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Large-scale Dirac–Fock–Breit method using density fitting and 2-spinor basis functions

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We present an efficient theory and algorithm for computing four-component relativistic Dirac–Fock wave functions using the Coulomb, Gaunt, and full Breit interactions. Our implementation is based on density fitting, and is routinely applicable to systems with 100 atoms and a few heavy elements. The small components are expanded using 2-spinor basis functions. We show that the factorization of 3-index half-transformed integrals before building Coulomb and exchange matrices is essential for efficient evaluation of the Fock matrix. With the Coulomb interaction, the computational cost for evaluating the Fock operator has been found to be only 70–90 times that in the non-relativistic density-fitted Hartree–Fock method. The prefactors have been 170 and 350–450 for the Gaunt and Breit interactions, respectively. The largest molecule to which we have applied the Dirac–Fock–Coulomb method is an Ac(III) motexafin complex (130 atoms, 556 electrons, 1289 basis functions), for which one self-consistent iteration takes around 1100 s using 1024 CPU cores. In addition, we have found that, while the standard fitting basis sets are accurate for Dirac–Fock–Coulomb calculations, their accuracy is very poor for Dirac–Fock–Gaunt and Breit calculations. We report a prototype of accurate fitting basis sets for these cases.

I. INTRODUCTION

Accurate simulation of properties of molecules containing heavy elements requires relativistic electronic structure theories. For instance, the spin–orbit effect in lanthanide complexes, such as single-molecule magnets and luminescent complexes, is too large to be modeled by perturbative treatments on the basis of the non-relativistic framework. Approaches based on the four-component Dirac equation are the natural extension of the non-relativistic theories to the relativistic framework, and considerable efforts have been made to realize four-component molecular mean-field theories as well as electron correlation theories. There have also been many studies on four-component density functional theories (DFT) and electron correlation theories. There are many relativistic Dirac–Fock–Coulomb methods that have been used in atomic electronic structure calculations of molecules. Note that the Breit interaction is accurate to order $c^{-2}$, and has been used in atomic electronic structure calculations.

Similarly to the approaches by Quiney and co-workers and by Yanai et al., we use 2-spinor basis functions for the small component, which are generated by applying $\sigma \cdot \hat{\mathbf{p}} / 2c$ to large-component basis functions. Therefore, the number of the small-component basis functions is the same as that of the large components in our implementation, which is in contrast to those based on scalar basis functions. Theoretical advantages of this approach have been discussed by Yanai et al. in Ref. 71. Furthermore, our new algorithm does not require the $j$-adaptation of the basis functions, which leads to far less complicated equations than those in the work by Quiney and co-workers and by Yanai et al.

The computational cost of the four-component Dirac–Fock method will be shown to be only 70–90 times (with the Coulomb interaction) that of the non-relativistic Hartree–Fock method. This means that a four-component calculation on a medium-sized computer cluster with 80 nodes will be performed with a similar wall time as an analogous non-relativistic calculation on one node. The largest calculation we demonstrate in this work is the Dirac–Fock–Coulomb calculation of an Ac(III) motexafin complex (130 atoms,
556 electrons, 1289 basis functions), which takes around
1100 s per self-consistent iteration using 1024 CPU cores
(with parallel efficiency of about 50%). All the codes have
been implemented in the BAGEL package,72 which will be dis-
tributed under the GNU Public License.

The article is organized as follows. In Sec. II, we briefly
review the Dirac–Fock method with the full Breit interaction.
We present the working equations for the Coulomb and ex-
change matrices in Sec. IV. Numerical results and timing data
are presented in Sec. V, followed by concluding remarks in
Sec. VI.

II. DIRAC–FOCK–BREIT METHOD

In the following, we use \( \psi, \phi, \) and \( \chi \) for scalar functions,
while 4-spinors are represented by \( \Phi \) and \( \Psi \). We use the fol-
lowing notation for orbital indices: \( r, s, t, \) and \( u \) label
atomic orbitals; \( i \) and \( j \) label occupied molecular orbitals;
and \( \gamma \) and \( \delta \) are indices for the auxiliary basis functions.
In addition, \( X, Y, Z, \) and \( W \) denote large components
\((L \pm)\) or small components \((S \pm)\). The Cartesian components
are labeled by \( w \) and \( w' \).

The Dirac Hamiltonian for molecular systems is
\[
\hat{H} = \sum_i \hat{h}(i) + \sum_{i < j} \hat{g}(i,j). \tag{1}
\]

The first term is the one-electron operator
\[
\hat{h}(i) = c^2(\beta - I_4) + c(\alpha \cdot \hat{p}_i) - \sum_A \frac{Z_A}{r_{iA}},
\tag{2}
\]
where \( c \) is the speed of light, \( \hat{p}_i \) is the momentum operator
of electron \( i \), and \( I_4 \) is the \( 4 \times 4 \) identity matrix. The
matrices \( \alpha \) and \( \beta \) are Dirac’s \( 4 \times 4 \) matrices,
\[
\beta = \begin{pmatrix}
I_2 & 0_2 \\
0_2 & -I_2
\end{pmatrix},
\]
\[
\alpha = \begin{pmatrix}
0_2 & \sigma \\
\sigma & 0_2
\end{pmatrix},
\tag{3}
\]
in which we used the \( 2 \times 2 \) identity and zero matrices
\((I_2 \) and \( 0_2 \), respectively). \( \sigma \) are the Pauli matrices, i.e.,
\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\tag{4}
\]

The second term of Eq. (1) is the electron–electron interac-
tion, for which we use the Breit interaction,
\[
\hat{g}(1,2) = \frac{1}{r_{12}} - \frac{\alpha_1 \cdot \alpha_2}{r_{12}^3} - \frac{\{\alpha_1 \cdot (V_r)\alpha_2 \cdot (V_r)r_{12}\}}{2},
\tag{5}
\]
The first term is the Coulomb term. The second term
\((-\alpha_1 \cdot \alpha_2/r_{12})\) is generally referred to as the Gaunt
term, and it is often an order of magnitude larger than the last term.67–70
Equation (5) can be shown identical to the following:
\[
\hat{g}(1,2) = \frac{1}{r_{12}} - \frac{\alpha_1 \cdot \alpha_2}{2r_{12}} - \frac{\{\alpha_1 \cdot r_{12}\alpha_2 \cdot r_{12}\}}{2r_{12}^3},
\tag{6}
\]
which we use throughout this work since the associated two-
electron integrals can be easily computed by the algorithm
developed by one of the authors.73

In this work, small-component basis spinors \((\Phi_r^{\pm})\) are
derived from the large-component spinors \((\Phi_r^{L \pm})\) by applying
\( \alpha \cdot \hat{p}/2c \) to avoid variational collapse as
\[
\Phi_r^{\pm} = \frac{1}{2c} \alpha \cdot \hat{p} \Phi_r^{L \pm}.
\tag{7}
\]
The explicit expressions of the basis spinors in terms of scalar
Gaussian basis functions are
\[
\Phi_r^{L \pm} = \begin{pmatrix} \phi^L_r \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \Phi_r^{L -} = \begin{pmatrix} 0 \\ \phi^L_r \\ 0 \\ 0 \end{pmatrix},
\tag{8}
\]
\[
\Phi_r^{S +} = -\frac{i}{\sqrt{\epsilon}} \begin{pmatrix} 0 \\ \phi^I_r \\ \phi^S_r + i\phi^I_r \end{pmatrix}, \quad \Phi_r^{S -} = -\frac{i}{\sqrt{\epsilon}} \begin{pmatrix} 0 \\ \phi^I_r - i\phi^S_r \end{pmatrix}.
\]

Here \( \phi^w_r(r) \) is a scalar basis function or its derivative with
respect to \( x, y, \) and \( z \), i.e.,
\[
\frac{\partial \phi^w_r(r)}{\partial w} = \begin{pmatrix} \phi^w_r(r) \\ w = l, \\ \partial \phi^w_r(r)/\partial w \\ w = x, y, z \end{pmatrix}.
\tag{9}
\]

The definition of the small-component basis functions in
this work is equivalent to those used by Quiney and co-
workers19,20 and by Yanai et al.21–23 We have decided not to use
different basis-set contractions for \( L^+ \) and \( L^- \) components
for performance reasons (though it is straightforward to
generalize our program to handle separate basis-set contrac-
tions). Note that the number of small-component basis functions
is smaller than that used by the standard packages. An
occupied molecular orbital (4-spinor) is expanded as
\[
\Psi_l = \sum_x \Psi^X_l = \sum_x \sum_r \Phi^X_l C^X_r.
\tag{10}
\]

The Dirac–Fock equation in this basis is
\[
FC = SC\epsilon,
\tag{11}
\]
in which \( \epsilon \) is a diagonal matrix whose elements are an orbital
energy, \( S \) is an overlap matrix between 4-spinor basis functions
[Eq. (8)], and \( C \) is a coefficient matrix,
\[
C = \begin{pmatrix} C^{L+} \\ C^{L-} \\ C^{S+} \\ C^{S-} \end{pmatrix}.
\tag{12}
\]

\( F \) is the Fock matrix,
\[
F = \mathbf{h} + \mathbf{J} - \mathbf{K},
\tag{13}
\]
in which \( \mathbf{h} \) is the one-body part,
\[
(h^{XY})_{ij} = \int \Phi^X_i(r_1)\hat{h}(1)\Phi^Y_j(r_1)dr_1.
\tag{14}
\]
J and K are Coulomb and exchange matrices, respectively, which are formally defined as

\[
(J^{XY})_{rs} = \sum_{ZW} \sum_{tu} D_{tu}^{ZW} \int \Phi_i^X(r_1) \Phi_j^Y(r_2) \hat{g}(1, 2) \Phi_i^X(r_1) \Phi_j^Y(r_2) dr_1 dr_2,
\]

(15)

\[
(K^{XY})_{rs} = \sum_{ZW} \sum_{tu} D_{tu}^{ZW} \int \Phi_i^X(r_1) \Phi_j^Y(r_2) \hat{g}(1, 2) \Phi_i^X(r_1) \Phi_j^Y(r_2) dr_1 dr_2,
\]

(16)

\[
D_{tu}^{ZW} = \text{density matrix}, \quad \Phi_i(r) = \text{basis functions from Eq. (8)}, \quad \text{the contribution to the Fock–Breit matrix}. \]

The exchange matrix has a contribution in every block as

\[
K = \begin{pmatrix}
K_{L+L+} & K_{L+L-} & K_{L+L+} & K_{L+L-} \\
K_{L-L+} & K_{L-L-} & K_{L-L+} & K_{L-L-} \\
K_{S+L-} & K_{S+L-} & K_{S+S+} & K_{S+S+} \\
K_{S-L+} & K_{S-L-} & K_{S+S-} & K_{S+S-}
\end{pmatrix},
\]

(19)

The total J and K matrices in Dirac–Fock–Breit calculations are

\[
J = J_C - \frac{1}{2} J_B \equiv J_C - \frac{1}{2} J_{bs} - \frac{1}{2} J_{bs},
\]

(20)

\[
K = K_C - \frac{1}{2} K_B \equiv K_C - \frac{1}{2} K_{bs} - \frac{1}{2} K_{bs},
\]

(21)

where \(J_{bs} (K_{bs})\) and \(J_{bs} (K_{bs})\) denote the individual contribution from the second and third term of Eq. (6), respectively. In Dirac–Fock–Gaunt calculations, we use

\[
J_G = J_C - J_{bs},
\]

(22)

\[
K_G = K_C - K_{bs},
\]

(23)

which are a subset (with a different prefactor) of the Dirac–Fock–Breit matrix.

III. VARIATIONAL PROCEDURES

In order to obtain Dirac–Fock solutions, we make the following energy expression stationary for any orbital rotations:

\[
E = \frac{1}{2} \text{Tr}[D(F + h)].
\]

(24)

The stationary point usually corresponds to a minimum. However, even though this variational procedure has been widely used, one needs to pay attention to the so-called Brown–Ravenhall disease\(^{72}\) to verify the procedure. The Brown–Ravenhall disease arises because the eigenvalues of the Dirac equation corresponding to the bound-state solutions are embedded in continuum states that spread over \([−∞, ∞]\).\(^{78, 79}\)

As recently noted by Kutzelnigg,\(^{12}\) the most consistent relativistic electronic-structure theories should be formulated in the Fock space, which correspond to low-order quantum electrodynamics (QED). Using Fock-space Hamiltonians, one can straightforwardly project the Hamiltonian onto the space spanned only by the positive energy states, curing the Brown–Ravenhall disease. The use of Fock-space Hamiltonians in many-electron systems is nevertheless not trivial. Some of recently developed 2-component quasi-relativistic Hamiltonians can be seen as an approximation to the Fock-space Hamiltonian. For instance, the so-called X2C method could use an approximate projector onto the positive energy states obtained from the one-electron Dirac Hamiltonian.\(^{51, 52}\)

The variational approach based on the configuration-space Dirac–Coulomb Hamiltonian [Eq. (1)] practically does not suffer from the Brown–Ravenhall disease because projection onto the positive energy states is automatically implied,\(^{75}\) even though one may argue that it is physically incorrect.\(^{12}\)

The situation with the Breit interaction appears to be more complicated. We chose to use the variational procedure for pragmatic reasons, encouraged by its successful use in numerical applications. Its numerical success could also be due to the resemblance between Eq. (7) and the stationary conditions for the minimax recipe.\(^{76, 77, 80}\)

The fundamental question on how to consistently, accurately, and efficiently model many-electron systems within the relativistic framework seems still unsolved, and theoretical and numerical assessments are warranted. Interested readers should refer to a recent review by Kutzelnigg.\(^{12}\)

IV. ALGORITHMS

In this section, we present an efficient algorithm for computing the Fock matrix [Eq. (11)]. We first describe the algorithm for the Coulomb interaction, followed by that for the Breit interaction. We use the density-fitting approximation for 4-index 2-electron integrals using auxiliary functions \(\chi\). The density-fitted Hartree–Fock methods have been described in detail, e.g., in Refs. 61–65. Note that our program can exploit neither time-reversal nor spatial symmetry so far, which is the subject of future extensions. The following algorithms for the Fock operator construction are equally applicable to closed and open-shell systems.
The density fitting approach approximates the Coulomb integrals as
\[
\int d\mathbf{r}_1 d\mathbf{r}_2 \int d\mathbf{r}_1 d\mathbf{r}_2 \phi^w_w(r_1) \phi^w_w(r_2) \sim \sum_{\gamma \delta} \langle \chi_\gamma | \phi^w_w | \chi_\delta \rangle (\mathcal{J}^{-1})_{\gamma \delta} (\chi_\delta | \phi^w_w | \chi_\gamma),
\]
where each element is defined with the Mulliken notation:
\[
\langle \phi^w_w | \chi_\gamma \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi^w_w(r_1) \chi_\gamma(r_2),
\]
and
\[
\langle \chi_\delta | \phi^w_w | \chi_\gamma \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi^w_w(r_1) \chi_\delta(r_2) \chi_\gamma(r_1).
\]

The evaluation of Eq. (26) is discussed in the Appendix. Furthermore, using a scalar transformed function,
\[
\psi^w_i^X(r) = \sum_r \phi^w_i(r) C^X_{ri},
\]
the half-transformed 3-index integrals \(\langle \phi^w_i^X \psi^w_i^X | \chi \rangle\) are likewise defined. Here we also introduce
\[
\langle \phi^w_i^X \psi^w_i^X | \chi \rangle = \sum_{\delta} \langle \phi^w_i^X \psi^w_i^X | \chi \rangle (\mathcal{J}^{-1/2})_{\delta \gamma},
\]
which will be used in Secs. IV A and IV B.

A. Two-electron Fock matrix for the Coulomb interaction

With density fitting, the elements of the exchange matrix \(K^C_{XY}\) are
\[
(K^C_{XY})_{rs} = \sum_{i=1}^{N_{occ}} \sum_{i'=1}^{N_{occ}} \sum_{\gamma \delta} \langle \chi_\gamma | \Phi^X_i^Y | \chi_\delta \rangle (\mathcal{J}^{-1})_{\gamma \delta},
\]
in which \(\langle \chi_\gamma | \Phi^X_i^Y | \chi_\delta \rangle\) is defined as
\[
\langle \chi_\gamma | \Phi^X_i^Y | \chi_\delta \rangle = \sum_{w,w'} \langle \chi_\gamma | \phi^w_i \phi^{w'}_{i'} | \chi_\delta \rangle k_{w w'}^{X Y}.
\]
The factor \(k_{w w'}^{X Y}\) in Eq. (32) is due to the definition of the basis functions in Eq. (8). For the Coulomb interaction, \(X\) and \(W\) must be both large components or both small components, i.e., integrals with the form \(\langle \Phi^X | \Phi^X | \chi \rangle\) or \(\langle \Phi^S | \Phi^S | \chi \rangle\). The factor \(k_{w w'}^{X Y}\) can be conveniently calculated as
\[
k_{w w'}^{X Y} = v^X_{w} \eta_{w} v^Y_{w},
\]
in which \(\eta_{w}\) is a 4 \(\times\) 4 matrix as
\[
\eta_{l} = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & 0_2 \end{pmatrix}, \quad \eta_{s} = -\frac{i}{2c} \begin{pmatrix} 0_2 & 0_2 \\ 0_2 & \sigma_s \end{pmatrix},
\]
\[
\eta_{y} = -\frac{i}{2c} \begin{pmatrix} 0_2 & 0_2 \\ 0_2 & \sigma_y \end{pmatrix}, \quad \eta_{z} = -\frac{i}{2c} \begin{pmatrix} 0_2 & 0_2 \\ 0_2 & \sigma_z \end{pmatrix},
\]
and \(v^X\) is a unit 4-vector, \(v^X = (\delta_{X,L+}, \delta_{X,L-}, \delta_{X,S+}, \delta_{X,S-})^T\).

In our algorithm, \(K^C_{XY}\) is computed using half-transformed 3-index integrals
\[
(K^C_{XY})_{rs} = \sum_{\gamma \delta} \langle \Phi^X_i^Y | \chi \rangle (\mathcal{J}^{-1})_{\gamma \delta} (\chi_\delta | \Phi^Y_i^X | \chi_\gamma),
\]
where each pair of the factorized objects. The location of the target is due to the definition of the basis functions, occupied orbitals, and auxiliary basis functions, respectively.

The simple definition of \(k_{w w'}^{X Y}\) using 4-vectors and 4 \(\times\) 4 matrices [Eq. (33)] has allowed us to implement a generic code for all possible combinations of \(L\) and \(S\) and Cartesian components. At runtime, we construct a list of half-transformed objects for \(\langle \Phi^X_i^Y | \Phi^X_i^Y | \chi \rangle\) that are index aware, automatically factorize the intermediates using the index information as in Eq. (36), evaluate an exchange matrix from each pair of the factorized objects. The location of the target Fock block is also automatically determined by the index information stored in the objects. This object-oriented design has been essential to arrive at a compact and efficient program.

The Coulomb matrix is similarly defined using density fitting as
\[
(J^C_{XY})_{rs} = \sum_{\gamma \delta} \langle \Phi^X_i^Y | \chi \rangle (\mathcal{J}^{-1})_{\gamma \delta} (\chi_\delta | \Phi^Y_i^X | \chi_\gamma),
\]
which are computed using factorized half-transformed integrals [Eq. (36)] as
\[
(J^C_{XY})_{rs} = \sum_{\gamma \delta} \langle \Phi^X_i^Y | \psi_\gamma \rangle C_\gamma,
\]
\[
C_\gamma = \sum_{\delta} (\mathcal{J}^{-1/2})_{\gamma \delta} D_\delta,
\]
\[
D_\gamma = \sum_{i,r} \langle \Phi^X_i^Y | \tilde{\psi}_\gamma \rangle C^*_\gamma.
\]
Note that the computation of the Coulomb matrix does not involve quartic scaling steps and, hence, is cheap.
B. Two-electron Fock matrix for the Breit interaction

The contributions to $K^B$ from the Breit interaction (other than the Coulomb interaction) are

$$ (K^B_{xy})_{rs} = \sum_{v \in \{x,y,z\}} \sum_{W} \sum_{tu} D_{tu}^{ZW} \sum_{\gamma \delta} (\Phi_r^X \alpha_v \Phi_s^Z | \chi_{\gamma}) (\mathcal{J}^{-1})_{\gamma \delta} \times (\chi_{\delta} | \Phi_u^W \alpha_v \Phi_s^Y). \quad (42) $$

$$ (K^B_{xy})_{rs} = \sum_{v \in \{x,y,z\}} \sum_{W} \sum_{tu} D_{tu}^{ZW} \sum_{\gamma \delta} (\Phi_r^X \alpha_v \Phi_s^Z | \chi_{\gamma}) \times (\mathcal{J}^{-1/2} B_{uv}^{\gamma \delta} \mathcal{J}^{-1/2} \gamma \delta) \times (\chi_{\delta} | \Phi_u^W \alpha_v \Phi_s^Y), \quad (43) $$

in which we have introduced the 2-index Breit integrals

$$ B_{uv}^{\gamma \delta} = \mathcal{J}^{-1/2} \mathcal{J}_B^{uv} \mathcal{J}^{-1/2} . $$

$$ (\mathcal{J}_B^{uv})_{\gamma \delta} = \int \int \chi_{\gamma}(r_1) (\frac{v_1 - v_2}{r_{12}} (v_1' - v_2') \chi_{\delta}(r_2) dr_1 dr_2. \quad (45) $$

The Breit integrals can be efficiently computed by the algorithm reported recently by one of the authors.\(^{73}\) In this work, we have not considered the so-called robust fitting\(^{62}\) for the Breit integrals, since the magnitude of the Breit contribution is much smaller than other contributions and that the Breit operator has a similar long-range tail to that of the Coulomb operator. The accuracy will be discussed below.

We compute $K^B$ using factorized intermediates similarly to the procedure for $K_C$:

$$ (K^B_{xy})_{rs} = \sum_{v \in \{x,y,z\}} \sum_{W} \sum_{i} (\Phi_r^X \alpha_v \Psi^i | \tilde{\chi}_{\gamma}) (\tilde{\chi}_{\delta} | \Psi^i \alpha_v \Phi_s^Y) \cdot \mathcal{B}^{uv}, \quad (46) $$

in which

$$ (\tilde{\chi}_{\gamma} | \Phi_r^X \alpha_v \Psi^i) = \sum_{W} (\tilde{\chi}_{\gamma} | \Phi_r^X \alpha_v \Psi^W). $$

$$ (\tilde{\chi}_{\delta} | \Psi^i \alpha_v \Phi_s^Y) = (\tilde{\chi}_{\delta} | \Psi^i \alpha_v \Phi_s^Y) + \sum_{v' \in \{x,y,z\}} \sum_{\delta}(\mathcal{B}^{uv'}) \gamma \delta (\tilde{\chi}_{\delta} | \Psi^i \alpha_v \Phi_s^Y). \quad (48) $$

The half-transformed quantities are computed directly as

$$ (\Phi_r^X \alpha_v \Psi^W | \tilde{\chi}_{\gamma}) = \sum_{w,w' \in \{x,y,z\}} (\phi^w_{\gamma} \phi^{w'}_{\delta} | \tilde{\chi}_{\gamma}) k^{XY}_{ww'}(\alpha_v), $$

in which we used $k^{XY}_{ww'}(\alpha_v)$ that is analogous to Eq. (33),

$$ k^{XY}_{ww'}(\alpha_v) = \int \int \chi_{\gamma}(r_1) \phi^{w'}_{\delta}(\alpha_v) \phi^w_{\gamma}(r_2) dr_1 dr_2. $$

with $\alpha_v$ being a Dirac matrix from Eq. (3). Note that non-zero contributions arise only from $X$ and $Y$ that are an opposite component with each other.

Similarly, the Breit contributions to $J^B$ are

$$ (J^B_{xy})_{rs} = \sum_{v' \in \{x,y,z\}} \sum_{W} \sum_{tu} D_{tu}^{ZW} \sum_{\gamma \delta} (\Phi_r^X \alpha_v \Phi_s^Y | \chi_{\gamma}) (\mathcal{J}^{-1})_{\gamma \delta} \times (\chi_{\delta} | \Phi_u^W \alpha_v \Phi_s^Y), \quad (51) $$

$$ (J^B_{xy})_{rs} = \sum_{v \in \{x,y,z\}} \sum_{W} \sum_{tu} D_{tu}^{ZW} \sum_{\gamma \delta} (\Phi_r^X \alpha_v \Phi_s^Y | \chi_{\gamma}) \times (\mathcal{J}^{-1/2} B_{uv}^{\gamma \delta} \mathcal{J}^{-1/2} \gamma \delta) \times (\chi_{\delta} | \Phi_u^W \alpha_v \Phi_s^Y), \quad (52) $$

which are computed by the following equations:

$$ (J^B_{xy})_{rs} = \sum_{v \in \{x,y,z\}} \sum_{\gamma} (\Phi_r^X \alpha_v \Phi_s^Y | \chi_{\gamma}) C^{uv}_{\gamma}, \quad (53) $$

$$ C^{uv}_{\gamma} = (\mathcal{J}^{-1/2} B_{uv}^{\gamma \delta} \mathcal{J}^{-1/2} \gamma \delta D^{uv}_{\delta}, \quad (54) $$

$$ D^{uv}_{\delta} = \sum_{x} \sum_{i,r} (\Phi_r^X \alpha_v \psi_i | \chi_{\delta}) B_{ci}^{Xx} . \quad (55) $$

Note that by removing terms with the Breit integrals, one can obtain the Gaunt contribution alone.

V. RESULTS

A. Accuracy of the relativistic density fitting

Table I compiles the errors due to density fitting in the Dirac–Fock–Coulomb, Gaunt, and Breit method. We have tested their accuracy on Cl$_2$ and Br$_2$, since there are systematic fitting basis sets. The bond length was set to 2.1783 Å and 2.3218 Å, respectively. We used the cc-pVDZ basis set\(^{85}\) for the orbital basis set. As a reference, we have calculated the energies using an even-tempered\(^{21}\)21p21d21f21g21h21l fitting basis set, in which the largest and smallest exponents are 100000.0, and 0.09536743, respectively (the ratio was set to 2.0).

Our findings are twofold. First, the standard cc-pVXZ-JKFIT basis sets\(^{61}\) that are designed for the Hartree–Fock method are equally accurate for the Dirac–Fock–Coulomb method. The fitting errors in the Dirac–Fock–Coulomb calculations for Cl$_2$ with respect to the reference values were found to be 0.053, 0.010, 0.006 mE$_h$ using cc-pVTZ-JKFIT, cc-pVQZ-JKFIT, and cc-pV5Z-JKFIT, respectively, which was almost identical to the errors in the Hartree–Fock calculations. We also observed the same tendency for Br$_2$: The errors were 0.077, 0.049, and 0.033 mE$_h$ with the same basis sets, which are within 0.005 mE$_h$ from the errors in the Hartree–Fock calculations. This result encourages the use of the standard fitting basis sets in the Dirac–Fock–Coulomb calculations.

Second, however, the standard fitting basis sets are very poor in describing the Gaunt and Breit term. The errors in the Dirac–Fock–Gaunt and Dirac–Fock–Breit calculations using the standard basis sets were 3–4 mE$_h$ for Cl$_2$, and even 30 mE$_h$ for Br$_2$, which are three orders of magnitude larger than the
TABLE I. Errors due to the density fitting approximation in Hartree–Fock and Dirac–Fock calculations (in mEh) relative to the energies computed by a very large even-tempered basis set. The reference values are listed in $E_{\text{ref}}$. XZ(JKfit) stands for the cc-pVXZ-JKFIT basis, while XZ(JKfit+1) is an augmented basis set as described in the main text.

<table>
<thead>
<tr>
<th>Fitting functions</th>
<th>Cl$_2$ / cc-pVDZ</th>
<th>B$_2$ / cc-pVDZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hartree–Fock</td>
<td>0.053</td>
<td>3.489</td>
</tr>
<tr>
<td>Dirac–Fock–Coulomb</td>
<td>0.053</td>
<td>–4.131</td>
</tr>
<tr>
<td>Dirac–Fock–Gaunt</td>
<td>–3.389</td>
<td>–4.004</td>
</tr>
<tr>
<td>Dirac–Fock–Breit</td>
<td>–3.389</td>
<td>–4.125</td>
</tr>
</tbody>
</table>

Table II shows the timing results from the Hartree–Fock, Dirac–Fock–Coulomb, Gaunt, and Breit calculations. (two significant digits are shown). A computer cluster with Xeon E5-2650 2.00 GHz was used. The energies are reported in the supplementary material.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atoms</th>
<th>Electrons</th>
<th>Orb. basis$^a$</th>
<th>Aux. basis$^b$</th>
<th>CPU cores</th>
<th>Non-rel.</th>
<th>Coulomb</th>
<th>Gaunt</th>
<th>Breit</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Au(Me$_2$-Imy)(cbz)]</td>
<td>37</td>
<td>218</td>
<td>SVP+DZ</td>
<td>TZ-JKfit</td>
<td>512</td>
<td>0.73</td>
<td>44</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>[Au$_2$(µ-L$_3$)$_2$]$_2^+$</td>
<td>64</td>
<td>376</td>
<td>SVP+DZ</td>
<td>TZ(JKfit+1)</td>
<td>4105</td>
<td>1.2</td>
<td>84</td>
<td>170</td>
<td>410</td>
</tr>
<tr>
<td>Ac-Motex$_2^+$</td>
<td>130</td>
<td>556</td>
<td>SVP+DZ</td>
<td>TZ-JKfit</td>
<td>7497</td>
<td>12</td>
<td>1100</td>
<td>…</td>
<td>…</td>
</tr>
</tbody>
</table>

$^a$An even-tempered [21s2p1d2f2/21s2p2d2f2/21s2p2d2f2] basis set. The largest exponent is 1000000.0 and the smallest exponent is 0.09536743.

$^b$ contracted fitting functions in the original cc-pVXZ-JKFIT are decontracted.

errors in the Hartree–Fock and Dirac–Fock–Coulomb calculations. We have found that these errors mainly stem from the lack of tight functions in the $p$, $d$, and $f$ shell. In Table I, we also report the results obtained by using the custom fitting basis sets [denoted as XZ(JKfit+1) in the table], in which we used the $s$ exponents of the cc-pVXZ-JKFIT basis set for the $s$ and $p$ shells, the $p$ exponents for the $d$ shell, the $d$ exponents for the $f$ shell, and so on. The results were remarkable: The errors in the Dirac–Fock–Gaunt and Breit calculations using these custom fitting basis sets were similar in magnitude to (or even smaller than) the errors in the Hartree–Fock and Dirac–Fock–Coulomb calculations. Of course, the size of the custom basis sets has been larger than the standard sets, but they are by no means optimal for this purpose. The development of fitting basis sets for the Dirac–Fock–Gaunt and Dirac–Fock–Breit method is highly warranted.

B. Cost analysis and timing data

In Dirac–Fock–Coulomb calculations, the computational cost of index transformation and application of $\mathcal{J}^{-1/2}$ [Eq. (30)] is 80 times that of the non-relativistic closed-shell Hartree–Fock method with the same basis sets because there are 20 complex-valued (i.e., 40 real-valued) intermediates and the number of occupied orbitals is doubled. In our implementation, the application of $\mathcal{J}^{-1/2}$ requires two transpositions of half-transformed integrals involving communication across nodes, and therefore, constitutes the most expensive step. As discussed above, the computational cost of building an exchange matrix is 216 times that of the Hartree–Fock, while the computational cost of a Coulomb matrix is usually marginal. From this analysis, the Dirac–Fock–Coulomb method is expected to be around 80–100 times more expensive than the closed-shell Hartree–Fock method. The additional cost of index transformation and application of $\mathcal{J}^{-1/2}$ in Dirac–Fock–Gaunt and Breit calculations is 32 times that of the Hartree–Fock method. Furthermore, there are 72 multiplication of $\mathcal{B}$ to a complex intermediate [Eq. (48)] in the Dirac–Fock–Breit method. An exchange build costs 3 times that of the Dirac–Fock–Coulomb method and is therefore 648 times more expensive than an exchange build in the Hartree–Fock method.

Table II shows the timing results from the Hartree–Fock, Dirac–Fock–Coulomb, Breit, and Gaunt calculations, which confirm the above analysis. The molecules we have tested are an Au(I) N-heterocyclic carbene carbazol complex ([Au(Me$_2$-Imy)(cbz)], or C$_{12}$H$_{10}$N$_{3}$Au), an Au(I) dicarbene complex ([Au$_2$(µ-$L^3$)$_2$]$_2^+$ with $L^3$ = Im$_{Me}$(CH)$_2$Im$_{Me}$ and Im$_{Me}$ = N-methylimidazol-N-yl-2-ylidine, or C$_{22}$H$_{32}$N$_{8}$Au$_{2}$ dication), and an Ac(III) metoxafin complex (Ac-Motex$_2^+$, or C$_{68}$H$_{66}$N$_{10}$Ac dication) which are depicted in Fig. 1. We used the def2-SVP basis set for light atoms and Dyll’s spin-free DZ basis set with valence flexibility for Au and Ac atoms. The fitting basis sets used were cc-pVTZ-JKFIT and the above TZ(JKfit+1) basis sets,

TABLE II. Wall times in seconds for an iteration of Hartree–Fock, Dirac–Fock–Coulomb, Gaunt, and Breit calculations (two significant digits are shown). A computer cluster with Xeon E5-2650 2.00 GHz was used. The energies are reported in the supplementary material.

<table>
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<th>Electrons</th>
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<tr>
<td>[Au(Me$_2$-Imy)(cbz)]</td>
<td>37</td>
<td>218</td>
<td>SVP+DZ</td>
<td>TZ-JKfit</td>
<td>521</td>
<td>0.73</td>
<td>44</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>[Au$_2$(µ-$L^3$)$_2$]$_2^+$</td>
<td>64</td>
<td>376</td>
<td>SVP+DZ</td>
<td>TZ(JKfit+1)</td>
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<td>SVP+DZ</td>
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<td>7497</td>
<td>12</td>
<td>1100</td>
<td>…</td>
<td>…</td>
</tr>
</tbody>
</table>
augmented by an uncontracted orbital basis set for Au and Ac. The molecular geometries were taken from the literature. No spatial symmetry was used. The converged Hartree–Fock and Dirac–Fock energies are compiled in the supplementary material.81

Our first benchmark complex, [Au(Me2-imy)(cbz)], consists of 37 atoms, 218 electrons, and 424 basis functions. This molecule is so small that the calculations were parallelized using 512 cores. The non-relativistic Hartree–Fock iteration with the standard fitting basis functions took less than a second (0.73 s), while the Dirac–Fock–Coulomb iteration took 44 s. Using extended fitting functions described above, the Hartree–Fock calculation cost around 1.2 s, while the wall times of the Dirac–Fock–Coulomb, Gaunt and Breit iterations were 84, 170, and 410 s, respectively, which are 70, 140, and 340 times that of a Hartree–Fock iteration. With the larger Au(I) dicarbene complex, [Au2(μ-L3)2]^2+ (64 atoms, 376 electrons, 708 basis functions), the wall times of a Hartree–Fock, Dirac–Fock–Coulomb, Gaunt, and Breit self-consistent iteration were found to be 3.8 (2.2), 310 (160), 640, and 1600 s, respectively (the numbers in parentheses are those using the standard fitting functions), which indicate that Dirac–Fock–Coulomb, Gaunt, and Breit calculations were 75–80, 170, and 420 times more expensive than the corresponding Hartree–Fock calculation, respectively.

The largest Dirac–Fock–Coulomb calculation in this work has been that of Ac-Motex^2+ (130 atoms, 556 electrons, and 1289 basis functions), which took only 1100 s per iteration using 1024 cores. This timing is 90 times that of the closed-shell Hartree–Fock method. Since our program in BAGEL so far stores all the atomic-orbital integrals on distributed memory, the size of Dirac–Fock calculations is limited by the memory requirement. This restriction could be partly lifted by implementing semi-direct algorithms to avoid storage of the atomic-orbital integrals. Alternatively, we could resort to larger computer hardware, since the Dirac–Fock methods consist of many independent equations and are expected to scale well with the so-called task-based parallelism.90

VI. CONCLUSIONS

In this work, we have proposed an efficient algorithm for evaluating the Fock operator in the four-component Dirac–Fock–Breit method. The key results of this work to arrive at an efficient program are intermediate factorization for exchange matrices [Eq. (36)]; simultaneous evaluation of the Gaunt and retardation terms [Eq. (48)]; and realization of a generic program using a simple scheme to evaluate the coefficient of each element [Eqs. (33) and (50)]. We have implemented the working equations into a parallel program in the BAGEL package, and demonstrated that the Dirac–Fock–Coulomb calculation of systems with more than a hundred atoms and a heavy element using a standard double-ζ basis set can be routinely performed on a research group’s computer cluster. The Dirac–Fock–Breit method was also applied to a molecule with 64 atoms containing two Au atoms, [Au2(μ-L3)2]^2+.

We have also found that the standard fitting basis sets, such as cc-pVQZ-JKFIT, provide similar accuracy in Dirac–Fock–Coulomb calculations to that of the non-relativistic Hartree–Fock calculations, while their performance is very poor for the Dirac–Fock–Gaunt and Breit methods. It has been shown that the tight fitting functions in higher angular shells are required for the Dirac–Fock–Gaunt and Breit methods. Together with the fact that there are no fitting basis sets available for most of the heavy elements, the development of optimized fitting basis sets is highly warranted.

Since the working equations of the Dirac–Fock methods consist of many independent contractions of intermediates, we plan to interface BAGEL to a task-based parallel runtime to execute them in massively parallel supercomputers in the future.90 The extension of this program to multi-configuration self-consistent-field methods26–28 with a Fock-matrix based algorithm is under way to address electronic structure problems of open-shell systems, especially of magnetic molecules containing heavy elements.

ACKNOWLEDGMENTS

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APPENDIX: COMPUTATION OF (χ^Lp|φ^L×p|φ^L×p)

We evaluate (χ^Lp|φ^L×p|φ^L×p) using the exact resolution of the identity. For instance, a batch of (χ^Lp|φ^Lp|φ^Lp) is computed by using Cartesian Gaussian functions, (φ^L), which are generated from a basis function shell {φ^L} of the angular momentum number l, to have the angular momentum number l ± 1 and the identical exponents. In each shell object, we pre-compute

FIG. 1. Molecules that are used for the timing benchmark in this work: (a) [Au(Me2-imy)(cbz)]; (b) [Au2(μ-L3)2]^2+; and (c) Ac-Motex^2+. See text for details.
and store
\[ \mathcal{M}_{i}^{\nu} = \sum_{u} \left( \mathbf{S}^{-1} \right)_{i u} \int \phi_u^*(\mathbf{r}) \frac{\partial}{\partial u} \phi_u(\mathbf{r}) d\mathbf{r}, \quad (A1) \]
\[ \left( \mathbf{S} \right)_{i u} = \int \phi_u(\mathbf{r}) \phi_u(\mathbf{r}) d\mathbf{r}. \quad (A2) \]
which are used when computing the 3-index integrals:
\[ (\chi_{\nu}) \phi_u^* \phi_s = \sum_{i} (\chi_{\nu}) \phi_u^* \phi_s \mathcal{M}_{i}^{\nu}, \quad (A3) \]
Note that \( \mathcal{M} \) is localized to each shell, and is not a global matrix.

1M. Reiher and A. Wolf, Relativistic Quantum Chemistry (Wiley-VCH, Germany, 2009).
31See supplementary material at http://dx.doi.org/10.1063/1.4807612 for the Hartree–Fock and Dirac–Fock energies.
38See supplementary material at http://dx.doi.org/10.1063/1.4807612 for the Hartree–Fock and Dirac–Fock energies.