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ABSTRACT

The frequency-independent Coulomb–Breit operator gives rise to the most accurate treatment of two-electron interaction in the non-quantum-electrodynamics regime. The Breit interaction in the Coulomb gauge consists of magnetic and gauge contributions. The high computational cost of the gauge term limits the application of the Breit interaction in relativistic molecular calculations. In this work, we apply the Pauli component integral–density matrix contraction scheme for gauge interaction with a maximum spin- and component separation scheme. We also present two different computational algorithms for evaluating gauge integrals. One is the generalized Obara–Saika algorithm, where the Laplace transformation is used to transform the gauge operator into Gaussian functions and the Obara–Saika recursion is used for reducing the angular momentum. The other algorithm is the second derivative of Coulomb interaction evaluated with Rys-quadrature. This work improves the efficiency of performing Dirac–Hartree–Fock with the variational treatment of Breit interaction for molecular systems. We use this formalism to examine relativistic trends in the Periodic Table and analyze the relativistic two-electron interaction contributions in heavy-element complexes.

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30 August 2023 18:32:25

I. INTRODUCTION

Four-component Dirac–Hartree–Fock (DHF) is the starting point for accurate all-electron relativistic calculations.[1–4] The frequency-independent instantaneous two-electron interaction provides the most accurate description[5–8] of electron–electron interaction before going to a genuine relativistic quantum electrodynamics theory of many-electron systems.[9–14] Derived from quantum electrodynamics, the form of the instantaneous two-electron interaction operator, accurate to $\mathcal{O}(c^{-2})$, depends on the choice of gauge. In the Feynman gauge, it can be written as

$$V_{ee}^{F} = \sum_{i=1}^{N} \sum_{j>i} (g^{C}(i,j) + g^{G}(i,j)), \tag{1}$$

$$g^{C}(i,j) = \frac{1}{r_{ij}}, \tag{2}$$

$$g^{G}(i,j) = -\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}}, \tag{3}$$

where $\{i,j\}$ are electron indices. Equation (3) is also known as the Gaunt term. The components of the $\boldsymbol{\alpha}$ matrices are defined as

$$\boldsymbol{\alpha}_{i,J} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_J \\ \boldsymbol{\sigma}_J & \mathbf{0}_2 \end{pmatrix}, \quad J = \{x,y,z\}, \tag{4}$$

and $\boldsymbol{\sigma}$ consists of Pauli matrices,

$$\mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5}$$

In the Coulomb gauge, the instantaneous two-electron operator is

$$V_{ee}^{C} = \sum_{i=1}^{N} \sum_{j>i} (g^{C}(i,j) + g^{B}(i,j)), \tag{6}$$

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$$g^B(i,j) = -\frac{1}{2}\left(\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} + \frac{\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij}\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3}\right), \tag{7}$$

where the Breit term [Eq. (7)] includes the magnetic interaction and an additional gauge term. Note that the magnetic interaction of the Breit term in the Coulomb gauge is half of the Gaunt term in the Feynman gauge.

While the Dirac–Coulomb operator accounts for the leading two-electron energy correction in the relativistic regime, the frequency-independent Breit or Gaunt term cannot be ignored for accurate description of electronic structures of late-row and heavy elements.[5–8] The difference in the two-electron interaction in Feynman and Coulomb gauge arises from different truncation schemes in the instantaneous interaction approximation, leading to gauge-dependent results. Although both forms of two-electron interactions [V_{ee}^F in Eq. (1) and V_{ee}^C in Eq. (6)] are accurate to $\mathcal{O}(c^{-2})$, there has been work showing that the Breit operator in the Coulomb gauge is more accurate than the Gaunt operator in the Feynman gauge.[7,8] It was also suggested that the variational treatment of the frequency-independent Breit interaction is important for both correlation calculations and property evaluations.[15,16] DHF with the Coulomb and Gaunt interactions has been implemented in quantum chemistry software packages for atomic and molecular systems.[17–30] However, the gauge term in the Breit interaction is computationally more expensive in both integral evaluation and integral–density contraction.

In the 1980s, frequency-dependent and -independent Breit interactions were included perturbatively in a multi-configuration Dirac-Fock formalism with finite difference methods in atomic systems.[31–33] Later on, variational treatment of the frequency-independent Breit term in atomic systems with kinetically balanced Slater type basis[34] and Gaussian basis[35–37] was realized computationally.

Molecular calculation with the Breit interaction came much later. Since radial-angular separation is not applicable for molecular systems, an analytical integral evaluation algorithm for the gauge term in Gaussian type orbitals is required.[38–40] The first practical gauge integral evaluation using the McMurchie–Davidson algorithm was implemented and applied for molecular systems by Quiney and co-workers.[41,42] Recently, a gauge integral with the generalized Rys-quadrature method was developed for molecules with the density fitting technique.[28,43] Still, the high computational cost of the gauge term limits its application in molecular relativistic calculations.[44]

Some techniques have been applied to reduce the computational cost of Dirac–Hartree–Fock calculations, such as the quaternion formalism,[23] resolution of the identity,[28,45] and quasi-four component approximations.[46,47] Recently, we introduced a Pauli matrix representation with an optimal spin- and component separation algorithm that results in a minimal floating-point count algorithm for integral–density contraction.[30]

In this work, we generalize the integral–density contraction in the Pauli spinor representation in the previous work[30] to gauge term contraction. A restricted kinetically balanced (RKB) Gaussian basis is used in this work. Component- and spin-separations[48] are applied for the Fock matrix and density matrices for maximal optimization of the contraction scheme. We also derived and developed two new methods for gauge term integral evaluation in Gaussian type orbitals: one uses the generalized Obara–Saika recursion, and the other is the second derivative of Coulomb interaction with Rys quadrature. This work includes the gauge term variationally in a relativistic four-component Dirac–Hartree–Fock framework for molecular calculations.

II. DIRAC–COULOMB–BREIT HARTREE–FOCK FORMALISM IN PAULI MATRIX REPRESENTATION

A. Restricted-kinetic-balanced Dirac–Coulomb–Breit Hartree–Fock equation

All expressions in this work are in atomic units. The eigenfunction of the Dirac Hamiltonian ψ has a four-spinor form,

$$\psi = \begin{pmatrix} \phi^L \\ \phi^S \end{pmatrix}, \tag{8}$$

where ϕ^L and ϕ^S are spinors of the large and small components, expanded in spinor basis,

$$\phi_p^L = \sum_{\tau}\sum_{\mu=1}^{N} c_{\mu\tau,p}^L \chi_{\mu\tau}^L, \quad \phi_p^S = \sum_{\tau}\sum_{\mu=1}^{N} c_{\mu\tau,p}^S \chi_{\mu\tau}^S, \tag{9}$$

where $\tau \in \{\alpha, \beta\}$ and N is the number of spatial basis functions. The large component basis is defined as

$$\chi_{\mu\alpha}^L = \begin{pmatrix} \chi_\mu \\ 0 \end{pmatrix}, \quad \chi_{\mu\beta}^L = \begin{pmatrix} 0 \\ \chi_\mu \end{pmatrix}, \tag{10}$$

where χ_μ is the one component spatial basis function. The relationship between the large and small component spinor basis can be defined via the restricted kinetic balance (RKB) condition[49–51] to ensure the correct nonrelativistic limit of the positive energy states.[52,53] The RKB condition can be written as

$$\chi_{\mu\tau}^S = \frac{1}{2c}\boldsymbol{\sigma} \cdot \mathbf{p}\chi_{\mu\tau}^L, \tag{11}$$

where c is the speed of light and $\mathbf{p} = -i\nabla$ is the linear momentum operator.

Introducing the RKB condition [Eq. (11)] into the Dirac equation results in the four-component Dirac formalism in matrix representation,[54]

$$\begin{pmatrix} \mathbf{F}^{LL} & \mathbf{F}^{LS} \\ \mathbf{F}^{SL} & \mathbf{F}^{SS} \end{pmatrix}\begin{pmatrix} \mathbf{C}_L^+ & \mathbf{C}_L^- \\ \mathbf{C}_S^+ & \mathbf{C}_S^- \end{pmatrix} = \begin{pmatrix} \mathbf{I}\otimes\mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}\otimes\frac{1}{2mc^2}\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{C}_L^+ & \mathbf{C}_L^- \\ \mathbf{C}_S^+ & \mathbf{C}_S^- \end{pmatrix}\begin{pmatrix} \boldsymbol{\epsilon}^+ & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\epsilon}^- \end{pmatrix}, \tag{12}$$

where $\mathbf{T}$ and $\mathbf{S}$ are the kinetic energy and overlap matrices, respectively. The solution of Eq. (12) consists of sets of positive/negative eigenvalues ($\{\epsilon^+\}$, $\{\epsilon^-\}$) with corresponding molecular orbital coefficients $\begin{pmatrix} \mathbf{C}_L^+ \\ \mathbf{C}_S^+ \end{pmatrix}$ and $\begin{pmatrix} \mathbf{C}_L^- \\ \mathbf{C}_S^- \end{pmatrix}$ for the positive/negative energy solutions.

30 August 2023 18:32:25

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The computation of integrals of operators in Eq. (6) is the dominant cost in building the Dirac–Coulomb–Breit Hartree–Fock matrix and is usually done in the atomic-orbital (AO) basis. To build the AO Dirac–Coulomb–Breit Hartree–Fock, one can scatter the four-component density matrix into 16 component- and spin-blocked density matrices,

$$D^{XY}_{\mu\tau_1,\nu\tau_2} = \sum_{i=1}^{N_e} c^{X}_{\mu\tau_1,i} c^{Y*}_{\nu\tau_2,i}, \quad X, Y = \{L, S\}, \tag{13}$$

where $\tau_1, \tau_2, \tau_3, \tau_4 \in \{\alpha, \beta\}$. With the RKB condition [Eq. (11)], component- and spin-blocked integrals can be constructed from four-index scalar AO integrals. Then, one can build the Fock matrix by contracting AO spinor integrals with component- and spin-blocked density matrices, resulting in the contraction scheme in the two-spinor basis [see Eqs. (A1)–(A4) in Appendix A].

B. Gauge term in Pauli matrix basis

In a recent study,[30] we introduced a minimal floating-point-operation (FLOP) count algorithm based on the Pauli quaternion formalism of maximal component- and spin-separation. In this approach, AO density matrices are further component- and spin-separated and directly contracted with scalar integrals with a minimal FLOP approach but at the cost of an increased arithmetic complexity.

In this work, we extend the Pauli quaternion formalism for building the gauge term in the Dirac–Coulomb–Breit Hartree–Fock equation. Note that the magnetic term [first term in Eq. (7)] is one-half of the Gaunt term, which was previously derived and implemented.[30] We refer readers to Ref. 30 for detailed implementation of the Gaunt term the with Pauli quaternion formalism.

In order to build the gauge term contribution in the Pauli component basis, both gauge integrals 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,[54]

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

for each component-block (LL, SS, LS, SL).

The separation of gauge integrals that contract with the density matrices in the Pauli component basis utilizes the Dirac identity and orthogonality of the quaternion. Mathematical derivations are lengthy and complex, and we only present the key equations and the final working expressions [Eqs. (A17)–(A30) in Appendix A].

Collecting all Pauli components, the two-spinor Fock matrix can be constructed:

$$\mathbf{F}^{XY} = \frac{1}{2}\begin{pmatrix} \mathbf{F}^{XY}_s + \mathbf{F}^{XY}_z & \mathbf{F}^{XY}_x - i\mathbf{F}^{XY}_y \\ \mathbf{F}^{XY}_x + i\mathbf{F}^{XY}_y & \mathbf{F}^{XY}_s - \mathbf{F}^{XY}_z \end{pmatrix}, \tag{14}$$

where $X, Y \in \{L, S\}$. The Dirac–Hartree–Fock equation can be solved self-consistently.

C. Gauge integral evaluation

In this work, we derived and implemented two methods to evaluate the gauge integral with the operator form defined as

$$\frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{2r_{12}^3} = \boldsymbol{\alpha}_1 \cdot \frac{\mathbf{r}_{12} \otimes \mathbf{r}_{12}}{2r_{12}^3} \cdot \boldsymbol{\alpha}_2.$$

In Appendix B, we show the working equations to evaluate the gauge integral using the Rys-quadrature approach in terms of second derivatives of the four-center two-electron Coulomb integral. In Appendix C, we derived the recursion relations using the generalized Obara–Saika algorithm. Both methods are implemented and benchmarked against each other, and the resulting integrals only differ by less than 10^{-12} a.u. Integral code optimization requires extensive work, and therefore, we will not provide timing comparisons between Rys-quadrature and Obara–Saika algorithms for the gauge term.

III. BENCHMARK AND DISCUSSION

A. Analysis of computational cost

In this section, we focus on analyzing the memory requirement and computational cost for building the Dirac–Fock matrix from four-index electron-repulsion-integrals (ERIs). We use the in-core formalism where all four-index integrals are computed and stored in memory for the theoretical cost analysis. In this analysis, we used a Kramers-unrestricted condition where all four Pauli components are non-zero. The memory requirement and FLOP count for Dirac–Coulomb and Gaunt have been previously analyzed in Ref. 30. Note that the magnetic contribution in the Breit term has the same computational cost as the Gaunt term. Therefore, the previous cost analyses were directly used in this work with the addition of the gauge contribution.

The gauge term is built from 16 four-index scalar (or one-component) integrals shown in Eqs. (A11)–(A14). In the two-spinor RKB approach, these 16 types of gauge ERIs are assembled into 64 two-spinor ERIs, and the integral–density contraction is carried out in the two-spinor form [see Eqs. (A1)–(A4)]. In contrast, the Pauli component approach does not assemble the 16 gauge ERIs into a large dimension, although several auxiliary scalar integrals [e.g., $(\sigma \cdot \sigma)$, $(\sigma \times \sigma)$, and $(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}$] can be constructed to reduce the cost of contraction. Instead, we scatter the Dirac–Fock and density matrices into the Pauli representation so that all gauge ERIs remain in the scalar form and the integral–density contraction is done in Pauli quaternion representation (see Sec. II B). Tables I and II list the estimated computational costs in terms of memory requirement and FLOP count for forming the Dirac–Fock matrix from integrals.

Table I shows that the Pauli matrix formalism has a much smaller memory storage requirement compared to the two-spinor matrix form. This is mainly because in the Pauli matrix basis, all integrals are stored in one-component real-valued scalar form. In contrast, in the two-spinor basis, scalar integrals are assembled into two-component complex-valued tensors. As a result, the in-core integral storage requirement is much bigger in the two-spinor basis than in the Pauli matrix basis.

Table II gives the FLOP count for each type of Coulomb **J** and exchange **K** contractions with the density. For both the

30 August 2023 18:32:25

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TABLE I. Analysis of memory requirement in terms of the equivalent number of unique real-valued one-component four-index electron-repulsion-integral tensors needed for forming the four-component Dirac–Coulomb–Breit Hamiltonian. N number of atomic basis functions are used in this estimate. Dense matrices with no integral or matrix symmetry are considered.

	Equivalent no. of real-valued N^4 ERI tensors		
Four-component scheme	Dirac–Coulomb[a]	Breit[b]	Total
Pauli matrix RKB basis	36	35	71
Two-spinor RKB basis[c]	96	128	224

[a]Dirac–Coulomb including the $(SS|SS)$ contribution.
[b]Analysis of the magnetic contribution in the Breit term is from Ref. 30.
[c]Two-spinor integrals are stored as complex-valued quantities, occupying two double-precision storage.

TABLE II. Analysis of FLOP count in double-precision operations for forming the four-component Dirac–Coulomb–Breit Fock matrix ($\mathbf{F}^{LL}, \mathbf{F}^{SS}, \mathbf{F}^{LS}$). N number of atomic basis functions are used in this estimate. FLOP count is separated into Coulomb **J** and exchange **K** contractions. Dense matrices with no integral or matrix symmetry are considered.

	Number of integral–density contractions $(\mathbf{J}, \mathbf{K})$		
Four-component scheme	Dirac–Coulomb[b]	Breit[c]	Total FLOP[a]
Pauli matrix RKB basis	$(21, 53)$	$(44, 189)$	$1228N^4$
Two-spinor RKB basis	$(64, 48)$	$(64, 96)$	$2176N^4$

[a]Floating point operation (FLOP) is defined as an arithmetic procedure $(+, -, \times, \div)$ of two double-precision numbers. Because integrals for the Pauli matrix RKB basis are stored as real-valued matrices and density matrices are complex-valued, each contraction step requires $4N^4$ FLOPs. For the two-spinor RKB basis, because integrals are complex-valued, each contraction step requires $8N^4$ FLOPs.
[b]Dirac–Coulomb including the $(SS|SS)$ contribution.
[c]Analysis of the magnetic contribution in the Breit term is from Ref. 30.

Dirac–Coulomb and the Breit terms, we see that the Pauli matrix formalism requires a much smaller number of **J** contractions than the two-spinor approach. However, the number of **K** matrix formations is much bigger in the Pauli basis than in the two-spinor basis. Since all integrals and density matrices in the two-spinor basis are complex-valued, each integral–density contraction requires $8N^4$ FLOPs. In contrast, each integral–density contraction needs $4N^4$ FLOPs in the Pauli basis because integrals are real-valued. As a result, the computational cost in terms of FLOP count is much more efficient in the Pauli basis.

B. Atomic periodic trend

The purpose of the data presented here is to display the magnitude of the effect of the Dirac–Coulomb–Breit Hamiltonian in atomic systems. In particular, DHF energies are compared to one another in this section. Integral computation is performed with the LIBCINT integral library.[55] All calculations in this section are performed with a development version of the Chronus Quantum software package.[56] The speed of light utilized in this section is 137.035 999 679 94 a.u.

Ground state DHF energies were computed utilizing the Dirac–Coulomb and Dirac–Coulomb–Breit Hamiltonians. All atoms are defined to be neutral in these calculations. A core Hamiltonian guess is utilized, such that no spin multiplicity need to be defined for the wavefunction guess. The self-consistent-field optimization proceeds in the Kramers unrestricted framework in which the lowest N_e number of positive energy orbitals is singly occupied. In order to analyze the importance of relativistic two-electron corrections in Dirac Hartree–Fock, we also compare the results obtained using the $(LL|LL)$ approximation (previously referred to as the Bare–Coulomb[30] approximation), i.e., only $(LL|LL)$ integrals are used without contributions from the small component. The four-component Hamiltonians presented here differ only in their treatment of the two-electron interaction. This allows for the isolation of the effect of various two-electron corrections, particularly the terms of the Dirac–Coulomb–Breit Hamiltonian presented here.

The ground state energies of selected atomic species from across the Periodic Table were computed and relativistic two-electron contributions are compared in Table III. To obtain the ground state energies, we have carried out separate self-consistent-field (SCF) calculations with each of the three Hamiltonians and the $(LL|LL)$ approximation. Relativistic two-electron corrections are defined as the differences between different SCF energies (see the caption of Table III). The uncontracted ANO-RCC basis[57–59] set was utilized for all cases. The results are listed in Table III and plotted in Fig. 1. As the atomic number Z increases, the Dirac–Coulomb (ΔE^{DC}) and Breit ($\Delta E^{\mathrm{Breit}}$) corrections increase as expected, as shown in Fig. 1(a). Compared to ΔE^{DC}, the Breit correction becomes less important as the atomic number increases, as indicated by the decreasing ratio of $\frac{\Delta E^{\mathrm{Breit}}}{\Delta E^{\mathrm{DC}}}$ [see Fig. 1(b)].

We plot in Fig. 1(c) the magnetic and gauge contributions (ΔE^{Mag} and $\Delta E^{\mathrm{Gauge}}$) in the Dirac–Coulomb–Breit Hamiltonian and their ratio $\frac{\Delta E^{\mathrm{Gauge}}}{\Delta E^{\mathrm{Mag}}}$ in Fig. 1(d). Both the magnetic and gauge

30 August 2023 18:32:25

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TABLE III. Ground state SCF energies (Hartrees) for selected atoms using finite width nuclei and the uncontracted ANO-RCC basis.[57–59] $\Delta E^{DC} = E^{DC} - E^{LLLL}$, $\Delta E^{Breit} = E^{DCB} - E^{DC}$, $\Delta E^{Mag.} = \frac{1}{2}(E^{DCG} - E^{DC})$, and $\Delta E^{Gauge} = \Delta E^{Breit} - \Delta E^{Mag.}$, where E^{DCB}, E^{DCG}, E^{DC}, and E^{LLLL} are the ground state SCF energies calculated with the Dirac–Coulomb–Breit (DCB), Dirac–Coulomb–Gaunt (DCG), and Dirac–Coulomb (DC) Hamiltonians, respectively, and the $(LL|LL)$ approximation.

Element	Z	E^{LLLL}	E^{DC}	ΔE^{DC}	E^{DCB}	ΔE^{Breit}	$\Delta E^{Mag.}$	ΔE^{Gauge}
F	9	−99.540 92	−99.504 74	0.036 18	−99.493 29	0.011 44	0.005 99	0.005 46
Na	11	−162.159 79	−162.077 29	0.082 49	−162.053 92	0.023 37	0.012 38	0.010 99
Si	14	−289.662 42	−289.448 67	0.213 76	−289.393 78	0.054 89	0.029 42	0.025 47
Cl	17	−461.406 68	−460.947 16	0.459 51	−460.838 80	0.108 36	0.058 57	0.049 79
Ca	20	−680.572 25	−679.709 87	0.862 37	−679.518 88	0.191 00	0.103 88	0.087 11
Ti	22	−854.108 69	−852.857 54	1.251 14	−852.592 70	0.264 84	0.144 48	0.120 36
Cu	29	−1 657.190 12	−1 653.453 40	3.736 72	−1 652.775 81	0.677 59	0.372 57	0.305 02
Ag	47	−5 339.393 10	−5 314.625 70	24.767 40	−5 311.055 72	3.569 98	1.985 61	1.584 36
I	53	−7 155.395 18	−7 115.798 49	39.596 69	−7 110.390 59	5.407 90	3.014 22	2.393 67
Ce	58	−8 917.383 68	−8 861.043 87	56.339 81	−8 853.658 36	7.385 51	4.121 82	3.263 68
Pr	59	−9 298.560 18	−9 238.265 44	60.294 74	−9 230.432 81	7.832 63	4.372 22	3.460 41
Pm	61	−10 091.178 92	−10 022.330 95	68.847 97	−10 013.546 34	8.784 62	4.905 35	3.879 26
Sm	62	−10 502.861 37	−10 429.356 22	73.505 15	−10 420.062 39	9.293 83	5.190 33	4.103 50
Tb	65	−11 801.625 31	−11 712.825 12	88.800 18	−11 701.892 28	10.932 8	6.108 49	4.824 36
Ho	67	−12 721.922 60	−12 621.573 98	100.348 62	−12 609.433 93	12.140 05	6.784 47	5.355 58
Lu	71	−14 699.426 40	−14 572.526 42	126.899 98	−14 557.677 23	14.849 19	8.301 18	6.548 01
Au	79	−19 231.541 95	−19 035.579 05	195.962 91	−19 013.938 49	21.640 56	12.101 75	9.538 81

terms grow exponentially with respect to the atomic number and both contributions are equally important in the Breit Hamiltonian. Figure 1(d) shows that the ratio $\frac{\Delta E^{Gauge}}{\Delta E^{Mag}}$ approaches unity toward light elements and ~0.78 toward heavy elements. Recall that the Breit operator is the Gaunt term in the Feynman gauge, and in the Coulomb gauge, consists of half of the Gaunt term (i.e., magnetic contribution) and the gauge term. Therefore, another way to understand Fig. 1(d) is that the energetic difference between the Feynman gauge and the Coulomb gauge is approaching ~0% for light elements and ~20% for heavy elements.

C. Heavy-element molecules

In this section, we analyze the contribution of the Breit Hamiltonian to the ground state energy and its effect on the electronic structure characteristics of selected heavy-element compounds from the actinyl oxycation series. Linear geometries and experimental bond lengths of 1.76, 1.75, and 1.74 Å were utilized for uranyl, neptunyl, and plutonyl, respectively.[60]

Table IV gives the energetic decomposition of different relativistic two-electron interaction terms in the total energy of uranyl, neptunyl, and plutonyl. The uncontracted ANO-RCC-VDZP basis set was used for both the oxygen and actinide atoms. The main trends seen across the actinyl series reflect the growing nuclear charge of the actinide atom and mirror the atomic periodic trends seen in Sec. III B. Although the relative contribution of the Breit term is small (~0.1% of the total energy), its effect on electronic structure characteristics of the molecular bonding could be significant.

Density of states plots were generated using the occupied Dirac–Coulomb and Dirac–Coulomb–Breit molecular orbitals for the three actinyls presented in Table IV. These plots are presented in Fig. 2 and show a total large component density as well as a large component contribution from each angular momentum orbital type, i.e., s, p, d, and f characters. Orbital character is summed over the three atoms in the molecule.

Figures 2(a) and 2(b) show that the highest occupied orbitals of uranyl consist of six $5f$-$2p$ and six $6d$-$2p$ bonding orbitals with a very small contribution of s character. The occupied nonbonding $5f$ electron molecular orbitals in neptunyl and plutonyl are the next highest energy orbitals, appearing lower in energy than the 12 bonding orbitals.

Comparing the DOS plots for this series, the energies of bonding molecular orbitals in neptunyl are more spread out than for those of uranyl and plutonyl. Comparing the DOS plots computed using the Dirac–Coulomb and Dirac–Coulomb–Breit Hamiltonians, we see that the Breit term does not significantly alter the character of the orbitals or the general ordering of the molecular orbitals presented here, but it does alter their relative energetics. For example, a distinct sharpening of the highest energy peak in each of these systems can be observed in the Dirac–Coulomb–Breit case. This is a result of narrowing of the frontier orbital energy gap near HOMO. However, for deeper valence orbitals, there is no noticeable difference in the DOS plots computed using Dirac–Coulomb and Dirac–Coulomb–Breit Hamiltonians.

In order to investigate the effect of the Breit operator on energetic observables, the dissociation energies of uranyl, neptunyl, and plutonyl into $2 \times O^{2-}$ and U(VI), Np(VI), and Pu(VI), respectively, were calculated with both Dirac–Coulomb and Dirac–Coulomb–Breit. To compute the SCF energies of atomic An(VI) cations, a core Hamiltonian guess is utilized, such that no spin multiplicity need to be defined for the wavefunction guess. The SCF optimization proceeds in the Kramers unrestricted framework in which the lowest N_e number of positive energy orbitals is singly occupied. These dissociation energies are given in Table V. Note that

30 August 2023 18:32:25

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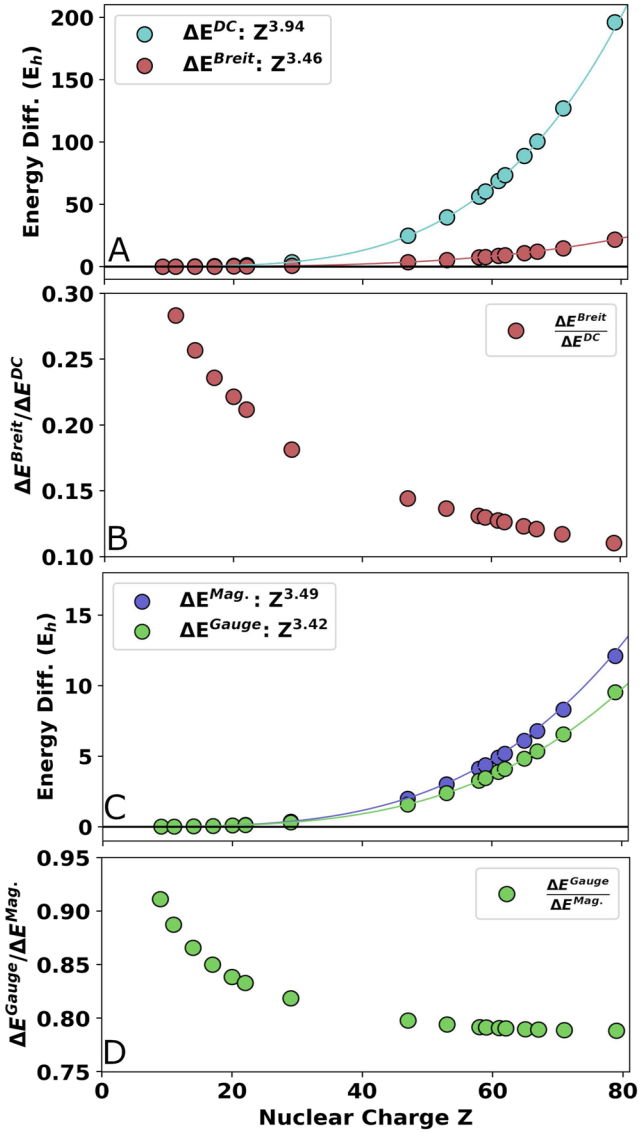


FIG. 1. (a) Contributions of Dirac–Coulomb and Breit relativistic corrections to the ground state SCF energy for selected elements. (b) Ratio between ΔE^{Breit} and ΔE^{DC} ground state energies. (c) Contribution of magnetic and gauge terms of the Breit Hamiltonian to the ground state SCF energy for selected elements. (d) Ratio between the gauge and magnetic portions of the Breit contribution to ground state energies.

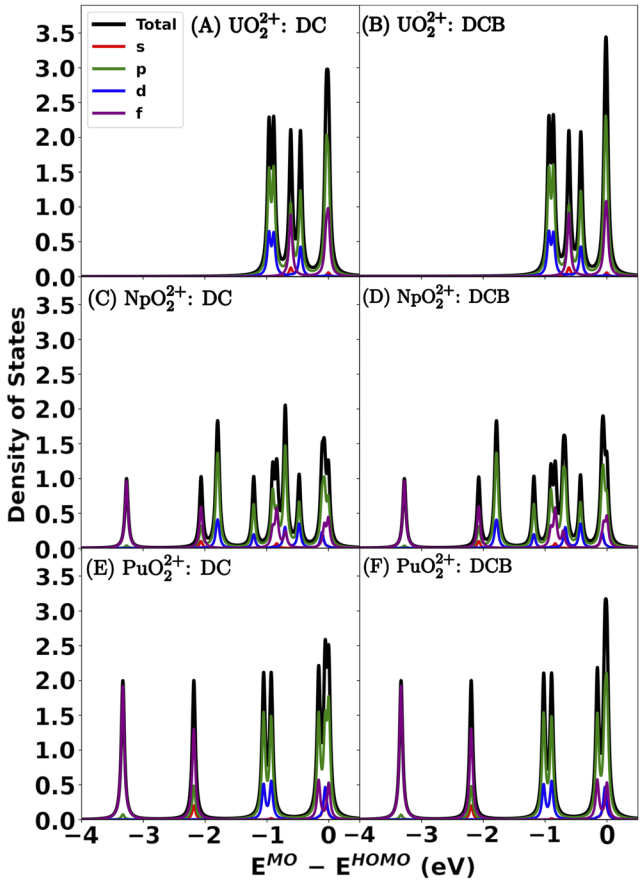


FIG. 2. Dirac–Hartree–Fock density of states plots of frontier molecular orbitals of actinyls with Dirac–Coulomb and Dirac–Coulomb–Breit Hamiltonians. Occupied molecular orbitals are shown with energies shifted with respect to the highest occupied molecular orbital (HOMO) for (a) UO_2^{2+} using Dirac–Coulomb, (b) UO_2^{2+} using Dirac–Coulomb–Breit, (c) NpO_2^{2+} using Dirac–Coulomb, (d) NpO_2^{2+} using Dirac–Coulomb–Breit, (e) PuO_2^{2+} using Dirac–Coulomb, and (f) PuO_2^{2+} using Dirac–Coulomb–Breit. Each orbital is broadened using Lorentzian broadening with a half-width at half-maximum of 0.03 eV. Partial density of states is calculated using Mulliken population analysis. The *s*, *p*, *d*, and *f* characters are summed over each of the three atoms in the molecule.

this study is meant to analyze the importance of the Breit contribution to bond dissociation energy at the Dirac–Hartree–Fock level. Accurate bond dissociation energies will require calculations using electron correlation methods.

TABLE IV. Ground state SCF energies (Hartrees) and relativistic two-electron contributions in three actinyls using finite width nuclei and uncontracted ANO-RCC-VDZP basis. $\Delta E^{\text{DC}} = E^{\text{DC}} - E^{\text{LLLL}}$, $\Delta E^{\text{Breit}} = E^{\text{DCB}} - E^{\text{DC}}$, $\Delta E^{\text{Mag.}} = \frac{1}{2}(E^{\text{DCG}} - E^{\text{DC}})$, and $\Delta E^{\text{Gauge}} = \Delta E^{\text{Breit}} - \Delta E^{\text{Mag}}$, where E^{DCB}, E^{DCG}, E^{DC}, and E^{LLLL} are the ground state SCF energies calculated with the Dirac–Coulomb–Breit (DCB), Dirac–Coulomb–Gaunt (DCG), and Dirac–Coulomb (DC) Hamiltonians, respectively, and the $(LL|LL)$ approximation.

Compound	Formula	E^{LLLL}	E^{DC}	ΔE^{DC}	E^{DCB}	ΔE^{Breit}	$\Delta E^{\text{Mag.}}$	ΔE^{Gauge}
Uranyl	UO_2^{2+}	−28 572.422 12	−28 202.267 63	370.154 49	−28 164.716 23	37.551 40	20.984 33	16.567 07
Neptunyl	NpO_2^{2+}	−29 383.809 43	−28 996.386 29	387.423 14	−28 957.313 71	39.072 57	21.831 54	17.241 03
Plutonyl	PuO_2^{2+}	−30 211.253 61	−29 805.949 66	405.303 94	−29 765.307 59	40.642 07	22.705 34	17.936 74

30 August 2023 18:32:25

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TABLE V. Ground state bond dissociation energies of three actinyls using finite width nuclei and uncontracted ANO-RCC-VDZP basis. $E_{\text{dissoc.}} = 2 \times E(O^{2-}) + E(\text{An(VI)}) - E(AnO_2^{2+})$. $\Delta E^{\text{Breit}}_{\text{dissoc.}} = E^{\text{DCB}}_{\text{dissoc.}} - E^{\text{DC}}_{\text{dissoc.}}$.

Compound	Formula	$E^{\text{DC}}_{\text{dissoc.}}$ (eV)	$E^{\text{DCB}}_{\text{dissoc.}}$ (eV)	$\Delta E^{\text{Breit}}_{\text{dissoc.}}$ (eV)
Uranyl	UO_2^{2+}	178.907 65	179.108 90	0.201 25
Neptunyl	NpO_2^{2+}	182.579 94	182.802 70	0.222 76
Plutonyl	PuO_2^{2+}	186.566 79	186.810 01	0.243 22

Dissociation energies, and therefore bonding energies, can be seen to be higher when calculated with Dirac–Coulomb–Breit than with the Dirac–Coulomb Hamiltonian in these compounds, suggesting that the Breit Hamiltonian stabilizes the chemical bonds between actinide and oxygen. This can be understood from the DOS plots in Fig. 2. The Breit Hamiltonian narrows the energy gap among frontier orbitals near HOMO. As a result, orbitals lower than HOMO will contribute more to the molecular bonding with Dirac–Coulomb–Breit than with the Dirac–Coulomb Hamiltonian. The difference between the calculated dissociation energies grows larger with an increasing atomic number of the actinide atom.

IV. CONCLUSION AND PERSPECTIVE

In this work, we applied Pauli spinor representation in the restricted–kinetic–balance condition for four-component Dirac–Hartree–Fock calculations with the Coulomb–Breit two-electron interaction. Along with the density–integral contraction formalism, we introduced two different methods for calculating frequency-independent gauge term integrals with the Gaussian basis. One method utilizes the generalized Obara–Saika algorithm, and the other is the second derivative of Coulomb interaction with Rys quadrature.

With this maximally component- and spin-separated formalism, the computational cost of density–integral contraction for gauge term in the Breit interaction is minimized. It is shown that this Pauli spinor representation is equivalent to the two-spinor formalism but with a much lower computational cost.

We applied this method for calculating atomic energies in order to analyze the periodic trend of the Breit term. It was shown that the Breit contribution becomes relatively less important compared to the Dirac–Coulomb term as the atomic number increases. The analysis also suggests that the difference between the Breit terms in the Feynman gauge and the Coulomb gauge approaches ~20% toward the heavy elements.

We also studied the effect of the Breit term on the electronic structure characteristics of actinyl oxycations. The analysis shows that the Breit term modifies the relative energies of frontier molecular orbitals near HOMO. As a result, it leads to a slightly stronger chemical bond.

Future development will be focused on combining this Pauli spinor formalism with atomic balance[52,61] and minimal-FLOP Cholesky integral decomposition[62] to further reduce the computational cost of four-component Dirac–Hartree–Fock.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Shichao Sun: Data curation (equal); Formal analysis (lead); Investigation (lead); Methodology (lead); Writing – original draft (equal); Writing – review & editing (equal). **Jordan Ehrman**: Data curation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Qiming Sun**: Conceptualization (supporting); Software (supporting); Writing – original draft (supporting); Writing – review & editing (supporting). **Xiaosong Li**: Conceptualization (equal); Software (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 A: COMPONENT- AND SPIN-SEPARATION IN GAUGE TERM

The gauge term contribution to the Fock matrix in the two-spinor basis reads

$$V^{g,LL}_{\mu\tau_1,\nu\tau_2} = \frac{1}{2}\sum_{\lambda\tau_4\kappa\tau_3} D^{SS}_{\lambda\tau_4,\kappa\tau_3}(\mu^L_{\tau_1}\boldsymbol{\sigma}\lambda^S_{\tau_4}|\kappa^S_{\tau_3}\boldsymbol{\sigma}\nu^L_{\tau_2})_3, \tag{A1}$$

$$V^{g,SS}_{\mu\tau_1,\nu\tau_2} = \frac{1}{2}\sum_{\lambda\tau_4\kappa\tau_3} D^{LL}_{\lambda_{\tau_4},\kappa_{\tau_3}}(\mu^S_{\tau_1}\boldsymbol{\sigma}\lambda^L_{\tau_4}|\kappa^L_{\tau_3}\boldsymbol{\sigma}\nu^S_{\tau_2})_3, \tag{A2}$$

$$V^{g,LS}_{\mu\tau_1,\nu\tau_2} = -\frac{1}{2}\sum_{\lambda\tau_4\kappa\tau_3}\Big\{D^{LS}_{\lambda\tau_4,\kappa\tau_3}(\mu^L_{\tau_1}\boldsymbol{\sigma}\nu^S_{\tau_2}|\kappa^S_{\tau_3}\boldsymbol{\sigma}\lambda^L_{\tau_4})_3 + D^{SL}_{\lambda\tau_4,\kappa\tau_3} \times\big[(\mu^L_{\tau_1}\boldsymbol{\sigma}\nu^S_{\tau_2}|\kappa^L_{\tau_3}\boldsymbol{\sigma}\lambda^S_{\tau_4})_3 - (\mu^L_{\tau_1}\boldsymbol{\sigma}\lambda^S_{\tau_4}|\kappa^L_{\tau_3}\boldsymbol{\sigma}\nu^S_{\tau_2})_3\big]\Big\}, \tag{A3}$$

$$V^{g,SL}_{\mu\tau_1,\nu\tau_2} = -\frac{1}{2}\sum_{\lambda\tau_4\kappa\tau_3}\Big\{D^{SL}_{\lambda\tau_4,\kappa\tau_3}(\mu^S_{\tau_1}\boldsymbol{\sigma}\nu^L_{\tau_2}|\kappa^L_{\tau_3}\boldsymbol{\sigma}\lambda^S_{\tau_4})_3 + D^{LS}_{\lambda\tau_4,\kappa\tau_3} \times\big[(\mu^S_{\tau_1}\boldsymbol{\sigma}\nu^L_{\tau_2}|\kappa^S_{\tau_3}\boldsymbol{\sigma}\lambda^L_{\tau_4})_3 - (\mu^S_{\tau_1}\boldsymbol{\sigma}\lambda^L_{\tau_4}|\kappa^S_{\tau_3}\boldsymbol{\sigma}\nu^L_{\tau_2})_3\big]\Big\}, \tag{A4}$$

where subscript "3" denotes that the integral is $\frac{1}{r_{12}^3}$ in contrast to $\frac{1}{r_{12}}$ and superscript g denotes the gauge term contribution.

In this work, we perform component- and spin-separation for gauge integrals. We use the Dirac identity,[1]

30 August 2023 18:32:25

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$(\boldsymbol{\sigma}\cdot\boldsymbol{\mu})(\boldsymbol{\sigma}\cdot\boldsymbol{\nu}) = \mathbf{I}\ (\boldsymbol{\mu}\cdot\boldsymbol{\nu}) + i\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\times\boldsymbol{\nu}$, and introduce ξ_τ as the spin representation,

$$\xi_\alpha = \begin{pmatrix}1\\0\end{pmatrix}, \qquad \xi_\beta = \begin{pmatrix}0\\1\end{pmatrix}.$$

We have the following identities:

$$\begin{aligned}
\xi_\alpha^\dagger\boldsymbol{\sigma}_x\xi_\beta &= 1, \quad \xi_\beta^\dagger\boldsymbol{\sigma}_x\xi_\alpha = 1,\\
\xi_\alpha^\dagger\boldsymbol{\sigma}_y\xi_\beta &= -i, \quad \xi_\beta^\dagger\boldsymbol{\sigma}_y\xi_\alpha = i,\\
\xi_\alpha^\dagger\boldsymbol{\sigma}_z\xi_\alpha &= 1, \quad \xi_\beta^\dagger\boldsymbol{\sigma}_z\xi_\beta = -1,\\
\xi_\alpha^\dagger\,\mathbf{I}\,\xi_\alpha &= 1, \quad \xi_\beta^\dagger\,\mathbf{I}\,\xi_\beta = 1,
\end{aligned}$$

otherwise zero.

The gauge integral in Eq. (A1) can be written as

$$\begin{aligned}
&(\mu^L_{\tau_1}\boldsymbol{\sigma}(1)\lambda^S_{\tau_4}|\kappa^S_{\tau_3}\boldsymbol{\sigma}(2)\nu^L_{\tau_2})_3\\
&\quad= \xi^\dagger_{\tau_1}(1)\xi_{\tau_4}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_2}(2)[\mathbf{I}(1)\mathbf{I}(2)\nabla_\kappa\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\lambda\\
&\qquad+ i\mathbf{I}(2)\nabla_\kappa\cdot\mathbf{r}_{12}\,\boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\lambda\\
&\qquad+ i\mathbf{I}(1)\boldsymbol{\sigma}(2)\cdot\nabla_\kappa\times\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\lambda\\
&\qquad- \boldsymbol{\sigma}(2)\cdot\nabla_\kappa\times\mathbf{r}_{12}\boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\lambda](\mu\lambda|\kappa\nu)_3. \qquad \text{(A5)}
\end{aligned}$$

Similarly, the integral in the first term of Eq. (A3) is

$$\begin{aligned}
&(\mu^L_{\tau_1}\boldsymbol{\sigma}(1)\nu^S_{\tau_2}|\kappa^S_{\tau_3}\boldsymbol{\sigma}(2)\lambda^L_{\tau_4})_3\\
&\quad= \xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[\mathbf{I}(1)\mathbf{I}(2)\nabla_\nu\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\kappa\\
&\qquad+ i\mathbf{I}(2)\mathbf{r}_{12}\cdot\nabla_\kappa\boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\nu + i\mathbf{I}(1)\nabla_\nu\cdot\mathbf{r}_{12}\boldsymbol{\sigma}(2)\cdot\nabla_\kappa\times\mathbf{r}_{12}\\
&\qquad- \boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\nu\boldsymbol{\sigma}(2)\cdot\nabla_\kappa\times\mathbf{r}_{12}](\mu\nu|\kappa\lambda)_3. \qquad \text{(A6)}
\end{aligned}$$

The integral in the second term of Eq. (A3) is

$$\begin{aligned}
&(\mu^L_{\tau_1}\boldsymbol{\sigma}(1)\nu^S_{\tau_2}|\kappa^L_{\tau_3}\boldsymbol{\sigma}(2)\lambda^S_{\tau_4})_3\\
&\quad= -\xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[\mathbf{I}(1)\mathbf{I}(2)\nabla_\nu\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\lambda\\
&\qquad+ i\mathbf{I}_1\nabla_\nu\cdot\mathbf{r}_{12}\boldsymbol{\sigma}(2)\cdot\mathbf{r}_{12}\times\nabla_\lambda + i\mathbf{I}_2\boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\nu\mathbf{r}_{12}\cdot\nabla_\lambda\\
&\qquad- \boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\nu\boldsymbol{\sigma}(2)\cdot\mathbf{r}_{12}\times\nabla_\lambda](\mu\nu|\kappa\lambda)_3, \qquad \text{(A7)}
\end{aligned}$$

and the exchange integral of Eq. (A3) is

$$\begin{aligned}
&(\mu^L_{\tau_1}\boldsymbol{\sigma}(1)\lambda^S_{\tau_4}|\kappa^L_{\tau_3}\boldsymbol{\sigma}(2)\nu^S_{\tau_2})_3\\
&\quad= -\xi^\dagger_{\tau_1}(1)\xi_{\tau_4}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_2}(2)[\mathbf{I}(1)\mathbf{I}(2)\nabla_\lambda\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\nu\\
&\qquad+ i\mathbf{I}(1)\nabla_\lambda\cdot\mathbf{r}_{12}\boldsymbol{\sigma}(2)\cdot\mathbf{r}_{12}\times\nabla_\nu + i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\lambda\mathbf{r}_{12}\cdot\nabla_\nu\\
&\qquad- \boldsymbol{\sigma}(1)\cdot\mathbf{r}_{12}\times\nabla_\lambda\boldsymbol{\sigma}(2)\cdot\mathbf{r}_{12}\times\nabla_\nu](\mu\lambda|\kappa\nu)_3, \qquad \text{(A8)}
\end{aligned}$$

and the exchange integral of Eq. (A2),

$$\begin{aligned}
&(\mu^S_{\tau_1}\boldsymbol{\sigma}(1)\lambda^L_{\tau_4}|\kappa^L_{\tau_3}\boldsymbol{\sigma}(2)\nu^S_{\tau_2})_3\\
&\quad= \xi^\dagger_{\tau_1}(1)\xi_{\tau_4}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_2}(2)\big[\mathbf{I}(1)\mathbf{I}(2)\nabla_\mu\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\nu\\
&\qquad+ i\mathbf{I}(1)\nabla_\mu\cdot\mathbf{r}_{12}\boldsymbol{\sigma}(2)\cdot\mathbf{r}_{12}\times\nabla_\nu + i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot\nabla_\mu\times\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\nu\\
&\qquad- \boldsymbol{\sigma}(1)\cdot\nabla_\mu\times\mathbf{r}_{12}\boldsymbol{\sigma}(2)\cdot\mathbf{r}_{12}\times\nabla_\nu\big](\mu\lambda|\kappa\nu)_3, \qquad \text{(A9)}
\end{aligned}$$

where ∇_κ is the nuclear coordinate derivative of the atomic basis χ_κ. $\mathbf{I}(2)$ and $\boldsymbol{\sigma}(2)$ are the identity and Pauli matrix for electron 2.

For simplicity and brevity, we introduce a simplified notation for two-spinor integrals,

$$\begin{aligned}
(\mu^L_{\tau_1}\boldsymbol{\sigma}\nu^S_{\tau_2}|\kappa^S_{\tau_3}\boldsymbol{\sigma}\lambda^L_{\tau_4})_3 &= \xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[\mathbf{I}(1)\mathbf{I}(2)(ss)\\
&\quad+ i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot(\sigma s) + i\mathbf{I}(1)(s\sigma)\cdot\boldsymbol{\sigma}(2)\\
&\quad+ \boldsymbol{\sigma}(1)\cdot(\sigma\sigma)\cdot\boldsymbol{\sigma}(2)](\mu\bar{\nu}|\bar{\kappa}\lambda)_3. \qquad \text{(A10)}
\end{aligned}$$

The "-" over ν,κ means derivatives are taken of these orbitals. To expand the spinor basis integral $(\mu^L_{\tau_1}\boldsymbol{\sigma}\nu^S_{\tau_2}|\kappa^S_{\tau_3}\boldsymbol{\sigma}\lambda^L_{\tau_4})_3$ as linear combination of second derivatives of spatial basis integrals as shown in Eq. (A10), we introduce the following short notations for the second derivative of spatial basis gauge integrals:

$$(ss)(\mu\bar{\nu}|\bar{\kappa}\lambda)_3 = \nabla_\nu\cdot\mathbf{r}_{12}\,\mathbf{r}_{12}\cdot\nabla_\kappa(\mu\nu|\kappa\lambda)_3, \qquad \text{(A11)}$$

$$(\sigma s)_J(\mu\bar{\nu}|\bar{\kappa}\lambda)_3 = (\mathbf{r}_{12}\times\nabla_\nu)_J(\mathbf{r}_{12}\cdot\nabla_\kappa)(\mu\nu|\kappa\lambda)_3, \qquad \text{(A12)}$$

$$(s\sigma)_J(\mu\bar{\nu}|\bar{\kappa}\lambda)_3 = (\nabla_\nu\cdot\mathbf{r}_{12})(\nabla_\kappa\times\mathbf{r}_{12})_J(\mu\nu|\kappa\lambda)_3, \qquad \text{(A13)}$$

$$(\sigma\sigma)_{JK}(\mu\bar{\nu}|\bar{\kappa}\lambda)_3 = -(\mathbf{r}_{12}\times\nabla_\nu)_J(\nabla_\kappa\times\mathbf{r}_{12})_K(\mu\nu|\kappa\lambda)_3, \qquad \text{(A14)}$$
$$J,K\in\{x,y,z\},$$

where $\mathbf{r}_{12}\mathbf{r}_{12}$ in Eqs. (A11)–(A14) is the operator evaluated in the integral. We move it outside of the $()_3$ for brevity. We give the definition for integrals with derivatives on the second and third centers.

Other types of integrals where the derivatives are taken on the second and fourth centers, or the first and fourth centers, can be derived from Eqs. (A11)–(A14) using symmetry. For the $V^{g,LL}$, $V^{g,LS}$, and $V^{g,SS}$ terms, we need gauge spinor integrals of the type $(LS|SL)$, $(SL|LS)$, $(LS|LS)$. By using the symmetry of the spinor integrals, we can express the gauge integrals of the type $(SL|LS)$, $(LS|LS)$ by Pauli components of $(LS|SL)$. Comparing Eq. (A9) with Eq. (A6), we have

$$\begin{aligned}
(\mu^S_{\tau_1}\boldsymbol{\sigma}\nu^L_{\tau_2}|\kappa^L_{\tau_3}\boldsymbol{\sigma}\lambda^S_{\tau_4})_3 &= \xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[\mathbf{I}(1)\mathbf{I}(2)(ss)\\
&\quad+ i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot(\sigma s) + i\mathbf{I}(1)(s\sigma)\cdot\boldsymbol{\sigma}(2)\\
&\quad+ \boldsymbol{\sigma}(1)\cdot(\sigma\sigma)\cdot\boldsymbol{\sigma}(2)](\bar{\mu}\nu|\kappa\bar{\lambda})_3\\
&= \xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[\mathbf{I}(1)\mathbf{I}(2)(ss)\\
&\quad- i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot(\sigma s) - i\mathbf{I}(1)(s\sigma)\cdot\boldsymbol{\sigma}(2)\\
&\quad+ \boldsymbol{\sigma}(1)\cdot(\sigma\sigma)\cdot\boldsymbol{\sigma}(2)](\nu\bar{\mu}|\bar{\lambda}\kappa)_3. \qquad \text{(A15)}
\end{aligned}$$

Similarly, comparing Eq. (A7) with Eq. (A6), we have

$$\begin{aligned}
(\mu^L_{\tau_1}\boldsymbol{\sigma}\nu^S_{\tau_2}|\kappa^L_{\tau_3}\boldsymbol{\sigma}\lambda^S_{\tau_4})_3 &= \xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[\mathbf{I}(1)\mathbf{I}(2)(ss)\\
&\quad+ i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot(\sigma s) + i\mathbf{I}(1)(s\sigma)\cdot\boldsymbol{\sigma}(2)\\
&\quad+ \boldsymbol{\sigma}(1)\cdot(\sigma\sigma)\cdot\boldsymbol{\sigma}(2)](\mu\bar{\nu}|\kappa\bar{\lambda})_3\\
&= \xi^\dagger_{\tau_1}(1)\xi_{\tau_2}(1)\xi^\dagger_{\tau_3}(2)\xi_{\tau_4}(2)[-\mathbf{I}(1)\mathbf{I}(2)(ss)\\
&\quad- i\mathbf{I}(2)\boldsymbol{\sigma}(1)\cdot(\sigma s) + i\mathbf{I}(1)(s\sigma)\cdot\boldsymbol{\sigma}(2)\\
&\quad+ \boldsymbol{\sigma}(1)\cdot(\sigma\sigma)\cdot\boldsymbol{\sigma}(2)](\mu\bar{\nu}|\bar{\lambda}\kappa)_3. \qquad \text{(A16)}
\end{aligned}$$

The discussion above illustrates the mathematical expressions and notations needed to derive the gauge contribution to the Fock matrix in the component- and spin-separated form. We skip the

30 August 2023 18:32:25

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detailed derivations and only present final working expressions. Note that the gauge contribution to the Fock matrix has a prefactor of $\frac{1}{(2c)^2}$. For brevity, we omit the prefactor in all equations.

The gauge term contribution to the Pauli components of the *LL* block of the Fock matrix is an exchange type,

$$\begin{aligned} V^{g,LL}_{\mu\nu,s} = \frac{1}{2}\{&D^{SS}_{\lambda\kappa,s}(ss) + i\big[D^{SS}_{\lambda\kappa,z}(s\sigma)_z + D^{SS}_{\lambda\kappa,x}(s\sigma)_x + D^{SS}_{\lambda\kappa,y}(s\sigma)_y\big] \\ &+ i\big[D^{SS}_{\lambda\kappa,z}(\sigma s)_z + D^{SS}_{\lambda\kappa,x}(\sigma s)_x + D^{SS}_{\lambda\kappa,y}(\sigma s)_y\big] \\ &+ \big[D^{SS}_{\lambda\kappa,s}(\sigma\cdot\sigma) - iD^{SS}_{\lambda\kappa,z}(\sigma\times\sigma)_z - iD^{SS}_{\lambda\kappa,y}(\sigma\times\sigma)_y \\ &- iD^{SS}_{\lambda\kappa,x}(\sigma\times\sigma)_x\big]\}(\mu\bar{\lambda}|\bar{\kappa}\nu)_3, \end{aligned} \tag{A17}$$

$$\begin{aligned} V^{g,LL}_{\mu\nu,z} = \frac{1}{2}\{&D^{SS}_{\lambda\kappa,z}(ss) + i\big[D^{SS}_{\lambda\kappa,s}(s\sigma)_z - iD^{SS}_{\lambda\kappa,y}(s\sigma)_x \\ &+ iD^{SS}_{\lambda\kappa,x}(s\sigma)_y\big] + i\big[D^{SS}_{\lambda\kappa,s}(\sigma s)_z + iD^{SS}_{\lambda\kappa,y}(\sigma s)_x \\ &- iD^{SS}_{\lambda\kappa,x}(\sigma s)_y\big] + D^{SS}_{\lambda\kappa,z}[-(\sigma\sigma)_{xx} - (\sigma\sigma)_{yy} + (\sigma\sigma)_{zz}] \\ &+ iD^{SS}_{\lambda\kappa,s}(\sigma\times\sigma)_z + D^{SS}_{\lambda\kappa,x}[(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}] \\ &+ D^{SS}_{\lambda\kappa,y}[(\sigma\sigma)_{yz} + (\sigma\sigma)_{zy}]\}(\mu\bar{\lambda}|\bar{\kappa}\nu)_3, \end{aligned} \tag{A18}$$

$$\begin{aligned} V^{g,LL}_{\mu\nu,x} = \frac{1}{2}\{&D^{SS}_{\lambda\kappa,x}(ss) + i\big[iD^{SS}_{\lambda\kappa,y}(s\sigma)_z + D^{SS}_{\lambda\kappa,s}(s\sigma)_x \\ &- iD^{SS}_{\lambda\kappa,z}(s\sigma)_y\big] + i\big[-iD^{SS}_{\lambda\kappa,y}(\sigma s)_z + D^{SS}_{\lambda\kappa,s}(\sigma s)_x \\ &+ iD^{SS}_{\lambda\kappa,z}(\sigma s)_y\big] + D^{SS}_{\lambda\kappa,x}[(\sigma\sigma)_{xx} - (\sigma\sigma)_{yy} - (\sigma\sigma)_{zz}] \\ &+ D^{SS}_{\lambda\kappa,y}[(\sigma\sigma)_{xy} + (\sigma\sigma)_{yx}] + D^{SS}_{\lambda\kappa,z}[(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}] \\ &+ iD^{SS}_{\lambda\kappa,s}(\sigma\times\sigma)_x\}(\mu\bar{\lambda}|\bar{\kappa}\nu)_3, \end{aligned} \tag{A19}$$

$$\begin{aligned} V^{g,LL}_{\mu\nu,y} = \frac{1}{2}\{&D^{SS}_{\lambda\kappa,y}(ss) + i\big[-iD^{SS}_{\lambda\kappa,x}(s\sigma)_z + iD^{SS}_{\lambda\kappa,z}(s\sigma)_x \\ &+ D^{SS}_{\lambda\kappa,s}(s\sigma)_y\big] + i\big[iD^{SS}_{\lambda\kappa,x}(\sigma s)_z - iD^{SS}_{\lambda\kappa,z}(\sigma s)_x \\ &+ D^{SS}_{\lambda\kappa,s}(\sigma s)_y\big] + D^{SS}_{\lambda\kappa,y}[-(\sigma\sigma)_{xx} + (\sigma\sigma)_{yy} - (\sigma\sigma)_{zz}] \\ &+ D^{SS}_{\lambda\kappa,x}[(\sigma\sigma)_{xy} + (\sigma\sigma)_{yx}] + iD^{SS}_{\lambda\kappa,s}(\sigma\times\sigma)_y \\ &+ D^{SS}_{\lambda\kappa,z}[(\sigma\sigma)_{yz} + (\sigma\sigma)_{zy}]\}(\mu\bar{\lambda}|\bar{\kappa}\nu)_3, \end{aligned} \tag{A20}$$

where $(\sigma\times\sigma)_x, (\sigma\times\sigma)_y, (\sigma\times\sigma)_z$ denote $(\sigma\sigma)_{yz} - (\sigma\sigma)_{zy}$, $(\sigma\sigma)_{zx} - (\sigma\sigma)_{xz}$, $(\sigma\sigma)_{xy} - (\sigma\sigma)_{yx}$, respectively.

Similarly, the Pauli components of the *SS* block of the Fock matrix are also an exchange type,

$$\begin{aligned} V^{g,SS}_{\mu\nu,s} = \frac{1}{2}\{&D^{LL}_{\lambda\kappa,s}(ss) + i\big[D^{LL}_{\lambda\kappa,z}(s\sigma)_z + D^{LL}_{\lambda\kappa,x}(s\sigma)_x + D^{LL}_{\lambda\kappa,y}(s\sigma)_y\big] \\ &+ i\big[D^{LL}_{\lambda\kappa,z}(\sigma s)_z + D^{LL}_{\lambda\kappa,x}(\sigma s)_x + D^{LL}_{\lambda\kappa,y}(\sigma s)_y\big] \\ &+ \big[D^{LL}_{\lambda\kappa,s}(\sigma\cdot\sigma) - iD^{LL}_{\lambda\kappa,z}(\sigma\times\sigma)_z - iD^{LL}_{\lambda\kappa,y}(\sigma\times\sigma)_y \\ &- iD^{LL}_{\lambda\kappa,x}(\sigma\times\sigma)_x\big]\}(\bar{\mu}\lambda|\kappa\bar{\nu})_3, \end{aligned} \tag{A21}$$

$$\begin{aligned} V^{g,SS}_{\mu\nu,z} = \frac{1}{2}\{&D^{LL}_{\lambda\kappa,z}(ss) + i\big[D^{LL}_{\lambda\kappa,s}(s\sigma)_z - iD^{LL}_{\lambda\kappa,y}(s\sigma)_x \\ &+ iD^{LL}_{\lambda\kappa,x}(s\sigma)_y\big] + i\big[D^{LL}_{\lambda\kappa,s}(\sigma s)_z + iD^{LL}_{\lambda\kappa,y}(\sigma s)_x \\ &- iD^{LL}_{\lambda\kappa,x}(\sigma s)_y\big] + D^{LL}_{\lambda\kappa,z}[-(\sigma\sigma)_{xx} - (\sigma\sigma)_{yy} + (\sigma\sigma)_{zz}] \\ &+ iD^{LL}_{\lambda\kappa,s}(\sigma\times\sigma)_z + D^{LL}_{\lambda\kappa,x}[(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}] \\ &+ D^{LL}_{\lambda\kappa,y}[(\sigma\sigma)_{yz} + (\sigma\sigma)_{zy}]\}(\bar{\mu}\lambda|\kappa\bar{\nu})_3, \end{aligned} \tag{A22}$$

$$\begin{aligned} V^{g,SS}_{\mu\nu,x} = \frac{1}{2}\{&D^{LL}_{\lambda\kappa,x}(ss) + i\big[iD^{LL}_{\lambda\kappa,y}(s\sigma)_z + D^{LL}_{\lambda\kappa,s}(s\sigma)_x \\ &- iD^{LL}_{\lambda\kappa,z}(s\sigma)_y\big] + i\big[-iD^{LL}_{\lambda\kappa,y}(\sigma s)_z + D^{LL}_{\lambda\kappa,s}(\sigma s)_x \\ &+ iD^{LL}_{\lambda\kappa,z}(\sigma s)_y\big] + D^{LL}_{\lambda\kappa,x}[(\sigma\sigma)_{xx} - (\sigma\sigma)_{yy} - (\sigma\sigma)_{zz}] \\ &+ D^{LL}_{\lambda\kappa,y}[(\sigma\sigma)_{xy} + (\sigma\sigma)_{yx}] + D^{LL}_{\lambda\kappa,z}[(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}] \\ &+ iD^{LL}_{\lambda\kappa,s}(\sigma\times\sigma)_x\}(\bar{\mu}\lambda|\kappa\bar{\nu})_3, \end{aligned} \tag{A23}$$

$$\begin{aligned} V^{g,SS}_{\mu\nu,y} = \frac{1}{2}\{&D^{LL}_{\lambda\kappa,y}(ss) + i\big[-iD^{LL}_{\lambda\kappa,x}(s\sigma)_z + iD^{LL}_{\lambda\kappa,z}(s\sigma)_x \\ &+ D^{LL}_{\lambda\kappa,s}(s\sigma)_y\big] + i\big[iD^{LL}_{\lambda\kappa,x}(\sigma s)_z - iD^{LL}_{\lambda\kappa,z}(\sigma s)_x \\ &+ D^{LL}_{\lambda\kappa,s}(\sigma s)_y\big] + D^{LL}_{\lambda\kappa,y}[-(\sigma\sigma)_{xx} + (\sigma\sigma)_{yy} - (\sigma\sigma)_{zz}] \\ &+ D^{LL}_{\lambda\kappa,x}[(\sigma\sigma)_{xy} + (\sigma\sigma)_{yx}] + iD^{LL}_{\lambda\kappa,s}(\sigma\times\sigma)_y \\ &+ D^{LL}_{\lambda\kappa,z}[(\sigma\sigma)_{yz} + (\sigma\sigma)_{zy}]\}(\bar{\mu}\lambda|\kappa\bar{\nu})_3. \end{aligned} \tag{A24}$$

The gauge contribution to the Pauli components of the *LS* and *SL* blocks of the Fock matrix includes both Coulomb and exchange types of integrals. For the *LS* block, the Coulomb part is

$$\begin{aligned} V^{g,LS}_{\mu\nu,s} = -\Bigg\{&\Bigg[D^{LS}_{\lambda\kappa,s}(ss) + i\sum_{J=x,y,z} D^{LS}_{\lambda\kappa J}(s\sigma)_J\Bigg](\mu\bar{\nu}|\bar{\kappa}\lambda)_3 \\ &+ \Bigg[D^{SL}_{\lambda\kappa,s}(ss) + i\sum_{J=x,y,z} D^{SL}_{\lambda\kappa J}(s\sigma)_J\Bigg](\mu\bar{\nu}|\kappa\bar{\lambda})_3\Bigg\}, \end{aligned} \tag{A25}$$

$$\begin{aligned} V^{g,LS}_{\mu\nu,J} = -\Bigg\{&\Bigg[iD^{LS}_{\lambda\kappa,s}(\sigma s)_J + \sum_{K=x,y,z} D^{LS}_{\lambda\kappa,K}(\sigma\sigma)_{JK}\Bigg](\mu\bar{\nu}|\bar{\kappa}\lambda)_3 \\ &+ \Bigg[iD^{SL}_{\lambda\kappa,s}(\sigma s)_J + \sum_{K=x,y,z} D^{SL}_{\lambda\kappa,K}(\sigma\sigma)_{JK}\Bigg](\mu\bar{\nu}|\kappa\bar{\lambda})_3\Bigg\}, \\ &J,K \in \{x,y,z\}. \end{aligned} \tag{A26}$$

The exchange part of *LS* block is

$$\begin{aligned} V^{g,LS}_{\mu\nu,s} = \frac{1}{2}\{&D^{SL}_{\lambda\kappa,s}(ss) + i\big[D^{SL}_{\lambda\kappa,z}(s\sigma)_z + D^{SL}_{\lambda\kappa,x}(s\sigma)_x \\ &+ D^{SL}_{\lambda\kappa,y}(s\sigma)_y\big] + i\big[D^{SL}_{\lambda\kappa,z}(\sigma s)_z + D^{SL}_{\lambda\kappa,x}(\sigma s)_x \\ &+ D^{SL}_{\lambda\kappa,y}(\sigma s)_y\big] + \big[D^{SL}_{\lambda\kappa,s}(\sigma\cdot\sigma) - iD^{SL}_{\lambda\kappa,z}(\sigma\times\sigma)_z \\ &- i\,D^{SL}_{\lambda\kappa,y}(\sigma\times\sigma)_y - iD^{SL}_{\lambda\kappa,x}(\sigma\times\sigma)_x\big]\}(\mu\bar{\lambda}|\kappa\bar{\nu})_3, \end{aligned} \tag{A27}$$

$$\begin{aligned} V^{g,LS}_{\mu\nu,z} = \frac{1}{2}\{&D^{SL}_{\lambda\kappa,z}(ss) + i\big[D^{SL}_{\lambda\kappa,s}(s\sigma)_z - iD^{SL}_{\lambda\kappa,y}(s\sigma)_x \\ &+ iD^{SL}_{\lambda\kappa,x}(s\sigma)_y\big] + i\big[D^{SL}_{\lambda\kappa,s}(\sigma s)_z + iD^{SL}_{\lambda\kappa,y}(\sigma s)_x \\ &- iD^{SL}_{\lambda\kappa,x}(\sigma s)_y\big] + D^{SL}_{\lambda\kappa,z}[-(\sigma\sigma)_{xx} - (\sigma\sigma)_{yy} + (\sigma\sigma)_{zz}] \\ &+ iD^{SL}_{\lambda\kappa,s}(\sigma\times\sigma)_z + D^{SL}_{\lambda\kappa,x}[(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}] \\ &+ D^{SL}_{\lambda\kappa,y}[(\sigma\sigma)_{yz} + (\sigma\sigma)_{zy}]\}(\mu\bar{\lambda}|\kappa\bar{\nu})_3, \end{aligned} \tag{A28}$$

$$\begin{aligned} V^{g,LS}_{\mu\nu,x} = \frac{1}{2}\{&D^{SL}_{\lambda\kappa,x}(ss) + i\big[iD^{SL}_{\lambda\kappa,y}(s\sigma)_z + D^{SL}_{\lambda\kappa,s}(s\sigma)_x - iD^{SL}_{\lambda\kappa,z}(s\sigma)_y\big] \\ &+ i\big[-iD^{SL}_{\lambda\kappa,y}(\sigma s)_z + D^{SL}_{\lambda\kappa,s}(\sigma s)_x + iD^{SL}_{\lambda\kappa,z}(\sigma s)_y\big] \\ &+ D^{SL}_{\lambda\kappa,x}[(\sigma\sigma)_{xx} - (\sigma\sigma)_{yy} - (\sigma\sigma)_{zz}] + D^{SL}_{\lambda\kappa,y}[(\sigma\sigma)_{xy} + (\sigma\sigma)_{yx}] \\ &+ D^{SL}_{\lambda\kappa,z}[(\sigma\sigma)_{xz} + (\sigma\sigma)_{zx}] + iD^{SL}_{\lambda\kappa,s}(\sigma\times\sigma)_x\}(\mu\bar{\lambda}|\kappa\bar{\nu})_3, \end{aligned} \tag{A29}$$

30 August 2023 18:32:25

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$$V^{g,LS}_{\mu\nu,y} = \frac{1}{2}\{D^{SL}_{\lambda\kappa,y}(ss) + i[-iD^{SL}_{\lambda\kappa,x}(s\sigma)_z + iD^{SL}_{\lambda\kappa,z}(s\sigma)_x + D^{SL}_{\lambda\kappa,s}(s\sigma)_y] + i[iD^{SL}_{\lambda\kappa,x}(\sigma s)_z - iD^{SL}_{\lambda\kappa,z}(\sigma s)_x + D^{SL}_{\lambda\kappa,s}(\sigma s)_y] + D^{SL}_{\lambda\kappa,y}[-(\sigma\sigma)_{xx} + (\sigma\sigma)_{yy} - (\sigma\sigma)_{zz}] + D^{SL}_{\lambda\kappa,x}[(\sigma\sigma)_{xy} + (\sigma\sigma)_{yx}] + iD^{SL}_{\lambda\kappa,s}(\sigma\times\sigma)_y + D^{SL}_{\lambda\kappa,z}[(\sigma\sigma)_{yz} + (\sigma\sigma)_{zy}]\}(\mu\tilde{\lambda}|\kappa\bar{\nu})_3. \quad \text{(A30)}$$

The *SL* block can be obtained by taking the complex conjugate transpose of the *LS* block,

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

APPENDIX B: GAUGE INTEGRAL EVALUATION WITH SECOND DERIVATIVES OF COULOMB INTEGRAL

The frequency independent gauge term operator is

$$\frac{(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})}{2r_{12}^3} = \boldsymbol{\alpha}_1\cdot\frac{\mathbf{r}_{12}\otimes\mathbf{r}_{12}}{2r_{12}^3}\cdot\boldsymbol{\alpha}_2. \quad \text{(B1)}$$

Define the Cartesian Gaussian basis function as

$$\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta) = (x-R_x)^{n_x}(y-R_y)^{n_y}(z-R_z)^{n_z}\exp[-\zeta(\mathbf{r}-\mathbf{R})^2]. \quad \text{(B2)}$$

The integral of the gauge operator in the Gaussian basis is a 3×3 second order tensor that has six independent elements: *xx*, *xy*, *xz*, *yy*, *yz*, and *zz*. A component of the gauge integral is defined as

$$(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3, \quad \text{(B3)}$$

where subscript 3 denotes $|\mathbf{r}_{12}|^{-3}$. $\mathbf{n}_{12} = (n_{12}^x, n_{12}^y, n_{12}^z)$ is a vector that denotes the component of the operator, $x_{12}^{n_{12}^x} y_{12}^{n_{12}^y} z_{12}^{n_{12}^z}$. Thus, *xx*, *xy*, *xz*, *yy*, *yz*, and *zz* components correspond to $\mathbf{n}_{12} = (2,0,0)$, $(1,1,0)$, $(1,0,1)$, $(0,2,0)$, $(0,1,1)$, and $(0,0,2)$, respectively.

The first-order derivative for the Coulomb operator is

$$\nabla_1\frac{1}{r_{12}} = -\frac{\mathbf{r}_{12}}{r_{12}^3}. \quad \text{(B4)}$$

We can use integration by parts to compute the first-order derivatives of the two-electron integrals,

$$-\left(\mathbf{ab}|\nabla_1\frac{1}{r_{12}}|\mathbf{cd}\right) = (\mathbf{a}^{(1)}\mathbf{b}|\mathbf{cd}) + (\mathbf{ab}^{(1)}|\mathbf{cd}). \quad \text{(B5)}$$

The superscript $(\mathbf{1})$ refers to the gradient of basis function with respect to electron 1. The four-index notations are

$$\left(\mathbf{ab}|\nabla_1\frac{1}{r_{12}}|\mathbf{cd}\right) = \int d\mathbf{r}_1\int d\mathbf{r}_1\varphi^*(\mathbf{r}_1-\mathbf{A};\mathbf{a})\varphi(\mathbf{r}_1-\mathbf{B};\mathbf{b})\nabla_1\frac{1}{r_{12}}\varphi^*(\mathbf{r}_2-\mathbf{C};\mathbf{c})\varphi(\mathbf{r}_2-\mathbf{D};\mathbf{d}),$$

$$(\mathbf{a}^{(u)}\mathbf{b}|\mathbf{cd}) = \int d\mathbf{r}_1\int d\mathbf{r}_1(\nabla_{1u}\varphi^*(\mathbf{r}_1-\mathbf{A};\mathbf{a}))\varphi(\mathbf{r}_1-\mathbf{B};\mathbf{b})\frac{1}{r_{12}}\varphi^*(\mathbf{r}_2-\mathbf{C};\mathbf{c})\varphi(\mathbf{r}_2-\mathbf{D};\mathbf{d}).$$

The superscript (u) in $(\mathbf{a}^{(u)}\mathbf{b}|\mathbf{cd})$ refers to taking the first derivative with respect to $u\in\{x,y,z\}$ for the particular basis function.

By using the relation [Eq. (B4)], we can decompose the gauge interactions into two terms,

$$\frac{(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})}{2r_{12}^3} = \frac{1}{2}(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})\boldsymbol{\alpha}_2\cdot\left(-\nabla_1\frac{1}{r_{12}}\right) = \frac{1}{2}(\boldsymbol{\alpha}_1\cdot\mathbf{r}_1)\boldsymbol{\alpha}_2\cdot\left(-\nabla_1\frac{1}{r_{12}}\right) - \frac{1}{2}(\boldsymbol{\alpha}_1\cdot\mathbf{r}_2)\boldsymbol{\alpha}_2\cdot\left(-\nabla_1\frac{1}{r_{12}}\right).$$

Taking the integration by parts relation [Eq. (B5)], we then derive an expression to compute a gauge integral from five regular Coulomb integrals,

$$\left(\mathbf{ab}|\frac{(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})}{2r_{12}^3}|\mathbf{cd}\right) = \frac{1}{2}\sum_{u,v=x,y,z}\alpha_{1,u}\alpha_{2,v}\times\left((\mathbf{a}^{(v)}r_{1u}\mathbf{b}|\mathbf{cd}) + (\mathbf{a}r_{1u}\mathbf{b}^{(v)}|\mathbf{cd}) + \delta_{uv}(\mathbf{ab}|\mathbf{cd}) - (\mathbf{a}^{(v)}\mathbf{b}|\mathbf{c}r_{2u}\mathbf{d}) - (\mathbf{ab}^{(v)}|\mathbf{c}r_{2u}\mathbf{d})\right). \quad \text{(B6)}$$

All five Coulomb integral terms above can be evaluated with the regular electron repulsion integral algorithms.

In the LIBCINT integral library,[55] the gauge integrals are computed using the Rys-quadrature approach. Based on the working expression in Eq. (B6), when calling Rys-quadrature for the regular Coulomb integrals, one needs to solve the Rys-polynomials for the total angular moment of the entire Coulomb integral with the total angular momentum raised by two. This roughly has the same cost as the second-order derivatives of Coulomb integrals. In addition, when the restricted–kinetic–balanced basis is used for small components, the total angular momentum of the Coulomb integral is raised by another two. This leads to roughly the same cost as fourth-order derivatives of regular Coulomb integrals.

APPENDIX C: GAUGE INTEGRAL EVALUATION WITH GENERALIZED OBARA–SAIKA ALGORITHM

1. Laplace transformation of the operator

In general, $(\frac{1}{|\mathbf{r}|})^\lambda$ can be written in the form of Laplace transform,

$$\left(\frac{1}{|\mathbf{r}|}\right)^\lambda = \int_0^\infty du\frac{2u^{\lambda-1}}{\Gamma(\lambda/2)}e^{-u^2\mathbf{r}^2} = \int_0^\infty du\frac{2u^{\lambda-1}}{\Gamma(\lambda/2)}\varphi(\mathbf{r};\mathbf{0},u^2). \quad \text{(C1)}$$

The μ, ν elements of the tensor operator can be expressed as the Laplace transform of Cartesian Gaussian with a total angular momentum of two,

$$\frac{(r_{12})_\mu(r_{12})_\nu}{r_{12}^3} = \int_0^\infty du\frac{2u^2}{\Gamma(3/2)}(r_{12})_\mu(r_{12})_\nu e^{-u^2(\mathbf{r}_{12})^2} = \int_0^\infty du\frac{2u^2}{\Gamma(3/2)}\varphi(\mathbf{r}_1-\mathbf{r}_2;\mathbf{1}_\mu+\mathbf{1}_\nu,u^2), \quad \text{(C2)}$$

30 August 2023 18:32:25

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where $\mathbf{1}_\mu$ denotes a vector whose μ component is 1, otherwise 0. Thus, the gauge integral can be written as Laplace transform,

$$(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3 = \int_0^\infty du \frac{2u^2}{\Gamma(3/2)}[\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd}], \tag{C3}$$

where $[\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd}]$ is the overlap integral,

$$[\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd}] = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \varphi^*(\mathbf{r}_1 - \mathbf{A}; \mathbf{a}, \zeta_a)\varphi(\mathbf{r}_1 - \mathbf{B}; \mathbf{b}, \zeta_b) \times \varphi(\mathbf{r}_1 - \mathbf{r}_2; \mathbf{n}_{12}, u^2)\varphi^*(\mathbf{r}_2 - \mathbf{C}; \mathbf{c}, \zeta_c)\varphi(\mathbf{r}_2 - \mathbf{D}; \mathbf{d}, \zeta_d). \tag{C4}$$

Similarly, integral of the operator $\frac{(r_{12})_x^{n_{12x}}(r_{12})_y^{n_{12y}}(r_{12})_z^{n_{12z}}}{|\mathbf{r}_{12}|}$ can be written as

$$(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_1 = \int_0^\infty du \frac{2u^2}{\Gamma(1/2)}[\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd}], \tag{C5}$$

and Eq. (C5) becomes the Coulomb integral when $\mathbf{n}_{12} = (0,0,0)$.

2. Recursion relations for auxiliary integrals

In order to use the generalized Obara–Saika recursion introduced in Ref. 63 to compute the gauge term, we define auxiliary integrals,

$$(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} = \int_0^\infty du \frac{2u^2}{\Gamma(3/2)}[\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd}]\left(\frac{u^2}{\rho+u^2}\right)^m,$$
$$(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_1^{(m)} = \int_0^\infty du \frac{2}{\Gamma(1/2)}[\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd}]\left(\frac{u^2}{\rho+u^2}\right)^m, \tag{C6}$$

where

$$\rho = \frac{\zeta\eta}{\zeta+\eta},$$
$$\zeta = \zeta_a + \zeta_b,$$
$$\eta = \zeta_c + \zeta_d,$$

and m is the non-negative integer. The gauge integral is $(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(0)}$.

First, we derived the recursion relation for $\mathbf{n}_{12}$ using Eq. (128) in Ref. 63,

$$\begin{aligned}(\mathbf{ab}|\mathbf{n}_{12}+\mathbf{1}_\mu|\mathbf{cd})_\lambda^{(m)} &= \frac{1}{2\zeta}N_\mu(\mathbf{n}_{12})\left\{(\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_\lambda^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_\lambda^{(m+1)}\right\} + \frac{1}{2\eta}N_\mu(\mathbf{n}_{12})\left\{(\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_\lambda^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_\lambda^{(m+1)}\right\} \\ &+ P_\mu\left\{(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m+1)}\right\} + \frac{1}{2\zeta}N_\mu(\mathbf{a})\left\{((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m)} - ((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m+1)}\right\} \\ &+ \frac{1}{2\zeta}N_\mu(\mathbf{b})\left\{(\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m)} - (\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m+1)}\right\} - \left\{Q_\mu\left[(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_\lambda^{(m+1)}\right]\right. \\ &+ \frac{1}{2\eta}N_\mu(\mathbf{c})\left[(\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}-\mathbf{1}_\mu)\mathbf{d})_\lambda^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}-\mathbf{1}_\mu)\mathbf{d})_\lambda^{(m+1)}\right] \\ &+ \left.\frac{1}{2\eta}N_\mu(\mathbf{d})\left[(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{c}(\mathbf{d}-\mathbf{1}_\mu))_\lambda^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|\mathbf{c}(\mathbf{d}-\mathbf{1}_\mu))_\lambda^{(m+1)}\right]\right\},\end{aligned} \tag{C7}$$

where λ can be 1 or 3. Although Eq. (C7) is not directly used in the integral evaluation, it is important for deriving the vertical recursion for electron 2 [Eq. (C11)] and the initial integral [Eq. (C14)].

The vertical recursion for the auxiliary Cartesian Gaussian integral for electron 1 ($\mathbf{a}$ and $\mathbf{b}$) is

$$\begin{aligned}((\mathbf{a}+\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} &= (\mathbf{P}-\mathbf{A})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} + (\mathbf{W}-\mathbf{P})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)} + \frac{\rho}{2\zeta}\frac{\Gamma(1/2)}{\Gamma(3/2)}N_\mu(\mathbf{n}_{12})(\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_1^{(m+1)} \\ &+ \frac{1}{2\zeta}N_\mu(\mathbf{a})\left\{((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} - \frac{\rho}{\zeta}((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)}\right\} + \frac{1}{2\zeta}N_\mu(\mathbf{b})\left\{(\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)}\right. \\ &- \left.\frac{\rho}{\zeta}(\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)}\right\} + \frac{1}{2(\zeta+\eta)}\left\{N_\mu(\mathbf{c})(\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}-\mathbf{1}_\mu)\mathbf{d})_3^{(m+1)} + N_\mu(\mathbf{d})(\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}(\mathbf{d}-\mathbf{1}_\mu))_3^{(m+1)}\right\},\end{aligned} \tag{C8}$$

where $\mu, \nu \in \{x, y, z\}$, $\mathbf{P} = \frac{\zeta_a\mathbf{A}+\zeta_b\mathbf{B}}{\zeta}$, $\mathbf{Q} = \frac{\zeta_c\mathbf{C}+\zeta_d\mathbf{D}}{\eta}$, and $\mathbf{W} = \frac{\zeta\mathbf{P}+\eta\mathbf{Q}}{\zeta+\eta}$. Since $n_{12}^x + n_{12}^y + n_{12}^z = 2$, we can define $\mathbf{n}_{12} - \mathbf{1}_\mu = \mathbf{1}_\nu$. The integral of the third term of Eq. (C8) can be split into three Coulomb integrals,

$$(\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_1^{(m+1)} = ((\mathbf{a}+\mathbf{1})_\nu\mathbf{b}|\mathbf{cd})_1^{(m+1)} - (\mathbf{ab}|(\mathbf{c}+\mathbf{1})_\nu\mathbf{d})_1^{(m+1)} + (\mathbf{A}-\mathbf{C})_\nu(\mathbf{ab}|\mathbf{cd})_1^{(m+1)}. \tag{C9}$$

To derive the vertical recursion for electron 2, we first note that

$$(\mathbf{ab}|\mathbf{n}_{12}+\mathbf{1}_\mu|\mathbf{cd})_3^{(m)} = ((\mathbf{a}+\mathbf{1})_\mu\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}+\mathbf{1})_\mu\mathbf{d})_3^{(m)} + (\mathbf{A}-\mathbf{C})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)}. \tag{C10}$$

Combining Eq. (C10) with the vertical recursion of electron 1 [Eq. (C8)] and the recursion for $\mathbf{n}_{12}$ [Eq. (C7)], we have

30 August 2023 18:32:25

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$$(\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}+\mathbf{1}_\mu)\mathbf{d})_3^{(m)} = (\mathbf{Q}-\mathbf{C})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} + (\mathbf{W}-\mathbf{Q})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)} - \frac{\rho}{2\eta}\frac{\Gamma(1/2)}{\Gamma(3/2)}N_\mu(\mathbf{n}_{12})(\mathbf{ab}|\mathbf{n}_{12}-\mathbf{1}_\mu|\mathbf{cd})_1^{(m+1)}$$
$$+\frac{1}{2\eta}N_\mu(\mathbf{c})\left\{(\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}-\mathbf{1}_\mu)\mathbf{d})_3^{(m)} - \frac{\rho}{\eta}(\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}-\mathbf{1}_\mu)\mathbf{d})_3^{(m+1)}\right\} + \frac{1}{2\eta}N_\mu(\mathbf{d})\left\{(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{c}(\mathbf{d}-\mathbf{1}_\mu))_3^{(m)}\right.$$
$$\left. - \frac{\rho}{\eta}(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{c}(\mathbf{d}-\mathbf{1}_\mu))_3^{(m+1)}\right\} + \frac{1}{2(\zeta+\eta)}\left\{N_\mu(\mathbf{a})((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)} + N_\mu(\mathbf{b})(\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{n}_{12}|(\mathbf{cd})_3^{(m+1)}\right\}. \quad \text{(C11)}$$

Note that the third term of Eq. (C11) is different from that in Eq. (C8) by a negative sign.

Horizontal recursions for electron 1 and 2 can be obtained from vertical recursions Eqs. (C8) and (C11), respectively,

$$(\mathbf{a}(\mathbf{b}+\mathbf{1}_\mu)|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} = ((\mathbf{a}+\mathbf{1}_\mu)\mathbf{b}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} + (\mathbf{A}-\mathbf{B})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)}, \quad \text{(C12)}$$

$$(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{c}(\mathbf{d}+\mathbf{1}_\mu))_3^{(m)} = (\mathbf{ab}|\mathbf{n}_{12}|(\mathbf{c}+\mathbf{1}_\mu)\mathbf{d})_3^{(m)} + (\mathbf{C}-\mathbf{D})_\mu(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)}. \quad \text{(C13)}$$

With horizontal [Eqs. (C12) and (C13)] and vertical recursion relations [Eqs. (C8) and (C11)], the gauge integral can be expressed in terms of regular ERIs and $(\mathbf{00}|\mathbf{n}_{12}|\mathbf{00})_3^{(m)}$ integrals.

3. $(\mathbf{00}|\mathbf{n}_{12}|\mathbf{00})_3^{(m)}$ auxiliary integrals

Since $\mathbf{n}_{12}$ has a total angular momentum of 2, we can write it as $\mathbf{n}_{12} = \mathbf{1}_\mu + \mathbf{1}_\nu$. The $(\mathbf{00}|\mathbf{n}_{12}|\mathbf{00})_3^{(m)}$ auxiliary integral of the gauge operator can be written in terms of auxiliary integrals of the Coulomb operator using Eq. (C7),

$$\begin{aligned}(\mathbf{00}|\mathbf{1}_\mu+\mathbf{1}_\nu|\mathbf{00})_3^{(m)} &= \left(\frac{1}{2\zeta}+\frac{1}{2\eta}\right)N_\mu(\mathbf{1}_\nu)\left\{(\mathbf{00}|\mathbf{1}_\nu-\mathbf{1}_\mu|\mathbf{00})_3^{(m)}\right.\\ &\quad\left.-(\mathbf{00}|\mathbf{1}_\nu-\mathbf{1}_\mu|\mathbf{00})_3^{(m+1)}\right\}\\ &\quad+(P_\mu-Q_\mu)\left\{(\mathbf{00}|\mathbf{1}_\nu|\mathbf{00})_3^{(m)}-(\mathbf{00}|\mathbf{1}_\nu|\mathbf{00})_3^{(m+1)}\right\}\\ &= \frac{\delta_{\mu\nu}}{2}\left(\frac{1}{\zeta}+\frac{1}{\eta}\right)(\mathbf{00}|\mathbf{0}|\mathbf{00})_1^{(m+1)}\frac{\Gamma(1/2)}{\Gamma(3/2)}\rho\\ &\quad+(P_\mu-Q_\mu)\frac{\Gamma(1/2)}{\Gamma(3/2)}\rho(P_\nu-Q_\nu)\\ &\quad\times\left\{(\mathbf{00}|\mathbf{0}|\mathbf{00})_1^{(m+1)}-(\mathbf{00}|\mathbf{0}|\mathbf{00})_1^{(m+2)}\right\}, \quad \text{(C14)}\end{aligned}$$

where we use the relation $(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)} = \frac{\Gamma(1/2)}{\Gamma(3/2)}\rho(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_1^{(m+1)}$. This relation can be derived

$$\begin{aligned}&(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m)} - (\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_3^{(m+1)}\\ &= \int_0^\infty du\frac{2u^2}{\Gamma(3/2)}(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})\left[\left(\frac{u^2}{\rho+u^2}\right)^m-\left(\frac{u^2}{\rho+u^2}\right)^{m+1}\right]\\ &= \int_0^\infty du\frac{2u^2}{\Gamma(3/2)}(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})\left(\frac{u^2}{\rho+u^2}\right)^m\left(1-\frac{u^2}{\rho+u^2}\right)\\ &= \int_0^1 dt\rho^{1/2}(1-t^2)^{-3/2}\frac{2}{\Gamma(3/2)}\left(\frac{\rho t^2}{1-t^2}\right)(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})t^{2m}(1-t^2)\\ &= \int_0^1 dt\rho^{1/2}(1-t^2)^{-3/2}\frac{2}{\Gamma(3/2)}\rho(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})t^{2m+2}\\ &= \int_0^\infty du\frac{2\rho}{\Gamma(3/2)}(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})\left(\frac{u^2}{\rho+u^2}\right)^{m+1}\\ &= \frac{\Gamma(1/2)}{\Gamma(3/2)}\rho\int_0^\infty du\frac{2}{\Gamma(1/2)}(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})\left(\frac{u^2}{\rho+u^2}\right)^{m+1}\\ &= \frac{\Gamma(1/2)}{\Gamma(3/2)}\rho(\mathbf{ab}|\mathbf{n}_{12}|\mathbf{cd})_1^{(m+1)}, \quad \text{(C15)}\end{aligned}$$

where we used $t^2 = \frac{u^2}{\rho+u^2}$, $du = \rho^{1/2}(1-t^2)^{-3/2}dt$, $(\frac{\rho}{\rho+u^2})^{3/2} = (1-t^2)^{3/2}$, and note that $\frac{\Gamma(1/2)}{\Gamma(3/2)} = 2$.

Using Eq. (C14), $(\mathbf{00}|\mathbf{n}_{12}|\mathbf{00})_3^{(m)}$ integral can be evaluated using

$$(\mathbf{00}|\mathbf{0}|\mathbf{00})_1^{(m)} = \frac{2\pi^{5/2}}{\zeta\eta\sqrt{\zeta+\eta}}K_{ab}K_{cd}F_m(T), \quad \text{(C16)}$$

$$K_{ab} = \exp\left(-\frac{\zeta_a\zeta_b}{\zeta}(\mathbf{A}-\mathbf{B})^2\right), \quad \text{(C17)}$$

$$K_{cd} = \exp\left(-\frac{\zeta_c\zeta_d}{\eta}(\mathbf{C}-\mathbf{D})^2\right), \quad \text{(C18)}$$

where the Boys function $F_m(T) = \int_0^1 dt\, t^{2m}\exp(-Tt^2)$ with $T = \rho(\mathbf{P}-\mathbf{Q})^2$.

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