DCG*	199.78	323.68	996.57	2183.79
^{4}DCG**	201.16	324.48	997.54	2185.01
^{2}DCG$^M(U_{mol})$	201.13	324.43	997.30	2184.40
^{2}DCG$^A(U_{nuc})$	194.86	321.45	994.49	2180.98
^{2}DCG$^0(U_{nuc})$	299.91	429.05	1145.17	2369.45
Expt.[a]	196.6	322.0	975.4	2091(40)

[a]References [68–70] and [74].

are observed when the free-particle projector P^+_{free} is employed, in line with the warning issued by Heully *et al.*[73] We furthermore observe that the use of fixed projection operators such as P^+_{nuc} and P^+_{free} systematically leads to lower energies compared to the continuously updated mean-field projector in a standard 4C calculation. This can be understood from the min-max principle since the introduction of ne solutions should raise the energy. In Table II we further report results of X2C calculations, using either transformed two-electron operators ^{2}DC(U_{nuc}) or the atomic mean field approximation ^{2}DC$^A(U_{nuc})$. The results obtained with the projected 4C Hamiltonian are formally equivalent to the full X2C approach and we indeed observe a very good agreement between the ^{4}DC(P_{nuc}) and the ^{2}DC(U_{nuc}) results reported by Seino and Hada[29] that were calculated in the same basis. The slight discrepancy for the heavier noble gases is thus probably due to the neglect of higher-order spin-dependent two-electron terms in the latter calculations. The errors introduced by the approximate treatment of the two-electron contributions can be assessed by comparing these results with those of the ^{2}DC$^A(U_{nuc})$ approach. For the heavier noble gases a significant deviation is observed, reaching almost 50 hartree for Uuo, although the relative error remains small.

The SO splitting in the ground state of the halogen monoxides is a convenient measure for the relevance for molecular applications of the errors introduced by the various approximations. We first consider the errors associated with the use of a decoupling transformation based on the 4C bare-nucleus Hamiltonian. In Table III we compare the SO splitting of the $^2\Pi$ ground state calculated using the unprojected H_{DC} and projected $P^+_{nuc}H_{DC}P^+_{nuc}$ DC Hamiltonian, again keeping in mind that the latter Hamiltonian is strictly equivalent to a fully transformed X2C Hamiltonian. It is clear that this approximation, which forms the basis for almost all approximate 2C schemes, does indeed result in errors much smaller than the typical accuracy of an electron correlation calculation.

We next add the Gaunt interaction and consider the effect of approximating the two-electron interaction in the ways described above. Compared to the experimental data the standard X2C method appears to perform best for the halogen monoxides (Table IV). The results for the PtH molecule (Table V) show, however, that this is the result of error cancellation: For PtH the results of the ^{4}DCG* calculation are closer to experiment as could be expected. From Table IV it is obvious that the error made by the unscreened X2C approach ^{2}DCG$^0(U_{nuc})$ is an order of magnitude larger than

the error in the other schemes. All other schemes give results in good agreement with the reference approach ^{4}DCG*, with the ^{2}DCG$^M(U_{mol})$ method deviating the least. It is interesting to see that the two ways to approximate the two electron interaction—leaving out the valence *SL* and *SS* part in a 4C approach, or apply the ^{2}DCG$^M(U_{mol})$ method—give nearly identical results. As shown in Sec. II B the two methods differ by the renormalization factor introduced in the X2C wave function, compare Eqs. (27) and (28). From Tables IV and V it is clear that the influence of this renormalization factor on the valence interactions is negligible for light molecules and becomes only significant for the heaviest atoms (iodine and platinum) studied in this work. As a side remark we note that our highest level calculations for BrO and IO still yield a small but consistent overestimation of the SO splittings. This is most likely due to core correlation or higher order correlation effects. Basis set effects were estimated by comparing TZ to QZ calculations for IO and were found to reduce the SO splitting by less than two wave numbers.

The main advantage of the original X2C method is the reduction in the time spent in the SCF procedure required to obtain the HF wave function. Table VI shows the dramatic reduction in CPU time in this step compared to the other schemes. Timings for the four-index transformation are similar, however, for the approximate schemes that all achieve almost a factor of 10 reduction compared to the reference method. Since for large-scale correlated calculations the time spent in the HF stage will become insignificant with respect to index transformation and the actual correlation calculation, there will be little reason to employ the more approximate atomic mean field X2C scheme compared to the molecular mean field approach. For calculations like the one

TABLE V. Excitation energies of the PtH molecule (in cm^{-1}), relative to the $\Omega=\frac{5}{2}$ ground state. See Table I for explanation of acronyms.

Method/Ω	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
^{4}DCG*	1030	3487	12 289	12 726
^{4}DCG**	1017	3488	12 293	12 728
^{2}DCG$^M(U_{mol})$	1030	3487	12 288	12 726
^{2}DCG$^A(U_{nuc})$	1093	3503	12 589	12 969
Expt.[a]		3254	11 608	

[a]Reference [75].

TABLE VI. Wall clock time (in minutes:seconds) of calculations with the various approximations for the IO molecule. See Table I for explanation of acronyms.

Method	HF	Four index	Correlation	Total
$^4DCG^*$	61:14	79:31	28:57	169:42
$^4DCG^{**}$	61:14	08:53	29:02	99:09
$^2DCG^M(U_{mol})$	61:24	08:45	29:12	99:21
$^2DCG^A(U_{nuc})$	06:14	07:37	29:09	43:00

reported here in which the SCF stage still presents a significant part of the effort, one may seek for a reduction relative to the full 4C scheme. It is for instance possible to combine the two schemes by first achieving SCF convergence in the atomic mean field X2C approximation, followed by a back-transformation of occupied MO coefficients to the 4C basis and restart of the calculation. This should yield convergence in very few cycles, rather than the 40 cycles typically needed in the normal procedure.

V. CONCLUSIONS

The X2C method, using a decoupling transformation based on the bare-nucleus Hamiltonian, is becoming an established method in relativistic quantum chemistry. We have shown that differences between a decoupling based on this simple model and that based on the more elaborate 4C HF potential are indeed small as is often implicitly assumed. Relatively large errors do occur if picture change errors on the 2C operator are entirely neglected because the two-electron SO contribution is important. This error can be largely compensated by adding a mean-field screening term to the Hamiltonian. We show that basing this mean-field operator on the molecular mean-field rather than on the sum of atomic mean fields is feasible and yields results that are very close to the 4C reference values.

Based on these experiences we recommend for accurate correlation calculations the molecular mean-field X2C method. The atomic mean field X2C method can be used for calculations in which SO effects are relatively unimportant and in cases in which the errors in the correlation treatment will surpass those made in the treatment of relativistic effects.

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