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Scalar Breit interaction for molecular calculations

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ABSTRACT

Variational treatment of the Dirac–Coulomb–Gaunt or Dirac–Coulomb–Breit two-electron interaction at the Dirac–Hartree–Fock level is the starting point of high-accuracy four-component calculations of atomic and molecular systems. In this work, we introduce, for the first time, the scalar Hamiltonians derived from the Dirac–Coulomb–Gaunt and Dirac–Coulomb–Breit operators based on spin separation in the Pauli quaternion basis. While the widely used spin-free Dirac–Coulomb Hamiltonian includes only the direct Coulomb and exchange terms that resemble nonrelativistic two-electron interactions, the scalar Gaunt operator adds a scalar spin–spin term. The spin separation of the gauge operator gives rise to an additional scalar orbit-orbit interaction in the scalar Breit Hamiltonian. Benchmark calculations of Au_n (n = 2–8) show that the scalar Dirac–Coulomb–Breit Hamiltonian can capture 99.99% of the total energy with only 10% of the computational cost when real-valued arithmetic is used, compared to the full Dirac–Coulomb–Breit Hamiltonian. The scalar relativistic formulation developed in this work lays the theoretical foundation for the development of high-accuracy, low-cost correlated variational relativistic many-body theory.

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INTRODUCTION

Variationally solving the four-component Dirac–Coulomb–Gaunt (DCG) or Dirac–Coulomb–Breit (DCB) Hartree–Fock equation is the starting point for high-accuracy relativistic calculations.[1–9] It is generally well understood that the Breit operator is more accurate than the Gaunt operator.[1,2,10–13] However, due to the large computational cost of the Breit term, the application of the Dirac–Coulomb–Breit Hamiltonian to molecules mostly remains in mean-field theory or is used as a perturbative treatment in correlated methods.[14–18]

Spin separation of the Dirac–Coulomb–Gaunt and Dirac–Coulomb–Breit Hamiltonians was proposed by Dyall in 1994.[19] For example, by applying the kinetic balance condition and the Dirac identity, the Coulomb interaction can be separated into spin-free and spin-own-orbit parts. The spin-free part of the Dirac–Coulomb Hamiltonian captures the majority of the interaction energy, whereas the spin-own-orbit term contributes to the energy level splitting. Due to their low computational cost, Hamiltonians based on the spin-free Dirac–Coulomb approximation have been widely used with perturbative spin–orbit coupling in four-component relativistic electronic structure methods.[20–24] In addition, the spin-free exact-two-component Hamiltonian has been successfully applied in multi-reference calculations.[25–27] However, to the best of our knowledge, the scalar Gaunt and scalar Breit Hamiltonians have never been developed and implemented for molecular calculations due to the high computational cost and complex mathematical form of the separation of the two-electron Gaunt and Breit operators.

In these Hamiltonians, there are terms that are not spin-free but are nevertheless spin-separated. These terms are products of a scalar spin operator and a scalar spatial operator, both of which transform into the totally symmetric irreducible representation of the point group. The spin–spin interaction, for example, couples states of the same spin, and the associated spatial operator couples states of the same spatial symmetry. Such operators are candidates for inclusion along with the spin-free terms in a Hamiltonian that preserves both spin and spatial symmetry. While the phrase "scalar relativistic" has

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been used interchangeably with "spin-free relativistic," the contributions from spin-dependent terms could justifiably be considered "scalar relativistic" as they can be incorporated into the scalar relativistic methods that traditionally have included only the spin-free contributions.

In the mathematical derivation of these terms, the use of the Dirac relation for spin reduction of the one-electron modified Dirac Hamiltonian[19] produces a scalar product, which is spin free, and a scalar triple product, which is the spin–orbit term. Likewise, the spin reduction of the electronic Coulomb interaction produces a spin-free term and a spin–orbit term from the $(LL|SS)$ integrals and various more complex terms from the $(SS|SS)$ integrals involving products of spin-free and spin–orbit terms. The spin reduction of the Gaunt and Breit interactions involves multiple applications of the Dirac relation and results in scalar triple and quadruple products as well as regular scalar products. The triple products are all of the spin–orbit type, which is not spin-free and does not preserve spin and spatial symmetry. The scalar quadruple product is a scalar product of vector products, which can be written in terms of the products of two scalar products. Of these, one term separates the spin from the spatial operators completely so that they can be treated separately, and the other includes terms that preserve spatial and spin symmetry, and from these terms arise contributions to the scalar relativistic Hamiltonian. Therefore, we propose that the term "scalar" not be considered synonymous with "spin-free" but include terms that contribute to the diagonal spin and spatial symmetry blocks of the Hamiltonian or Fock matrix. It should be noted that the quaternion-based SCF methods cannot separate out the double spin–orbit terms from the $(SS|SS)$ integrals because these terms are even in the number of spin operators. The same is true for the spin–spin terms derived from the Gaunt interaction. Hence, these methods are not really spin-free but fall under our proposed definition of scalar relativistic Hamiltonians.

As mentioned, the Gaunt and Breit terms,

$$g^G(i,j) = -\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}}, \tag{1}$$

$$g^B(i,j) = -\frac{1}{2}\left(\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} + \frac{\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij}\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3}\right), \tag{2}$$

can be decomposed into spin-free, spin-other-orbit, spin–spin, and orbit-orbit interactions.[3,28,29] Here, $\{i,j\}$ are electron indices, and the components of the $\boldsymbol{\alpha}$ matrices are defined as

$$\boldsymbol{\alpha}_{i,q} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_q \\ \boldsymbol{\sigma}_q & \mathbf{0}_2 \end{pmatrix}, \quad q = \{x,y,z\}, \tag{3}$$

where the $\boldsymbol{\sigma}_q$ are the Pauli matrices,

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{4}$$

and $\mathbf{0}_2$ is the 2×2 zero matrix.

Recent advances using the Pauli matrix quaternion basis have achieved the minimum floating-point count algorithm for building the full DCG and DCB Hamiltonians in spin-separated forms[28,29] and opened a pathway for the development of fully correlated DCG/DCB many-body methods. The current work builds upon the spin- and component-separation using the Pauli matrix quaternion representation and, for the first time, introduces the low-scaling scalar Breit Hamiltonian that allows for practical applications of the fully relativistic electronic structure theory. The mathematical derivations are lengthy and complex, especially for the spin- and component-separation of the Breit operator in the Pauli quaternion representation. We refer readers to Refs. 28 and 29 for detailed derivations. In this work, we present the key discussion and final working expressions (see the Appendix) of the scalar Breit Hamiltonian with benchmark calculations.

In the Dirac–Coulomb Hamiltonian, the spin-free $\mathcal{O}(c^{-2})$ integrals can be easily derived using the Dirac identity [Eq. (A2)] in the restricted kinetic balance condition,[30–32]

$$\nabla_\mu \cdot \nabla_\nu (\mu\nu|\kappa\lambda), \tag{5}$$

where ∇_μ operates on an atomic basis function μ. Equation (5) is the conventional spin-free term that does not depend on spin densities. The contraction of spin-free integrals with the large-component and small-component scalar densities gives rise to the spin-free Dirac–Coulomb term in the Pauli quaternion representation [Eq. (A7) and Eq. (A12) in the Appendix]. The $\mathcal{O}(c^{-4})$ spin-free contribution can be derived similarly from the $(SS|SS)$ integrals and leads to the integral $(\nabla_\mu \cdot \nabla_\nu)\,(\nabla_\kappa \cdot \nabla_\lambda)\,(\mu\nu|\kappa\lambda)$, which provides contributions like the nonrelativistic direct and exchange terms [Eqs. (A13)–(A16) in the Appendix] in the small-component block of the Fock matrix. It is easy to see that the spin-free Dirac–Coulomb Hamiltonian accounts for the direct $\mathcal{O}(c^{-2})$ Coulomb interaction between the large- and small-component electron densities and $\mathcal{O}(c^{-4})$ Coulomb and exchange interactions in the small-component space.

For the Gaunt operator, a spin-free term that is similar to the spin-free Dirac–Coulomb term arises after applying the Dirac identity twice. This term is of the form

$$\nabla_\kappa \cdot \nabla_\nu (\mu\nu|\kappa\lambda). \tag{6}$$

There are four terms of this kind, corresponding to the possible combinations of indices. Just like the spin-free Dirac–Coulomb case, this term accounts for $\mathcal{O}(c^{-2})$ direct and exchange contributions in the scalar Gaunt Hamiltonian. However, the scalar Gaunt term has more contributions from the Gaunt operator than the spin-free interaction. In the derivation of spin separation for the Gaunt term, the reduction of the scalar quadruple product of the spin–spin interaction yields two terms,

$$\begin{aligned}(\boldsymbol{\sigma}(2) \times \nabla_\kappa) \cdot (\boldsymbol{\sigma}(1) \times \nabla_\nu)(\mu\nu|\kappa\lambda) \\ = [(\boldsymbol{\sigma}(2) \cdot \boldsymbol{\sigma}(1))(\nabla_\kappa \cdot \nabla_\nu) - (\boldsymbol{\sigma}(2) \cdot \nabla_\nu)(\boldsymbol{\sigma}(1) \cdot \nabla_\kappa)](\mu\nu|\kappa\lambda).\end{aligned} \tag{7}$$

The first term is a product of a spin operator and a spatial operator, each of which preserves symmetry as they are tensors of rank 0. This term resembles in form the contribution from the spin-free integrals [Eq. (6)], except that it is contracted with spin densities instead of scalar densities. The second term couples the spin and spatial operators and contains operators that preserve spin and spatial symmetry (tensors of rank 0) and operators that break spin or spatial symmetry

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(tensors of rank 1 and 2). Both of these terms contribute to the Fermi contact and the spin–spin dipole terms of the Breit–Pauli Hamiltonian. In this work, only the contributions from tensors of rank 0 are included in the scalar Gaunt Hamiltonian.

In other words, in addition to the direct Coulomb-like interaction, the spin–spin interaction also contributes to the scalar Gaunt term. Compared to the spin-free Dirac–Coulomb term, scalar Gaunt contributions predominantly appear as exchange interactions in the *LL*, *SS*, and *LS* blocks of the Fock matrix. The working expressions of density-integral contractions of Eq. (7) are presented in Eqs. (A18)–(A23) of Appendix A 3.

The derivation of the scalar Breit operator is more complicated, mainly due to the gauge term in Eq. (2), which has the form $\frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3}$. The all-scalar product of the gauge operator in the restricted kinetic balance condition naturally leads to a scalar gauge contribution that resembles the direct Coulomb interaction,

$$(\mu\nu|\nabla_\nu \cdot \mathbf{r}_{12}\, \mathbf{r}_{12} \cdot \nabla_\kappa|\kappa\lambda)_3, \tag{8}$$

where the symbol $()_3$ stands for the integral of operator $\frac{1}{r_{12}^3}$ for simplicity. However, this all-scalar gauge term is incomplete for the scalar Breit operator. Another scalar term arises from the derivation of spin separation for the gauge operator,

$$(\mu\nu|(\mathbf{r}_{12} \times \nabla_\nu) \cdot (\mathbf{r}_{12} \times \nabla_\kappa)|\kappa\lambda)_3. \tag{9}$$

Since $\mathbf{r} \times \mathbf{p}$ is the angular momentum operator, $(\mathbf{r}_{12} \times \nabla_\nu) \cdot (\mathbf{r}_{12} \times \nabla_\kappa)$ is the scalar orbit-orbit interaction. This scalar quadruple product reduces to a product of scalar products, as for the spin–spin term. Like the Gaunt operator, the scalar Breit operator contributes predominantly through exchange interactions in all the component blocks of the Fock matrix.

In summary, the spin-free Dirac–Coulomb operator consists of direct and exchange terms that resemble non-relativistic two-electron interactions, and the scalar Gaunt operator adds scalar spin–spin interactions along with other direct and exchange terms. The scalar Breit operator adds a scalar orbit-orbit interaction. All working expressions in the Pauli quaternion representation are presented in the Appendix.

Figure 1 presents the computational scaling of Au_n chains and the accuracy of spin-free/scalar terms with respect to the full Dirac–Coulomb, Gaunt, and Breit Hamiltonians. All calculations in this section are performed with a development version of the Chronus Quantum software package.[33] The speed of light utilized is 137.035 999 679 94 a.u. The uncontracted ANO-RCC basis[34–36] set was utilized, resulting in 297 basis functions per Au atom with up to *h* orbital angular momentum (2376 basis functions for Au_8 with 16 *h*, 32 *g*, 88 *f*, 120 *d*, 168 *p*, and 192 *s* functions). The scalar and full relativistic calculations are carried out in complex arithmetic for a direct algorithmic and energy comparison.

It is evident from Fig. 1 that spin-free and scalar Hamiltonians are computationally much cheaper than the full Hamiltonian. For the Dirac–Coulomb case, building the spin-free Fock matrix is only ~27% of the cost of the full Hamiltonian, including integral formation and integral-density contraction, for Au_2. The scalar Gaunt and scalar gauge costs are only ~16% and ~24%, respectively, of the full Hamiltonian for Au_2.

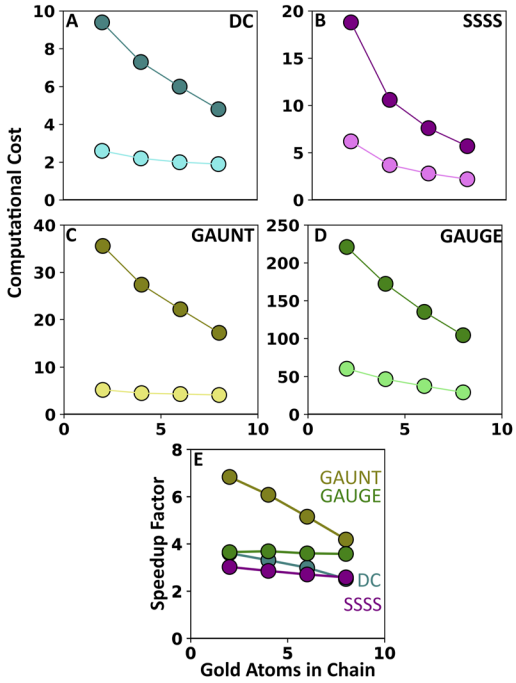


FIG. 1. Cost comparison of full (dark colors) and spin-free/scalar (light colors) Dirac-Coulomb-Breit Hamiltonian components. (a) Dirac–Coulomb (DC) without *SSSS*; (b) *SSSS*; (c) Gaunt; (d) Gauge. Cost is measured relative to the *LLLL* only calculation, $\frac{T}{T_{LLLL}}$, where T and T_{LLLL} are the CPU times to build the corresponding relativistic and the *LLLL* term. (d) Speedup factor = $\frac{T_{\text{full}}}{T_{\text{SF}}}$, where T_{full} and T_{SF} are the CPU times to build the full and spin-free/scalar (SF) Hamiltonian term. Schwarz integral screening threshold of 10^{-14} is used in the calculations.

As the system size increases, the advantage of using the scalar Hamiltonian decreases, although it is still much computationally cheaper than the full Hamiltonian. This is mainly due to the increased effectiveness of integral screening in the full

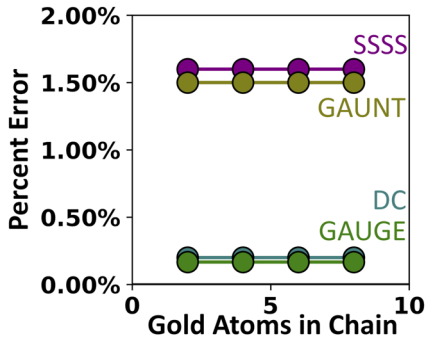


FIG. 2. Percent error of scalar Dirac-Coulomb-Breit interaction components relative to corresponding full operators. The percent error is computed as $\frac{|\Delta E_{\text{full}} - \Delta E_{\text{SF}}|}{|\Delta E_{\text{full}}|}$, where $\Delta E = E - E_{LLLL}$ is the relativistic energy contribution. The energy E is obtained by only adding the corresponding relativistic operator separately to the *LLLL* term, followed by a full self-consistent-field wave function optimization. Schwarz integral screening threshold of 10^{-14} is used in the calculations.

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TABLE I. Total energy (Hartrees) comparison between scalar Dirac–Coulomb–Breit and full Dirac–Coulomb–Breit calculations with the ANO-RCC basis set across the actinyl oxycation series. A Schwarz integral screening threshold of 10^{-14} was used in the uncontracted calculations. All molecules are in the linear form with An-O bond lengths of 1.76, 1.75, and 1.74 Å for UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}, respectively. For scalar calculations, the spin multiplicities are singlet, doublet, and triplet for UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}, respectively.

Formula	Full Hamiltonian	Scalar	Absolute error	Percent error (%)
UO_2^{2+}	−28 164.71	−28 165.47	0.75	0.0027
NpO_2^{2+}	−28 957.31	−28 958.14	0.83	0.0029
PuO_2^{2+}	−29 765.31	−29 766.19	0.88	0.0030

Hamiltonian build. The scalar Breit interaction is relatively more local than non-relativistic operators, dominated by the nearest-neighbor interaction, and as a result, less sensitive to the increased integral screening as the system size increases.

While exhibiting a strong computational advantage, Fig. 2 shows that these scalar Hamiltonians capture ~99% of the total two-electron interaction energy compared to those computed using the full Hamiltonian. It is worth emphasizing that ignoring the scalar spin–spin interaction from the Gaunt interaction or the scalar orbit-orbit interaction in the gauge term leads to a large discrepancy in total energy, strongly supporting the use of these terms in the scalar Breit Hamiltonian. For Au_n tests, the orbit-orbit interaction accounts for ~73% of the scalar gauge term, and the spin–spin interaction is ~56% of the scalar Gaunt term.

In order to study the scalar Hamiltonian's effect on total calculated energy in molecules, four-component Dirac–Hartree–Fock calculations were performed on three members of the actinyl oxycation series utilizing either the full Dirac–Coulomb–Breit or the scalar Dirac–Coulomb–Breit Hamiltonian. In the scalar case, the Dirac–Coulomb, Gaunt, and gauge terms are all chosen to be scalar only. The results in Table I show that over 99.99% of the total energy is captured by the scalar Breit Hamiltonian. Note that the percent errors shown here are much less than those in Fig. 2 because the errors here are displayed as a percentage of total energy, not as a percentage of the relativistic energy contribution attributable to a single operator.

CONCLUSION AND PERSPECTIVES

The scalar Dirac–Coulomb–Breit Hamiltonian introduced in this work includes direct and exchange spin-free terms from the Coulomb and Gaunt interactions and the scalar spin–spin and scalar orbit-orbit interactions from the Breit interaction, obtained through spin separation in the Pauli quaternion basis. Benchmark calculations show that the scalar Dirac–Coulomb–Breit Hamiltonian captures ~99% of the total relativistic two-electron interaction energy at only a fraction of the computational cost compared to the full Hamiltonian.

The scalar Dirac–Coulomb–Breit Hamiltonian consists of only real-valued matrix elements. Therefore, the computational cost can be further reduced by using real-valued arithmetic, resulting in another twofold reduction in computational cost in the Pauli quaternion basis relative to the full Dirac–Coulomb–Breit Hamiltonian. The reduction is only twofold because the full Dirac–Coulomb–Breit Hamiltonian in the Pauli quaternion basis already utilizes real-valued integrals in an optimal FLOP (floating point operation) algorithm.

Although important physics (including the spin-own-orbit, spin-other-orbit, and more complex spin-dependent interactions) is separated out, the scalar Dirac–Coulomb–Breit Hamiltonians are ideal for preparing zeroth-order four-component wave functions for the perturbative treatment of the spin physics in the state interaction framework. In addition, we suggest that the scalar Dirac–Coulomb–Breit operator can be used to capture relativistic electron correlation in many-body theory, laying the theoretical foundation for the future development of fully correlated Dirac–Coulomb–Breit ultra-high-accuracy computational methods.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Shichao Sun: Conceptualization (equal); Methodology (equal); Software (equal); Writing – original draft (equal); **Jordan N. Ehrman**: Data curation (equal); Validation (equal); Visualization (lead); Writing – review & editing (equal). **Tianyuan Zhang**: Software (equal); Validation (equal). **Qiming Sun**: Software (equal); Validation (equal). **Kenneth G. Dyall**: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Xiaosong Li**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal);

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Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX: SPIN-FREE DIRAC–COULOMB–BREIT HAMILTONIAN IN THE PAULI QUATERNION REPRESENTATION

The development of the scalar Gaunt and Breit Hamiltonians is based on the restricted kinetic balance (RKB) condition for the large component (χ^L) and small component (χ^S) basis,[30–32] $\chi^S = \frac{1}{2c}\boldsymbol{\sigma}\cdot\mathbf{p}\chi^L$, to ensure the correct nonrelativistic limit of the positive energy states,[37,38] where c is the speed of light and $\mathbf{p} = -i\nabla$ is the linear momentum operator. Mathematical derivations are lengthy and complex for the spin- and component-separation of the Dirac–Coulomb, Gaunt, and Breit operators in the Pauli quaternion representation. We refer to readers Refs. 28 and 29 for detailed derivations. We only present the key equations and the final working expressions here.

1. Pauli quaternion representation

In order to build the scalar Dirac–Coulomb–Breit Hamiltonian on the Pauli quaternion basis, all integrals (Dirac–Coulomb, Gaunt, and Breit) and density matrices need to be expressed in the Pauli matrix representation. The Pauli components of the density matrix can be transformed from the spin-blocked matrices,[39]

$$\begin{aligned}\mathbf{D}_s &= \mathbf{D}_{\alpha\alpha} + \mathbf{D}_{\beta\beta},\\ \mathbf{D}_z &= \mathbf{D}_{\alpha\alpha} - \mathbf{D}_{\beta\beta},\\ \mathbf{D}_x &= \mathbf{D}_{\alpha\beta} + \mathbf{D}_{\beta\alpha},\\ \mathbf{D}_y &= i(\mathbf{D}_{\alpha\beta} - \mathbf{D}_{\beta\alpha}),\end{aligned}$$

for each component-block (LL, SS, LS, SL). These density matrices are contracted with scalar integrals to build Fock matrices, all in the Pauli quaternion representation. Collecting all Pauli components, the four-component Fock matrix can be constructed,

$$\mathbf{F}^{XY} = \frac{1}{2}\begin{pmatrix}\mathbf{F}_s^{XY} + \mathbf{F}_z^{XY} & \mathbf{F}_x^{XY} - i\mathbf{F}_y^{XY}\\ \mathbf{F}_x^{XY} + i\mathbf{F}_y^{XY} & \mathbf{F}_s^{XY} - \mathbf{F}_z^{XY}\end{pmatrix}, \tag{A1}$$

where $X, Y \in \{L, S\}$.

2. Pauli quaternion spin-free Dirac–Coulomb

The derivation of the spin-free Dirac–Coulomb is straightforward, utilizing the Dirac identity,

$$(\boldsymbol{\sigma}\cdot\boldsymbol{\mu})(\boldsymbol{\sigma}\cdot\boldsymbol{\nu}) = \mathbf{I}\,(\boldsymbol{\mu}\cdot\boldsymbol{\nu}) + i\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\times\boldsymbol{\nu}, \tag{A2}$$

in the two-electron Coulomb integrals with the RKB condition. The first term in Eq. (A2) is known as the conventional spin-free contribution. The resulting Pauli quaternion spin-free Dirac–Coulomb expressions, including the $\mathcal{O}(c^{-4})$ order contribution from the $(SS|SS)$ term, are

$$V_{\mu\nu,s}^{C,LL} = D_{\lambda\kappa,s}^{LL}[2(\mu\nu|\kappa\lambda) - (\mu\lambda|\kappa\nu)], \tag{A3}$$

$$V_{\mu\nu,z}^{C,LL} = -D_{\lambda\kappa,z}^{LL}(\mu\lambda|\kappa\nu), \tag{A4}$$

$$V_{\mu\nu,x}^{C,LL} = -D_{\lambda\kappa,x}^{LL}(\mu\lambda|\kappa\nu), \tag{A5}$$

$$V_{\mu\nu,y}^{C,LL} = -D_{\lambda\kappa,y}^{LL}(\mu\lambda|\kappa\nu), \tag{A6}$$

$$V_{\mu\nu,s}^{C,LL} = 2D_{\lambda\kappa,s}^{SS}\nabla_\kappa\cdot\nabla_\lambda(\mu\nu|\kappa\lambda), \tag{A7}$$

$$V_{\mu\nu,s}^{C,LS} = -D_{\lambda\kappa,s}^{LS}\nabla_\kappa\cdot\nabla_\nu(\mu\lambda|\kappa\nu), \tag{A8}$$

$$V_{\mu\nu,z}^{C,LS} = -D_{\lambda\kappa,z}^{LS}\nabla_\kappa\cdot\nabla_\nu(\mu\lambda|\kappa\nu), \tag{A9}$$

$$V_{\mu\nu,x}^{C,LS} = -D_{\lambda\kappa,x}^{LS}\nabla_\kappa\cdot\nabla_\nu(\mu\lambda|\kappa\nu), \tag{A10}$$

$$V_{\mu\nu,y}^{C,LS} = -D_{\lambda\kappa,y}^{LS}\nabla_\kappa\cdot\nabla_\nu(\mu\lambda|\kappa\nu), \tag{A11}$$

$$V_{\mu\nu,s}^{C,SS} = 2D_{\lambda\kappa,s}^{LL}\nabla_\mu\cdot\nabla_\nu(\mu\nu|\kappa\lambda), \tag{A12}$$

$$\begin{aligned}V_{\mu\nu,s}^{C,SS} = 2D_{\lambda\kappa,s}^{SS}\big[&(\nabla_\mu\cdot\nabla_\nu)(\nabla_\kappa\cdot\nabla_\lambda)(\mu\nu|\kappa\lambda)\\ &- (\nabla_\mu\cdot\nabla_\lambda)(\nabla_\kappa\cdot\nabla_\nu)(\mu\lambda|\kappa\nu)\big],\end{aligned} \tag{A13}$$

$$V_{\mu\nu,z}^{C,SS} = -D_{\lambda\kappa,z}^{SS}(\nabla_\mu\cdot\nabla_\lambda)(\nabla_\kappa\cdot\nabla_\nu)(\mu\lambda|\kappa\nu), \tag{A14}$$

$$V_{\mu\nu,x}^{C,SS} = -D_{\lambda\kappa,x}^{SS}(\nabla_\mu\cdot\nabla_\lambda)(\nabla_\kappa\cdot\nabla_\nu)(\mu\lambda|\kappa\nu), \tag{A15}$$

$$V_{\mu\nu,y}^{C,SS} = -D_{\lambda\kappa,y}^{SS}(\nabla_\mu\cdot\nabla_\lambda)(\nabla_\kappa\cdot\nabla_\nu)(\mu\lambda|\kappa\nu), \tag{A16}$$

where ∇_κ is the nuclear coordinate derivative of the atomic basis function χ_κ.

3. Pauli quaternion scalar Gaunt

The mathematical expressions for the scalar Gaunt and Breit Hamiltonians cannot be easily obtained using the Dirac identity [Eq. (A2)]. Unlike the Dirac–Coulomb term, both the Gaunt and Breit operators [Eqs. (1) and (2)] are intrinsically dependent on Pauli matrices. As a result, the following vector identity:

$$\boldsymbol{\mu}\times\boldsymbol{\nu}\cdot\boldsymbol{\kappa}\times\boldsymbol{\lambda} = \boldsymbol{\mu}\cdot\boldsymbol{\kappa}\,\boldsymbol{\nu}\cdot\boldsymbol{\lambda} - \boldsymbol{\mu}\cdot\boldsymbol{\lambda}\,\boldsymbol{\nu}\cdot\boldsymbol{\kappa}, \tag{A17}$$

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must be applied, in addition to the Dirac identity, to achieve fully spin-separated expressions. The working expressions for the scalar Gaunt Hamiltonian in the Pauli quaternion representation are

$$V^{G,LL}_{\mu\nu,s} = 3D^{SS}_{\lambda\kappa,s}\nabla_\lambda\cdot\nabla_\kappa(\mu\lambda|\kappa\nu), \tag{A18}$$

$$V^{G,SS}_{\mu\nu,s} = 3D^{LL}_{\lambda\kappa,s}\nabla_\mu\cdot\nabla_\nu(\mu\lambda|\kappa\nu), \tag{A19}$$

$$\begin{aligned}V^{G,LS}_{\mu\nu,s} = -2\big[&D^{LS}_{\lambda\kappa,s}\nabla_\kappa\cdot\nabla_\nu(\mu\nu|\kappa\lambda) + D^{SL}_{\lambda\kappa,s}\nabla_\nu\cdot\nabla_\lambda(\mu\nu|\kappa\lambda)\\ &+ D^{SL}_{\lambda\kappa,s}\nabla_\lambda\cdot\nabla_\nu(\mu\lambda|\kappa\nu)\big],\end{aligned} \tag{A20}$$

$$\begin{aligned}V^{G,LS}_{\mu\nu,z} = -2\big[&D^{SL}_{\lambda\kappa,z}\nabla_\lambda\cdot\nabla_\nu(\mu\lambda|\kappa\nu) + D^{LS}_{\lambda\kappa,z}\nabla_\kappa\cdot\nabla_\nu(\mu\nu|\kappa\lambda)\\ &+ D^{SL}_{\lambda\kappa,z}\nabla_\nu\cdot\nabla_\lambda(\mu\nu|\kappa\lambda)\big],\end{aligned} \tag{A21}$$

$$\begin{aligned}V^{G,LS}_{\mu\nu,x} = -2\big[&D^{SL}_{\lambda\kappa,x}\nabla_\lambda\cdot\nabla_\nu(\mu\lambda|\kappa\nu) + D^{LS}_{\lambda\kappa,x}\nabla_\kappa\cdot\nabla_\nu(\mu\nu|\kappa\lambda)\\ &+ D^{SL}_{\lambda\kappa,x}\nabla_\nu\cdot\nabla_\lambda(\mu\nu|\kappa\lambda)\big],\end{aligned} \tag{A22}$$

$$\begin{aligned}V^{G,LS}_{\mu\nu,y} = -2\big[&D^{SL}_{\lambda\kappa,y}\nabla_\lambda\cdot\nabla_\nu(\mu\lambda|\kappa\nu) + D^{LS}_{\lambda\kappa,J}\nabla_\kappa\cdot\nabla_\nu(\mu\nu|\kappa\lambda)\\ &+ D^{SL}_{\lambda\kappa,y}\nabla_\nu\cdot\nabla_\lambda(\mu\nu|\kappa\lambda)\big].\end{aligned} \tag{A23}$$

4. Pauli quaternion scalar gauge

We introduce the following short notations for the gauge integrals that contribute to the scalar term:

$$(ss)(\mu\bar\nu|\bar\kappa\lambda)_3 = \left(\mu\nu\left|\frac{\nabla_\nu\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\kappa}{|\mathbf{r}_{12}|^3}\right|\kappa\lambda\right), \tag{A24}$$

$$\begin{aligned}(\sigma\sigma)_{JK}(\mu\bar\nu|\bar\kappa\lambda)_3 = -\left(\mu\nu\left|\frac{(\mathbf{r}_{12}\times\nabla_\nu)_J(\nabla_\kappa\times\mathbf{r}_{12})_K}{|\mathbf{r}_{12}|^3}\right|\kappa\lambda\right),\\ J,K\in\{x,y,z\},\end{aligned} \tag{A25}$$

$$(\sigma\cdot\sigma)(\mu\bar\nu|\bar\kappa\lambda)_3 = [(\sigma\sigma)_{xx} + (\sigma\sigma)_{yy} + (\sigma\sigma)_{zz}](\mu\bar\nu|\bar\kappa\lambda)_3, \tag{A26}$$

where subscript 3 denotes the $|\mathbf{r}_{12}|^{-3}$ operator for the gauge integral.

The scalar gauge Hamiltonian in the Pauli quaternion representation is

$$V^{g,LL}_{\mu\nu,s} = \frac{1}{2}\big[D^{SS}_{\lambda\kappa,s}(ss) + D^{SS}_{\lambda\kappa,s}(\sigma\cdot\sigma)\big](\mu\bar\lambda|\bar\kappa\nu)_3, \tag{A27}$$

$$V^{g,LL}_{\mu\nu,z} = \frac{1}{2}D^{SS}_{\lambda\kappa,z}(ss)(\mu\bar\lambda|\bar\kappa\nu)_3, \tag{A28}$$

$$V^{g,LL}_{\mu\nu,x} = \frac{1}{2}D^{SS}_{\lambda\kappa,x}(ss)(\mu\bar\lambda|\bar\kappa\nu)_3, \tag{A29}$$

$$V^{g,LL}_{\mu\nu,y} = \frac{1}{2}D^{SS}_{\lambda\kappa,y}(ss)(\mu\bar\lambda|\bar\kappa\nu)_3, \tag{A30}$$

$$V^{g,SS}_{\mu\nu,s} = \frac{1}{2}\big[D^{LL}_{\lambda\kappa,s}(ss) + D^{LL}_{\lambda\kappa,s}(\sigma\cdot\sigma)\big](\bar\mu\lambda|\kappa\bar\nu)_3, \tag{A31}$$

$$V^{g,SS}_{\mu\nu,z} = \frac{1}{2}D^{LL}_{\lambda\kappa,z}(ss)(\bar\mu\lambda|\kappa\bar\nu)_3, \tag{A32}$$

$$V^{g,SS}_{\mu\nu,x} = \frac{1}{2}D^{LL}_{\lambda\kappa,x}(ss)(\bar\mu\lambda|\kappa\bar\nu)_3, \tag{A33}$$

$$V^{g,SS}_{\mu\nu,y} = \frac{1}{2}D^{LL}_{\lambda\kappa,y}(ss)(\bar\mu\lambda|\kappa\bar\nu)_3, \tag{A34}$$

$$\begin{aligned}V^{g,LS}_{\mu\nu,s} = &-\big[D^{LS}_{\lambda\kappa,s}(ss) + D^{SL}_{\lambda\kappa,s}(ss)\big](\mu\bar\nu|\kappa\bar\lambda)_3\\ &-\frac{1}{2}\big[D^{SL}_{\lambda\kappa,s}(ss) + D^{SL}_{\lambda\kappa,s}(\sigma\cdot\sigma)\big](\mu\bar\lambda|\kappa\bar\nu)_3,\end{aligned} \tag{A35}$$

$$V^{g,LS}_{\mu\nu,z} = -\frac{1}{2}D^{SL}_{\lambda\kappa,z}(ss)(\mu\bar\lambda|\kappa\bar\nu)_3, \tag{A36}$$

$$V^{g,LS}_{\mu\nu,x} = -\frac{1}{2}D^{SL}_{\lambda\kappa,x}(ss)(\mu\bar\lambda|\kappa\bar\nu)_3, \tag{A37}$$

$$V^{g,LS}_{\mu\nu,y} = -\frac{1}{2}D^{SL}_{\lambda\kappa,y}(ss)(\mu\bar\lambda|\kappa\bar\nu)_3. \tag{A38}$$

For the *SL* blocks of Dirac–Coulomb, Gaunt, and Breit, we have the symmetry

$$V^{SL} = V^{\dagger LS}.$$

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