Exact exchange matrix of periodic Hartree-Fock theory for all-electron simulations

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This work presents an algorithm to evaluate Coulomb and exchange matrices in Fock operator using range separation techniques at various aspects. This algorithm is particularly favorable for the scenario of (1) all-electron calculations or (2) computing exchange matrix for a large number of $k$-point samples. An all electron Hartree-Fock calculation with 110k basis functions is demonstrated in this work.

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I. INTRODUCTION

In crystal electronic structure simulations, planewave basis is a natural choice because of the periodicity in wave function\textsuperscript{1–4}. When the atomic nature of electron density is taken into account, numerical basis and periodic Gaussian basis are also widely used\textsuperscript{5–7}. However, we can still find the footprint of planewaves in the intermediates. If the quantity of interests, e.g. the electron density, changes smoothly in the space, they can be efficiently evaluated with the assistance of planewaves and discrete Fourier transform (FT). As such, crystal simulations with density functional theory (DFT) were rapidly evolved. Large scale DFT calculations have reached \( \sim 100k \) atoms and millions of basis functions\textsuperscript{8,9}.

Along with the choice of planewave basis, electronic structure simulations for crystal face two challenges: the treatment of exact exchange and the quality of pseudo-potential.

Evaluating Hartree-Fock (HF) exchange in crystal simulations is not trivial. Treatments of divergence and finite size errors have been addressed by many pioneer works\textsuperscript{10–17}. Besides, various efforts have been made to improve the efficiency of building HF exchange in the context of planewave basis and the associated discrete FT\textsuperscript{18–24}. Regardless of the basis type or the algorithm or the approximations, the computational cost for HF exchange in terms of discrete FT scales as \( \mathcal{O}(N_A^2N_k^2N_G\log(N_G)) \) for a simulation of \( N_A \) atoms, \( N_k \) \( \mathbf{k} \)-points and \( N_G \) planewaves (or integration mesh grids in real space). It becomes unaffordable for systems which requires a relatively large number of planewaves. In the context of Gaussian type crystal basis, one would use auxiliary Gaussian basis to expand electron density and invoke density fitting (DF) technique to evaluate the Coulomb repulsion integral\textsuperscript{14,16,25–36}. It largely removes the demands to the planewaves (or integration grids) and reduces the formal scaling to \( \mathcal{O}(N_{AO}^2N_k^2) \) in computational costs and \( \mathcal{O}(N_{AO}^2N_k^2) \) in memory (or disk) footprint for \( N_{AO} \) Gaussian basis functions. Although DF can deliver great performance for simulations with moderate system size and a moderate number of \( \mathbf{k} \) points, occasionally, memory and disk usage can become a bottleneck when hundreds of \( \mathbf{k} \) points are requested. Another issue of DF is that it is picky on basis sets and auxiliary basis functions. Most auxiliary basis sets were developed and tested for specific atomic basis sets in the context of molecules. Their performance are yet extensively validated for systems with periodic boundaries.

The contradiction of efficiency and accuracy is rooted in the development of pseudo potential\textsuperscript{37–41}. Because of the limited choices of available soft pseudo potentials, one often would have to sacrifice the reliability in a real application, not to mention the limitations of pseudo potential if
one would like to study the problems beyond closed-shell valence properties, such as relativistic effects, core-valence correlations, core electron spectroscopy, spin polarization and so forth. All-electron simulations would be the key of these challenges.

Developing an algorithm suitable for arbitrary basis sets and arbitrary core treatment is the goal of the current work we would like to achieve. As shown in Irmler’s work\textsuperscript{35}, it is efficient to evaluate exchange matrix in the two-passes algorithm: First compute the exchange matrix based on Born-von Karman supercell in real space then transform to the representations adapted to \( \mathbf{k} \)-point symmetry in reciprocal space. In their work, they demonstrated several HF calculations with thousands of \( \mathbf{k} \) points. Nonetheless, the accuracy of Irmler’s work is affected by the artifacts of truncated Coulomb kernel near the truncation boundary. We adopt the similar 2-passes strategy to evaluate Coulomb and exchange matrices in our algorithm. In contrast to their treatment of Coulomb metric, we handle the full Coulomb metric without truncation.

The formulaism of the algorithm are established in Section II. The algorithm in the present work requires various integral screen thresholds and cutoffs. They are discussed in Section II D. Results and performance benchmark are presented in Section III.

### II. THEORY

#### A. Fock matrix computed in the range-separation of Coulomb metric

We consider here a periodic system which consists of repeated unit cells with translation vectors \( \mathbf{m} \) and lattice vectors \( \mathbf{a} \)

\[
\mathbf{m} = m_x \mathbf{a}_x + m_y \mathbf{a}_y + m_z \mathbf{a}_z.
\]  

(1)

Crystal orbitals for a crystal of \( N \to \infty \) unit cells can be expanded with a set of Bloch orbitals

\[
\phi_{\mu}^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{m}} e^{i \mathbf{k} \cdot \mathbf{m}} \mu^\mathbf{m}(\mathbf{r})
\]  

(2)

where \( \mu^\mathbf{m} \) is an real Gaussian-type orbital centered at \( \mathbf{R}_\mu \) in the unit cell regarding to the translation vector \( \mathbf{m} \)

\[
\mu^\mathbf{m}(\mathbf{r}) = \mu(\mathbf{r} - \mathbf{R}_\mu - \mathbf{m})
\]  

(3)

Solving the periodic HF model can lead us to the \( \mathbf{k} \)-point symmetry adapted Roothaan equations

\[
\mathbf{F}^\mathbf{k} \mathbf{C}^\mathbf{k} = \mathbf{S}^\mathbf{k} \mathbf{C}^\mathbf{k} \mathbf{\epsilon}^\mathbf{k},
\]  

(4)
and the corresponding \( k \)-point symmetry adapted Fock matrix and overlap matrix

\[
F^k = T^k + V^k_{\text{Nuc}} + J^k - K^k, \tag{5}
\]

\[
S_{\mu \nu}^k = \langle \phi_{\mu}^k | \phi_{\nu}^k \rangle \tag{6}
\]

The overlap matrix can be computed using discrete FT of the overlap integrals in real space

\[
S_{\mu \nu}^k = \sum_m e^{i k \cdot m} S_{\mu \nu}^0 m, \tag{7}
\]

\[
S_{\mu \nu}^0 m = \langle \mu^0 | \nu^m \rangle. \tag{8}
\]

In a similarly way, we can get the kinetic matrix in \( F^k \)

\[
T_{\mu \nu}^k = \sum_m e^{i k \cdot m} T_{\mu \nu}^0 m. \tag{9}
\]

When computing the nuclear attraction matrix \( V^k_{\text{Nuc}} \), we use model charge to screen the long-range interactions then compute separately the long-range and short-range parts of nuclear attraction integrals. Relevant techniques have been documented in our earlier work \cite{34}.

The HF Coulomb and exchange matrices in \( F^k \) are

\[
J_{\mu \nu}^k = \sum_{k'} \sum_{k' \lambda} D_{\lambda k'}^k (\phi_{\mu}^k \phi_{\nu}^k | \phi_{k'}^{k'} \phi_{\lambda}^{k'}), \tag{10}
\]

\[
K_{\mu \lambda}^k = \sum_{k'} \sum_{\lambda \nu} D_{\nu k'}^{k'} (\phi_{\mu}^k \phi_{\nu}^k | \phi_{k'}^{k'} \phi_{\lambda}^{k'}). \tag{11}
\]

The four-center two-electron repulsion integrals in equation (11) follow Mulliken notation

\[
(\phi_{\mu}^{k \mu} \phi_{\nu}^{k \nu} | \phi_{k}^{k} \phi_{\lambda}^{k}) = \int \int \phi_{\mu}^{k \mu}(r_1) \phi_{\nu}^{k \nu}(r_1) g(r_{12}) \phi_{k}^{k}(r_2) \phi_{\lambda}^{k}(r_2) d^3r_1 d^3r_2. \tag{12}
\]

By splitting the Coulomb metric \( g(r_{12}) \) into long-range (LR) plus short-range (SR) contributions

\[
g(r_{12}) = \frac{1}{r_{12}} = \frac{\text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erfc}(\omega r_{12})}{r_{12}}, \tag{13}
\]

we can evaluate the electron repulsion integrals of the two components separately in reciprocal space and real space.

We will focus on the computation of exchange matrix in the following context. The Coulomb matrix can be computed in a similar fashion. The LR component of the ERI \( (12) \) can be evaluated
in reciprocal space, yielding a summation over planewaves $G = \frac{(2\pi)^{3/2}}{\sqrt{N}} e^{iG \cdot r}$ inside the volume $\Omega$ of the unit cell.\(^{42}\)

\[
(\phi^k_\mu | \phi^k_{\mu'})_{LR} = \frac{1}{\Omega} \sum_G \frac{4\pi \exp(-\frac{|G+k'-k|^2}{4\omega})}{|G+k'-k|^2} \rho^{kk'}_{\mu\nu}(G) \rho^{kk'}_{\kappa\lambda}(-G),
\]

(14)

\[
\rho^{kk'}_{\mu\nu}(G) = \int e^{-i(G+k'-k) \cdot r} \phi^k_\mu(r) \phi^{k'}_{\nu}(r) d^3G = \sum_n e^{ik' \cdot n} \int e^{-i(G+k'-k) \cdot r} \mu(r) \nu(r-n) d^3G.
\]

(15)

In Eq. (14), a limited number of planewaves is required to converge the integrals thanks to the exponential decay quantity $\exp(-\frac{G^2}{4\omega})$. We then ready to obtain the LR contributions of the exchange matrix using Eq. (10) and Eq. (11).

SR Coulomb integrals can be evaluated in real space. Following the schemes developed in \(^{35}\), we first perform the SR part of the exchange matrix in the Born-von Karman (BvK) supercell

\[
K^\text{SR}_{\mu_0 \lambda_1} = \sum_{v+n} \sum_{L+m} \sum_{M+n} D_{\nu_0}^{m+n} (\mu_0 | \nu_0^{m+n}) D_{\nu_0}^{m+n} (\lambda_1 | \lambda_1^{m+n})^\text{SR}.
\]

(16)

Here involves two types of translation vectors, the super-lattice translation vectors for BvK supercell ($L$, $M$, $N$) and the translation inside a single BvK supercell ($l$, $m$, $n$). SR Coulomb integrals as well as the exchange matrix can be converged with a finite number of super lattice translation vectors. Similar to the treatment for overlap matrix in Eq. (7), a discrete FT can transform Eq. (16) to the $k$-point symmetry adapted exchange matrix. The quantity $D_{\nu_0}^{m+n}$ in Eq. (16) is density matrix of BvK supercell. The translation symmetry ensures that the density matrix is invariant against the super-lattice translations

\[
D_{\nu_0}^{m+n} = D_{\nu_0}^{m+n}.
\]

(17)

For the BvK supercell being filled with $N_{BvK}$ primitive cells, $D_{\nu_0}^{m+n}$ is obtained from back-FT of the $k$-adapted density matrices

\[
D_{\nu_0}^{m+n} = D_{\nu_0}^{m+n} = \frac{1}{N_{BvK}} \sum_k e^{-ik \cdot (m-n)} D_{\nu_k}^{k}.
\]

(18)

When comparing the so-obtained exchange matrix to the one based on discrete FT, we noticed that they are different at $G = 0$, whose contribution is

\[
K^k_{\mu\lambda} \bigg|_{G=0} = \frac{\pi}{\Omega \omega^2} \sum_{v+k} S^k_{\mu v} D^k_{v k} S^k_{k \lambda}.
\]

(19)
B. SR integrals in real space

When a system employs diffused basis functions, the integration scheme above may still require a huge number of repeated images of BvK supercell in the crystal to converge the SR integrals. It is efficient to compute the integrals in reciprocal space if the relevant basis functions are all smooth functions. We thus divided the entire basis sets into two groups based on their locality, using notation $\mathcal{D}$ and $\mathcal{C}$ to label the diffused functions and the compact functions. The products of two basis functions $\rho_{\mu\nu}$ have four possible combinations: $\rho_{\mu\nu} \sim \mathcal{D} \mathcal{D}$ is the product of two diffused functions; $\rho_{\mu\nu} \sim \mathcal{D} \mathcal{C}$ and $\rho_{\mu\nu} \sim \mathcal{C} \mathcal{D}$ are the product of one diffused function and one compact function; $\rho_{\mu\nu} \sim \mathcal{C} \mathcal{C}$ is the product of two compact functions.

When computing the two-electron SR integrals, the products $\rho_{\mu\nu} \cdot \rho_{\mu\nu}$ (in total 9 components) are evaluated analytically in real space. All other integrals are evaluated in reciprocal space, including: the long-range part of $\rho_{\mu\nu} \cdot \rho_{\mu\nu}$ and the full Coulomb integrals of $\rho_{\mu\nu} \cdot \rho_{\mu\nu}$, $\rho_{\mu\nu} \cdot \rho_{\mu\nu}$, and $\rho_{\mu\nu} \cdot \rho_{\mu\nu}$.

C. Integrals in reciprocal space

Integrals in the reciprocal space are computed

$$\langle \phi_{\mu}^{k} \phi_{\nu}^{k'} | \phi_{\kappa}^{k} \phi_{\lambda}^{k} \rangle = \frac{1}{\Omega} \sum_{G} g(G, k, k') \rho_{\mu\nu}^{k k'}(G) \rho_{\kappa\lambda}^{k' k}(-G),$$  \hspace{1cm} (20)

where the Coulomb kernel $g(G, k, k')$ can be

$$g(G, k, k') = \frac{4\pi}{|G + k' - k|^2}$$  \hspace{1cm} (21)

for the regular full Coulomb interactions and

$$g_{LR}(G, k, k') = \frac{4\pi \exp\left(-\frac{|G + k' - k|^2}{4\omega}\right)}{|G + k' - k|^2}$$  \hspace{1cm} (22)

for the long-range Coulomb attenuation. By using the notations $D$ and $C$ for diffused and compact basis functions, we get 7 types of two-electron integrals computed with the full Coulomb kernel \(^{21}\). They are $\mathcal{D} \mathcal{D} | \mathcal{D} \mathcal{D}$, $\mathcal{D} \mathcal{D} | \mathcal{C} \mathcal{D}$, $\mathcal{D} \mathcal{D} | \mathcal{D} \mathcal{C}$, $\mathcal{D} \mathcal{D} | \mathcal{C} \mathcal{C}$, $\mathcal{C} \mathcal{D} | \mathcal{D} \mathcal{D}$, $\mathcal{D} \mathcal{C} | \mathcal{D} \mathcal{D}$, and $\mathcal{C} \mathcal{C} | \mathcal{D} \mathcal{D}$. There
are 9 types of integrals \( (CC|CC), (CC|CD), (CC|DC), (CD|CD), (CD|CC), (DC|CD), (DC|DC), (DC|CC) \) associated with the LR Coulomb attenuation kernel (22). For the 9 types of LR integrals, the contributions of \( \mathbf{G} = 0 \) as shown in (19) which was brought by the real-space analytical integration need to be subtracted.

D. Truncation criteria

1. Coulomb attenuation parameter

Our first parameter to determine is the range-separation parameter \( \omega \) in the attenuated Coulomb metric. The optimal choice would be the one that can balance the cost of reciprocal space and real space computation. It can be influenced by many factors, e.g. the lattice parameters, the ratio of diffused functions in the entire basis sets, the desired numerical precision, the performance of underlying integral engine and FT engine. In our current implementation, the reciprocal space computation is dominated by the analytical FT (15), in which we need to invoke \( N_k \) times the analytical FT for \( N_G \) planewaves. In each call of the FT, the complexity is \( \mathcal{O}(N_G^2 N_t) \) regarding to the \( N_{AO} \) basis functions and \( N_t \) the number translation vectors in lattice sum. We thus target that, with certain value of \( \omega \) and its associated \( N_G \), the complexity of the dominant step in the real space computation \( \mathcal{O}(N_A^4 N_I^3) \) is comparable to the FT complexity. Under this guideline, we adjust certain factors and utilize the estimation expression for \( \omega \)

\[
\omega \approx 0.01 \left( \frac{N_{AO} N_I \Omega}{N_k} \right)^{\frac{1}{3}}.
\]  

(23)

2. Integral prescreening

We employ two types of Schwarz inequalities

\[
(\mu \nu | \kappa \lambda) < \sqrt{(\mu \nu | \mu \nu)(\kappa \lambda | \kappa \lambda)},
\]  

(24)

\[
(\mu \nu | \kappa \lambda) < \min(\sqrt{(\mu \mu | \kappa \kappa)(\nu \nu | \lambda \lambda)}, \sqrt{(\mu \mu | \lambda \lambda)(\nu \nu | \kappa \kappa)}).
\]  

(25)

The second condition is not quite useful for regular Coulomb metric due to the LR character of Coulomb interactions. Neither \( \sqrt{(\mu \mu | \kappa \kappa)(\nu \nu | \lambda \lambda)} \) nor \( \sqrt{(\mu \mu | \lambda \lambda)(\nu \nu | \kappa \kappa)} \) will vanish regardless how the underlying basis functions are separated. In contrast to regular Coulomb, this
condition filters about 50% terms for SR integrals. These cases are corresponding to the interactions between the remotely separated bra and ket functions which are quite common to the lattice sum integration.

3. Energy cutoff

Given Coulomb attenuation parameter $\omega$ and the desired numerical precision $\varepsilon$, the energy cutoff $E_{\text{cut}} = \frac{1}{2} |G_{\text{max}}|^2$ to converge LR integrals in reciprocal space is ready to obtain

$$
\frac{1}{\Omega} \sum_{G=0}^{\infty} \rho(G) \frac{4\pi \exp(-\frac{G^2}{4\omega^2})}{G^2} \rho(-G) = \frac{1}{\Omega} \sum_{G=0}^{E_{\text{cut}}} \rho(G) \frac{4\pi \exp(-\frac{G^2}{4\omega^2})}{G^2} \rho(-G) + \delta. \tag{26}
$$

Our estimation for the error $\delta$ is

$$
\delta = \frac{1}{\Omega} \sum_{|G|>E_{\text{cut}}} \rho(G) \frac{4\pi \exp(-\frac{G^2}{4\omega^2})}{G^2} \rho(-G) \approx \int_{G_{\text{max}}-\frac{1}{2}G_{\text{min}}}^{\infty} \rho(G) \frac{4\pi \exp(-\frac{G^2}{4\omega^2})}{G^2} \rho(-G)d^3G. \tag{27}
$$

$G_{\text{min}}$ is the smallest non-zero $G$. The Fourier transformed Gaussian product $\rho(G)$ is a Gaussian distribution. $\rho(G)$ is always smaller than 1. The error estimation can be reduction to

$$
\delta < \int_{G_{\text{max}}-\frac{1}{2}G_{\text{min}}}^{\infty} \frac{4\pi \exp(-\frac{G^2}{4\omega^2})}{G^2}d^3G = \int_{G_{\text{max}}-\frac{1}{2}G_{\text{min}}}^{\infty} 16\pi^2 \exp(-\frac{G^2}{4\omega^2})dG < \frac{1}{G_{\text{max}}} \int_{G_{\text{max}}-\frac{1}{2}G_{\text{min}}}^{\infty} 16\pi^2 G \exp(-\frac{G^2}{4\omega^2})dG < \frac{32\pi^2 \omega^2 \exp(-\frac{(G_{\text{max}}-\frac{1}{2}G_{\text{min}})^2}{4\omega^2})}{G_{\text{max}}}. \tag{28}
$$

We can set the energy cutoff

$$
E_{\text{cut}} = \frac{1}{2} |G_{\text{max}}|^2 > 2\omega^2 \log(\frac{32\pi^2 \omega^2}{\varepsilon}) \tag{29}
$$

which ensures the integral error $\delta$ of LR integrals smaller than the required precision $\varepsilon$ for all basis functions.
4. Basis locality

We are now targeting a criteria to classify the diffused functions and the compact basis functions. Based on this partitioning criteria $\rho_D$ the product of two diffused functions needs to be smooth enough to converge the reciprocal integration \[ (20) \] under the full Coulomb kernel.

This error is estimated

$$\delta = \frac{1}{\Omega} \sum_{G \sim \sqrt{2E_{\text{cut}}}} \rho_D(G) \frac{4\pi}{G^2} \rho(-G) \approx \int_{\sqrt{2E_{\text{cut}}}}^{\infty} \rho_D(G) \frac{4\pi}{G^2} \rho(-G) d^3G. \quad (30)$$

$\rho(-G)$ is smaller than 1 in any circumstance.

$$\delta < \int_{\sqrt{2E_{\text{cut}}}}^{\infty} \rho_D(G) \frac{4\pi}{G^2} d^3G. \quad (31)$$

If $\rho_D$ is formed from the same primitive $s$-type Gaussians at the same center, we have

$$(\rho_D)_{\mu \nu}(r) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} \exp(-\alpha (r - R_{\mu})^2) \exp(-\alpha (r - R_{\nu})^2). \quad (32)$$

The product under FT appears

$$(\rho_D)_{\mu \nu}(G) = \exp\left(-\frac{G^2}{8\alpha}\right) \exp\left(-\frac{i}{2} G \cdot (R_{\mu} + R_{\nu})\right)$$

$$| (\rho_D)_{\mu \nu}(G) | < \exp\left(-\frac{G^2}{8\alpha}\right)$$

We then derive the integration error

$$\delta < \int_{\sqrt{2E_{\text{cut}}}}^{\infty} 16\pi^2 \exp\left(-\frac{G^2}{8\alpha}\right) dG < \frac{64\pi^2 \alpha \exp\left(-\frac{E_{\text{cut}}}{4\alpha}\right)}{\sqrt{2E_{\text{cut}}}} \quad (33)$$

which yields the boundary of the Gaussian exponent

$$\alpha_{\text{cut}} < \frac{E_{\text{cut}}}{4 \log\left(\frac{64\pi^2}{\sqrt{2E_{\text{cut}}} \epsilon}\right)}. \quad (34)$$

For basis functions of angular momentum $l$, we analyze the leading term of the Fourier transformed orbital products in the similar manner and obtain an estimation of the boundary

$$\alpha_{\text{cut}} < \frac{E_{\text{cut}}}{4 \log\left(\frac{64\pi^2 E_{\text{cut}}^{l - \frac{1}{2}}}{2^{l + \frac{1}{2}} (2l + 1)! \epsilon}\right)}. \quad (35)$$

We use the threshold $\alpha_{\text{cut}}$ to classify the characters of basis functions. The basis functions in the smooth set are the primitive Gaussians with exponents smaller than $\alpha_{\text{cut}}$. The rest basis functions are grouped in the compact set. For contracted basis functions, we first de-contract the bases then carry out the partitioning for the primitive functions.
5. **Lattice sum boundary**

Lattice sum in real space is required in two places. First is the FT of the orbital product (15). Second is the SR integrals (16) computed in the real space.

For simplicity, we ignore the $k$ points in Eq. (15)

$$\rho_{\mu\nu}(G) = \sum_N \int e^{-iG \cdot r} \mu(r)\nu(r-N) d^3r.$$  \hspace{1cm} (35)

The real space truncation error is

$$\delta = \sum_{|N|>R_{cut}} \int e^{-iG \cdot r} \mu(r)\nu(r-N) d^3r < \sum_{|N|>R_{cut}} S_{\mu\nu}^N,$$ \hspace{1cm} (36)

$$S_{\mu\nu}^N = \int \mu(r)\nu(r-N) d^3r.$$ \hspace{1cm} (37)

The overlap $S_{\mu\nu}^N$ in terms of $s$-type Gaussians is

$$S_{\mu\nu}^N = \left(\frac{4\alpha_{\mu}\alpha_{\nu}}{\alpha_{\mu\nu}^2}\right)^{3/4} e^{-\eta_{\mu\nu}^N}$$ \hspace{1cm} (38)

where

$$\alpha_{\mu\nu} = \alpha_\mu + \alpha_\nu,$$ \hspace{1cm} (39)

$$\eta_{\mu\nu}^N = \frac{\alpha_{\mu}\alpha_\nu}{\alpha_{\mu\nu}} |R_\mu - R_\nu - N|^2.$$ \hspace{1cm} (40)

The error $\delta$ would be maximized when $\mu$ and $\nu$ are located at the same atomic center. The upper bound of the error for large distance $|N|$ is

$$\frac{2\pi\alpha_{\mu\nu}|N|}{\alpha_\mu\alpha_\nu} \left(\frac{4\alpha_{\mu}\alpha_{\nu}}{\alpha_{\mu\nu}^2}\right)^{3/4} \exp\left(-\frac{\alpha_{\mu}\alpha_\nu (|N| - \frac{3\sqrt{2}}{2})^2}{\alpha_{\mu\nu}}\right).$$ \hspace{1cm} (41)

We use this equation to filter the translation vectors in analytical FT (15).

The SR integral of four primitive $s$-type Gaussians on different centers has analytical form

$$(\mu\nu|\kappa\lambda)_{SR,\omega} = \int \rho_{\mu\nu}(r_1) \frac{\text{erfc}(\omega r_{12})}{r_{12}} \rho_{\kappa\lambda}(r_2) d^3r_1 d^3r_2$$

$$= \frac{8(\alpha_\mu\alpha_\nu\alpha_\kappa\alpha_\lambda)^{3/4}}{\pi^3} \int e^{\alpha_{\mu\nu}(r_1-R_{\mu\nu})^2} \frac{\text{erfc}(\omega r_{12})}{r_{12}} e^{\alpha_{\kappa\lambda}(r_2-R_{\kappa\lambda})^2} d^3r_1 d^3r_2$$

$$= \frac{8(\alpha_\mu\alpha_\nu\alpha_\kappa\alpha_\lambda)^{3/4}}{\alpha_{\mu\nu}^2\alpha_{\kappa\lambda}^2} \left(\frac{e^{-\eta_{\mu\nu}-\eta_{\kappa\lambda}}}{s}\right) \text{erf}(\sqrt{\beta s}) - \text{erf}\left(\frac{\omega \sqrt{\beta}}{\sqrt{\omega^2 + \beta}}s\right)$$ \hspace{1cm} (42)
\[ \beta = \frac{\alpha_{\mu \nu} \alpha_{\kappa \lambda}}{\alpha_{\mu \nu} + \alpha_{\kappa \lambda}}, \quad (43) \]
\[ s = |\mathbf{R}_{\mu \nu} - \mathbf{R}_{\kappa \lambda}|, \quad (44) \]
\[ \mathbf{R}_{\mu \nu} = \frac{\alpha_{\mu} \mathbf{R}_{\mu} + \alpha_{\nu} \mathbf{R}_{\nu}}{\alpha_{\mu} + \alpha_{\nu}}. \quad (45) \]

In the \textit{(DC|DC)}-type integrals, both \( \rho_{\mu \nu}(\mathbf{r}) \) and \( \rho_{\kappa \lambda}(\mathbf{r}) \) are the product of a diffused Gaussian and a compact Gaussian. \( \mathbf{R}_{\mu \nu} \), the center of the product \( \rho_{\mu \nu} \), should be close to the center of the compact function \( v(\mathbf{r}) \). So is the center \( \mathbf{R}_{\kappa \lambda} \) in \( \rho_{\kappa \lambda} \). If function \( \lambda(\mathbf{r}) \) is close to function \( v(\mathbf{r}) \), the distance \( s \) between \( \rho_{\mu \nu}(\mathbf{r}) \) and \( \rho_{\kappa \lambda}(\mathbf{r}) \) is relatively a small value otherwise the SR Coulomb attenuation would rapidly decay to zero. Employing the formula

\[ \frac{\text{erf}(ts)}{s} < \lim_{s \to 0} \frac{\text{erf}(ts)}{s} = \frac{2t}{\sqrt{\pi}}, \quad (46) \]

the SR ERI is approximately

\[ \langle \mu \nu | \kappa \lambda \rangle_{\text{SR}, \omega} \approx 8 \left( \frac{\alpha_{\mu} \alpha_{\nu} \alpha_{\kappa} \alpha_{\lambda}}{\alpha_{\mu \nu}^2 \alpha_{\kappa \lambda}} \right)^{3/4} e^{-\eta_{\mu \nu} - \eta_{\kappa \lambda}} \frac{2}{\sqrt{\pi}} \left( \sqrt{\beta} - \frac{\omega \sqrt{\beta}}{\sqrt{\omega^2 + \beta}} \right) \]
\[ < 16 \sqrt{\frac{\beta}{\pi}} \left( \frac{\alpha_{\mu} \alpha_{\nu} \alpha_{\kappa} \alpha_{\lambda}}{\alpha_{\mu \nu}^2 \alpha_{\kappa \lambda}} \right)^{3/4} \exp \left( - \frac{\alpha_{\mu} \alpha_{\nu}}{\alpha_{\mu \nu}} |\mathbf{R}_{\mu} - \mathbf{R}_{\mu \nu}|^2 - \frac{\alpha_{\kappa} \alpha_{\lambda}}{\alpha_{\kappa \lambda}} |\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa \lambda}|^2 \right). \quad (47) \]

Without loss of generality, we can assume \( \alpha_{\mu} = \alpha_{\kappa} \) and \( \alpha_{\nu} = \alpha_{\lambda} \) and \( \mu < \nu \)

\[ \langle \mu \nu | \kappa \lambda \rangle_{\text{SR}, \omega} < 16 \sqrt{\frac{\alpha_{\mu \nu}}{2\pi}} \left( \frac{\alpha_{\mu} \alpha_{\nu}}{\alpha_{\mu \nu}^2} \right)^{3/2} \exp \left( - \frac{\alpha_{\mu} \alpha_{\nu}}{\alpha_{\mu \nu}} \left( |\mathbf{R}_{\mu} - \mathbf{R}_{\mu \nu}|^2 + |\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa \lambda}|^2 \right) \right). \quad (48) \]

Due to the inequality (46), we would get the maximum value of (48) at \( s = \mathbf{R}_{\mu \nu} - \mathbf{R}_{\kappa \lambda} = 0 \). It indicates the condition to filter the translation vector \( \mathbf{M} \) in SR integration (16)

\[ 16 \sqrt{\frac{\alpha_{\mu \nu}}{2\pi}} \left( \frac{\alpha_{\mu} \alpha_{\nu}}{\alpha_{\mu \nu}^2} \right)^{3/2} \exp \left( - \frac{\alpha_{\mu} \alpha_{\nu}}{2\alpha_{\mu \nu}} \left( |\mathbf{R}_{\mu} - \mathbf{R}_{\mu \nu}|^2 - (\mathbf{R}_{\kappa} + \mathbf{M}) \right)^2 \right) < \epsilon. \quad (49) \]

For \textit{(CC|CC)}-type integrals, the orbital product \( \rho \) decays rapidly. The lattice sum in (16) is dominated by the terms of which \( \mathbf{N} = 0 \) and \( \mathbf{L} = 0 \). For simplicity, we can analyze the special case \( \mu = \nu \) and \( \kappa = \lambda \), and in addition the products \( \rho_{\mu \nu} \) and \( \rho_{\kappa \lambda} \) being separated by the translation vector \( \mathbf{M} \). We then transform Eq. (42) to

\[ \frac{\text{erfc}(\frac{\omega \sqrt{\beta}}{\sqrt{\omega^2 + \beta}} s) - \text{erfc}(\sqrt{\beta} s)}{s} < \sqrt{\frac{\omega^2 + \alpha_{\mu}}{\omega \sqrt{\alpha_{\mu}}}} \exp\left( -\frac{\omega^2 \alpha_{\mu}}{\omega^2 + \alpha_{\mu}} s \right) \frac{2s^2}{2s^2}. \]
Applying lattice sum to this equation, we get the filter condition
\[
\sqrt{\omega^2 + \alpha^2} \exp\left( - \frac{\omega^2 \alpha}{\omega^2 + \alpha^2} (|M| - \frac{\sqrt{\Omega}}{2})^2 \right).
\] (50)

Depending on whether the system has diffused functions, we adopted either condition (49) or condition (50) for the lattice sum index \(M\) in (16).

In the \((DC|CC)\)-type integrals, the maximum value of \((\mu \nu | \kappa \lambda)\) can be approximated with Eq. (48). The maximum value of this integral appears around \(R_\kappa = R_\lambda \approx R_\mu \approx R_\nu\) and \(\alpha_\kappa = \alpha_\lambda\), i.e., the three compact basis functions in the 4 centers are standing on the same atomic center and two of which are the same basis functions, leading to the error estimation proportional to the regular overlap of two basis functions
\[
\frac{4(\alpha_{\mu} \alpha_{\nu})^{3/4}}{\sqrt{\pi \alpha_{\mu \nu}}} \langle \mu | v^N \rangle.
\] (51)

By applying the effects of lattice sum (Appendix A), we would get the condition to filter translation vector \(N\) in equation (16) for \((DC|CC)\)-type integrals (or vector \(L\) for \((CC|DC)\)-type integrals)
\[
\frac{2\sqrt{\pi} |N|}{(\alpha_{\mu} \alpha_{\nu})^{1/4}} \langle \mu | v^N \rangle.
\]

III. BENCHMARK

In this section, we benchmark the \(k\)-point HF calculations. Our program is available in PySCF-1.7.6. In these benchmark calculations, the ERI prescreening parameter for J/K builder was set to \(10^{-13}\). The precision parameter \(\varepsilon\) was set to \(10^{-8}\) when estimating energy cutoff (29), and the basis locality partitioning parameter (II D 4) and the lattice sum boundary of FT (41). All timings were obtained on a desktop equipped with Intel I9-7940X CPU and 64 GB memory.

Table II lists the KHF (HF with \(k\)-point sampling) results for diamond crystal in the cubic unit cell with GTH-SZV basis and pseudo potential GTH-pade. In each unit cell, this calculation contains 8 Carbon atoms and 32 basis functions. The largest calculation involves \(15 \times 15 \times 15 = 3375\) samples in the first Brillouin zone, corresponding to in total 27000 atoms or 108000 basis functions. For comparison, evaluating the Coulomb integrals in reciprocal space would require at least \(N_G = 49^3\) planewaves to converge the integrals to the desired accuracy. The discrete FT engine in PySCF requires at least \(\frac{1}{2} \times 3 \times 8 \times N^2 \beta^N \alpha^N_k \) FLOPs to process the FT in K-matrix constructor (factor 8 is obtained from the complex matrix multiplication; 3 is due to the 3 passes.
TABLE I. KHF for diamond crystal with GTH-SZV basis and pseudo potential GTH-pade. The unit cell is cubic structure with lattice parameter 3.5668 Å.

| $\mathbf{k}$ mesh | $E/E_h$ per cell | $\omega$ | CPU hours | Error $\times 10^9/E_h$ $^a$ |
|-------------------|-----------------|---------|-----------|-----------------------------|
| 1 $\times$ 1 $\times$ 1 | -43.8468002862 | 2.512 | 2.76 | +0.13 |
| 2 $\times$ 2 $\times$ 2 | -44.0506288397 | 0.5 | 11.7 | +2.89 |
| 3 $\times$ 3 $\times$ 3 | -44.0240243649 | 0.5 | 13.4 | -0.75 |
| 4 $\times$ 4 $\times$ 4 | -44.0136700424 | 0.5 | 20.0 | - |
| 6 $\times$ 6 $\times$ 6 | -44.0077526217 | 0.4 | 70.7 | - |
| 8 $\times$ 8 $\times$ 8 | -44.0062794104 | 0.4 | 125 | - |
| 10 $\times$ 10 $\times$ 10 | -44.0057532951 | 0.237 | 294 | - |
| 15 $\times$ 15 $\times$ 15 | - | | | |

$^a$ Difference w.r.t. results of discrete FT formulism

in the 3D-FT; $\frac{1}{2}$ is due to the hermiticity in the intermediate tensors). For $4 \times 4 \times 4$ $\mathbf{k}$-mesh, the cost is roughly $2.9 \times 10^{14}$ FLOPs.

When moving to all-electron calculations, as shown in Table II, it is inappropriate to call the discrete FT engine because of the steep basis functions for core electrons. The STO-3G basis would require about $183^3$ planewaves for Coulomb repulsion integrals. This number becomes about $954^3$ for cc-pVDZ basis due to the more compact functions presented in the basis set. Even the minimal basis with minimal $2 \times 2 \times 2$ $\mathbf{k}$-mesh can easily reach $10^{15}$ FLOPs to build K-matrix, not to mention the TB level memory footprint to hold the intermediates. The present new algorithm would be able to finish the calculation of cc-pVDZ basis with $4 \times 4 \times 4$ $\mathbf{k}$-mesh in a couple of hours on a dedicated multi-core CPU machine. The largest all-electron calculation which consists of 112000 basis functions only requires 784 CPU hours and memory footprint less than 6 GB.

IV. CONCLUSIONS

We presented an algorithm to evaluate Coulomb repulsion integrals and construct Fock matrix using periodic GTOs for all-electron crystals simulations. In the algorithm, we split Coulomb integrals into smooth and compact components based on the locality of underlying Coulomb operator and basis functions. We then computed the intermediates either in real space or in the reciprocal
TABLE II. All-electron KHF for diamond crystal with STO-3G and cc-pVDZ. The unit cell is cubic structure with lattice parameter 3.5668 Å.

|  | STO-3G |  | cc-pVDZ |  |
|---|---|---|---|---|
| **k mesh** | $E/E_h$ per cell | $\omega$ | CPU/h | $E/E_h$ per cell | $\omega$ | CPU/h |
| 1\times1\times1 | -299.328100921 | 0.6 | 2.82 | -302.870240306 | 0.5 | 54.3 |
| 2\times2\times2 | -299.551273686 | 0.6 | 2.58 | -303.076048519 | 0.609 | 19.3 |
| 3\times3\times3 | -299.525889782 | 0.579 | 6.17 | -303.054159127 | 0.609 | 30.1 |
| 4\times4\times4 | -299.516149849 | 0.579 | 16.1 | -303.044553455 | 0.616 | 79.5 |
| 6\times6\times6 | -299.510659684 | 0.332 | 25.3 | -303.038977867 | 0.474 | 260 |
| 10\times10\times10 | -299.508816002 | 0.237 | 95.2 | -303.037088495 | 0.237 | 784 |

space and gain great efficiency in both space. The algorithm does not have restrictions on the basis sets, the k-point mesh, or other preliminary knowledges of the system. HF self-consistency for systems of 10k atoms and 100k basis functions can be handled on regular desktops without difficulty.

The performance of this algorithm relies on the thresholds and cutoffs in the integrator. We discussed the prescreening thresholds and cutoffs in our implementation based on the estimation of Coulomb integral values and lattice sum formulaism. The estimations in this work are quite conservative. There are plenty rooms to optimize the thresholds for better performance.

**Appendix A: Appendix**

We demonstrate here how the lattice sum is applied to the estimation of integral values.

- Lattice sum for overlap

$$\sum_{|L|>R_{cut}} \exp \left( -\frac{\alpha_\mu \alpha_\nu L^2}{\alpha_{\mu\nu}} \right)$$

$$\approx \frac{1}{\Omega} \int_{R_{cut} - \frac{\sqrt{\Omega}}{2}}^{\infty} \exp \left( -\frac{\alpha_\mu \alpha_\nu L^2}{\alpha_{\mu\nu}} \right) d^3L$$

$$= \frac{4\pi}{\Omega} \int_{R_{cut} - \frac{\sqrt{\Omega}}{2}}^{\infty} \exp \left( -\frac{\alpha_\mu \alpha_\nu L^2}{\alpha_{\mu\nu}} \right) L^2 dL$$

$$= \frac{4\pi}{\Omega} \frac{\alpha_{\mu\nu}}{2\alpha_\mu \alpha_\nu} \left( R_{cut} - \frac{\sqrt{\Omega}}{2} \right) \exp \left( -\frac{\alpha_\mu \alpha_\nu \left( R_{cut} - \frac{\sqrt{\Omega}}{2} \right)^2}{\alpha_{\mu\nu}} \right) + \int_{R_{cut} - \frac{\sqrt{\Omega}}{2}}^{\infty} \exp \left( -\frac{\alpha_\mu \alpha_\nu R^2}{\alpha_{\mu\nu}} \right) dR$$
\[
\approx \frac{2\pi(R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2})\alpha_{\mu\nu}}{\Omega \alpha_{\mu} \alpha_{\nu}} \exp \left( - \frac{\alpha_{\mu} \alpha_{\nu}(R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2})^2}{\alpha_{\mu\nu}} \right) (1 + \frac{\alpha_{\mu\nu}}{2\alpha_{\mu} \alpha_{\nu}(R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2})^2})
\]
\[
< \frac{2\pi R_{\text{cut}} \alpha_{\mu\nu}}{\Omega \alpha_{\mu} \alpha_{\nu}} \exp \left( - \frac{\alpha_{\mu} \alpha_{\nu}(R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2})^2}{\alpha_{\mu\nu}} \right)
\]

• Lattice sum for Coulomb integrals

\[
\int_{R_{\text{cut}} = \frac{3\sqrt{\Omega}}{2}}^{\infty} \frac{\sqrt{\omega^2 + \alpha_{\mu}}}{\omega \sqrt{\alpha_{\mu}}} \exp \left( - \frac{\omega^2 \alpha_{\mu} s}{\omega^2 + \alpha_{\mu}} \right) d^3 s
\]
\[
= \frac{2\pi \sqrt{\omega^2 + \alpha_{\mu}}}{\omega \sqrt{\alpha_{\mu}}} \int_{R_{\text{cut}} = \frac{3\sqrt{\Omega}}{2}}^{\infty} \exp \left( - \frac{\omega^2 \alpha_{\mu}}{\omega^2 + \alpha_{\mu}} s \right) ds
\]
\[
= \frac{\omega \sqrt{\alpha_{\mu}}}{\sqrt{\pi} \sqrt{\omega^2 + \alpha_{\mu}}} \text{erfc} \left( \frac{\omega \sqrt{\alpha_{\mu}}}{\sqrt{\omega^2 + \alpha_{\mu}}} (R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2}) \right)
\]
\[
\approx \frac{\sqrt{\omega^2 + \alpha_{\mu}}}{\omega \sqrt{\alpha_{\mu}}} \exp \left( - \frac{\omega^2 \alpha_{\mu}}{\omega^2 + \alpha_{\mu}} (R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2})^2 \right) \frac{R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2}}{R_{\text{cut}} - \frac{3\sqrt{\Omega}}{2}}
\]
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