Efficient evaluation of Gaussian integrals in periodic systems

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By using Poisson’s summation formula, we calculate periodic integrals over Gaussian basis functions by partitioning the lattice summations between the real and reciprocal space, where both sums converge exponentially fast with a large exponent. We demonstrate that the summation can be performed efficiently to calculate 2-center Gaussian integrals over various kernels including overlap, kinetic, and Coulomb. The summation in real space is performed using an efficient flavor of the McMurchie-Davidson Recurrence Relation (MDRR). The expressions for performing summation in the reciprocal space are also derived and implemented. We find that the resulting algorithm is only between a factor of 5 to 15 slower than that for molecular integrals, indicating the very small number of terms needed in both the real and reciprocal space summations. An outline of the algorithm for calculating 3-center Coulomb integrals is also provided.

I. INTRODUCTION

Electronic structure calculations of molecular systems often use the Gaussian basis sets since they allow fast evaluation of the kinetic, overlap, and Coulomb integrals. Further, they offer a compact representation of the wavefunctions both in mean-field and correlated calculations. For these reasons there has been an increasing interest in using the Gaussian basis set for calculations on periodic systems. In one popular approach, the Gaussians are first partitioned into diffuse and sharp functions. The integrals over diffuse Gaussians are effectively calculated using the fast Fourier transform (FFT) whereby plane waves are used to fit the product of two Gaussians, whereas the integrals over sharp Gaussians are calculated explicitly. This approach is implemented in the PySCF software package, an algorithm that utilizes a mixture of Gaussians basis functions and plane waves to evaluate the integrals using the density fitting procedure. However, the cost of the integral evaluation remains high, especially if one uses standard basis sets containing exponents that spans several orders of magnitude typical in molecular calculations.

For periodic systems, the plane waves are the most commonly used basis sets because they automatically honor the translation symmetry of the system so that various integrals, including the Coulomb integrals, are trivially evaluated. However, plane waves do not yield a particularly compact representation. For example, several thousand plane waves are routinely needed and it is difficult if not impossible to treat core electrons without the use of pseudo-potentials or projected augmented waves. Both of these shortcomings can be overcome by using Gaussian basis sets. However, one of the major bottlenecks that prevented a more widespread use of Gaussian basis sets for periodic systems is the cost of calculating the Coulomb integrals that is significantly more expensive than that for molecules. In fact many Gaussian-based mean-field calculations avoid using such bases all together.

In this paper, we present an efficient algorithm for evaluation of the 2-center integrals,

$$\langle a | K | b \rangle = \int \int \phi_a (r_1) K (r_{12}) \phi_b (r_2) \, dr_1 dr_2,$$  \hspace{1cm} (1)

where the kernel $K(r_{12})$ is a function of the inter-electron distance $r_{12} = ||r_1 - r_2||$ and the associated lattice sum

$$\langle a | K | b \rangle^{\text{her}} = \sum_{P} \int \int \phi_a (r_1) K (||r_1 - r_2 + P||) \phi_b (r_2) \, dr_1 dr_2$$  \hspace{1cm} (2)

where $P = n_1 a_1 + n_2 a_2 + n_3 a_3$ are the lattice translations vectors. The kernel $K$ can be the Coulomb kernel $1/r_{12}$, the attenuated Coulomb kernel $\text{erf}(r_{12})/r_{12}$, the Laplace kernel $\nabla_1 \delta_{12}$ for kinetic energy operator or the overlap kernel $\delta_{12}$, where $\delta_{12} = \delta (r_1 - r_2)$. The algorithm can be extended to evaluate other integrals including those involving derivative operators (e.g. nuclear gradients) or multipole operators. Extensions of the current algorithm for 3-center integrals is discussed towards the end of the paper.

The current algorithm is built on top of a particularly efficient version of the McMurchie-Davidson Recurrence Relation (MDRR) scheme proposed recently for calculating the two center integrals. We begin by presenting the
salient features of this algorithm and then show how it can be extended to treat periodic integrals. As in most approaches, we calculate periodic integrals over Gaussian basis functions by partitioning the lattice summations between the real and reciprocal space.

II. GAUSSIAN INTEGRALS FOR MOLECULAR SYSTEMS

The Gaussian type basis sets used in calculations include a pure Gaussian multiplied by solid harmonics, a set of $2l_a + 1$ basis function of the form

$$\phi_a (r) = S_{l_a}^{m_a} (r - A) \exp \left(-a \|r - A\|^2\right)$$

where $m_a$ takes the $2l_a + 1$ values from $-l_a, \ldots, l_a$. The solid harmonics are given in terms of homogeneous monomials,

$$S_{l_a}^{m_a} (r - A) = \sum_{a_x, a_y, a_z = 1} \rho S_{a_x, a_y, a_z}^{l_a, m_a} (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z},$$

where the summation is such that $a_x + a_y + a_z = l_a$.

A useful relation (known as Hobson’s theorem\textsuperscript{16,17}),

$$\left(\frac{1}{2a}\right)^l_a S_{l_a}^{m_a} (\nabla A) \exp \left(-a \|r - A\|^2\right) = S_{l_a}^{m_a} (r - A) \exp \left(-a \|r - A\|^2\right),$$

shows that a Gaussian basis function with non-zero $l_a$ can be obtained by differentiating a simple Gaussian an appropriate number of times with respect to its center. Using this relation, we can rewrite Equation 11 as

$$\langle a|K|b \rangle = \left(\frac{1}{2a}\right)^{l_a} S_{l_a}^{m_a} (\nabla A) \left(\frac{1}{2b}\right)^{l_b} S_{l_b}^{m_b} (\nabla B) I_0 (a, b, T),$$

$$I_0 (a, b, T) = \int \exp \left(-a \|r - A\|^2\right) K (r_{12}) \exp \left(-b \|r - B\|^2\right) dr_1 dr_2$$

$$= \left(\frac{\pi}{a + b}\right)^{3/2} \int e^{-\rho\|A - B - r\|^2} K (r) dr$$

$$= \left(\frac{\pi}{a + b}\right)^{3/2} 2\pi e^{-\rho\|A - B\|^2} \int_0^{\infty} \int_0^{\infty} e^{-\rho r^2} e^{2\rho\|A - B\| r^2 \cos \theta} K (r) r^2 dr \sin \theta d\theta$$

$$= \left(\frac{\pi}{a + b}\right)^{3/2} 2\pi e^{-\rho\|A - B\|^2} \int_0^{\infty} e^{-\rho r^2} r \sinh \left(2\rho\|A - B\|r\right) K (r) dr$$

$$= \left(\frac{\pi}{a + b}\right)^{3/2} G_0 (\rho, T)$$

where $r = \|r\|, \rho = \frac{ab}{\pi \rho}, T = \rho \|A - B\|^2$ and $G_0 (\rho, T)$ ends up being a 1-D integral that can be evaluated analytically for several commonly used kernels.

It is expensive to directly evaluate all $(2l_a + 1)(2l_b + 1)$ derivatives of Equation 11 to compute the integrals. Instead, we can use the MDRR motivated by the observation that

$$S_{l_a}^{m_a} (\nabla A) = S_{l_a}^{m_a} (\nabla R)$$

$$S_{l_a}^{m_a} (\nabla B) = -S_{l_a}^{m_a} (\nabla R)$$

where $R = A - B$. Combining Equations 1, 4, 3 and 11, we obtain

$$\langle a|K|b \rangle = \left(\frac{\pi}{a + b}\right)^{3/2} \left(\frac{1}{2a}\right)^{l_a} \left(\frac{-1}{2b}\right)^{l_b} \sum_{a_x, a_y, a_z = 1} \rho S_{a_x, a_y, a_z}^{l_a, m_a} \sum_{b_x, b_y, b_z = 1} S_{b_x, b_y, b_z}^{l_b, m_b} [c]^{(0)},$$
where $\mathbf{c} = \mathbf{a} + \mathbf{b}$ and we have used the shorthand notation following $^{18,19}$,

$$
[c]^{(m)} = (2\rho)^m \frac{\partial^m}{\partial R_c^m} G_0(\rho, T)
$$

$$
= (-2\rho)^m \frac{\partial^m}{\partial R_c^m} G_m(\rho, T)
$$

where $G_m(\rho, T) = \left(-\frac{\partial}{\partial T}\right)^m G_0(\rho, T)$. We have introduced the extra index $m$ which tells us the order of derivative of $G_0(\rho, T)$ with respect to $T$. In the final integrals we always have $m = 0$ but values with non-zero $m$ are useful intermediates that appear in the recursion of the MDRR scheme,

$$
[c]^{(m)} = R_i [c - \mathbf{1}_i]^{(m+1)} + (r_i - 1) [c - \mathbf{2}_i]^{(m+1)},
$$

where $\mathbf{1}_i$ is a unit vector along direction $i \in \{x, y, z\}$ and $\mathbf{2}_i = 2\mathbf{1}_i$. In the MDRR scheme one begins by evaluation of $[0]^{(m)}$ for all $m \leq l_a + l_b$. Then, by using the recursion relation in Equation $^{15}$ we obtain the integrals $[c]^{(0)}$ for all possible vectors $c = \{c_x, c_y, c_z\}$ such that $c_x + c_y + c_z = l_a + l_b$. These $[c]^{(0)}$ can then be inserted in Equation $^{12}$ along with the known coefficients $S_{a_i,a_j,a_k}$ to evaluate the desired integrals.

As a result, the calculation of molecular 2-electron integrals involves the following three steps:

1. Calculate the $2(l_a + l_b) + 1$ quantities $[0]^{(m)} = (-2\rho)^m G_m(\rho, T)$, where $m$ can take any value from $-l_a - l_b, \cdots, l_a + l_b$. As an example, expression for $G_m(\rho, T)$ are tabulated in Table III for several kernels where

$$
F_m(T) = \left(-\frac{\partial}{\partial T}\right)^m F_0(T)
$$

and

$$
F_0(T) = \frac{1}{2} \sqrt{\frac{\pi}{T}} \text{erf} \left(\sqrt{T}\right)
$$

is the Boys function.

2. Use MDRR scheme to evaluate $(2l_a + 1) (2l_b + 1)$ integrals $[c]^{(0)}$ where $c_x + c_y + c_z = l_a + l_b$.

3. Use the solid harmonics coefficients to generate the desired integral $\langle a|K|b \rangle$ from $[c]^{(0)}$.

III. GAUSSIAN INTEGRALS FOR PERIODIC SYSTEMS

Having outlined the MDRR scheme to calculate the molecular integrals, we now describe modifications needed to generate integrals over periodic systems. In periodic systems the integrals of interest are

$$
\langle a|K|b \rangle^{\text{per}} = \sum_{P} \int \int \phi_a(\mathbf{r}_1) K(||\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{P}||) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2
$$

$$
= \sum_{P} \int \int \phi_a(\mathbf{r}_1) K(||\mathbf{r}_1 - \mathbf{r}_2||) \phi_b(\mathbf{r}_2 + \mathbf{P}) d\mathbf{r}_1 d\mathbf{r}_2
$$

$$
= \sum_{P} \langle a|K|b\mathbf{P} \rangle
$$

where $\mathbf{P} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ are the lattice translations vectors, $n_i$ are the integers, $\mathbf{a}_i$ are the three primitive lattice translations vectors and $| b\mathbf{P} \rangle$ represents the Gaussian type orbital $| b \rangle$ that has been translated by the vector $\mathbf{P}$. The equation is useful for calculating the Gamma point integrals and conversion to integrals with translational symmetry. Notice that in Equation $^{12}$ only the quantity $[c]^{(0)}$ depends on $\mathbf{P}$. In particular, the periodic integral can be written as

$$
\langle a|K|b \rangle^{\text{per}} = \left(\frac{\pi}{a + b}\right)^{3/2} \left(\frac{1}{2a}\right)^{l_a} \left(-\frac{1}{2b}\right)^{l_b}
$$

$$
\sum_{a_x,a_y,a_z \in I_a} S_{a_x,a_y,a_z}^{(l_a)} \sum_{b_x,b_y,b_z \in I_b} S_{b_x,b_y,b_z}^{(l_b)} \sum_{P} [c(\mathbf{P})]^{(0)},
$$

where $\mathbf{c} = \mathbf{a} + \mathbf{b}$. This equation generalizes the Boys' function.

$$
\partial F_{m}(T) = \left(-\frac{\partial}{\partial T}\right)^{m} F_0(T)
$$

and

$$
F_0(T) = \frac{1}{2} \sqrt{\frac{\pi}{T}} \text{erf} \left(\sqrt{T}\right)
$$

is the Boys function.
Since, as written, the sum diverges; see next section) the sum converge slowly when either
Poisson’s summation formula which states that
a straightforward technique for avoiding this is to perform the summation in reciprocal space by making use of the
\[
\hat{c}(\mathbf{p}) = \frac{2\pi}{\mathbf{P}} P(\mathbf{p}) T(\mathbf{p})^2 \pi \left( \frac{\mathbf{p}}{\rho} \right)^{3/2} \exp(-i\mathbf{G} \cdot \mathbf{R}) \exp \left( -\frac{\mathbf{p}^2}{4\rho} \right) / (4\Omega G^2)
\]

where
\[
[c(\mathbf{P})]^{(0)} = \frac{\partial^x}{\partial R^x} \frac{\partial^y}{\partial R^y} \frac{\partial^z}{\partial R^z} G_0(\rho, T(\mathbf{P}))
\]

\( T(\mathbf{P}) = \rho \| \mathbf{A} - \mathbf{B} - \mathbf{P} \|^2 \) and three Cartesian coordinates of \( \mathbf{R} \) are \( R_i = A_i - B_i - P_i \). It is also useful to observe that
\[
\sum_{\mathbf{P}} [c(\mathbf{P})]^{(0)} = \frac{\partial^x}{\partial R^x} \frac{\partial^y}{\partial R^y} \frac{\partial^z}{\partial R^z} \sum_{\mathbf{P}} [C(\mathbf{P})]
\]
\[
= \frac{\partial^x}{\partial R^x} \frac{\partial^y}{\partial R^y} \frac{\partial^z}{\partial R^z} \sum_{\mathbf{P}} G_0(\rho, T(\mathbf{P}))
\]

which means that the summation and the derivatives commute. We will make use of this property when performing
summation in reciprocal space (see Section IIIA).

These equations give a straightforward way of performing lattice summation and the only difference from the
molecular algorithm is that one performs steps 1 and 2 (see the end of previous section) for each value of \( \mathbf{P} \) to
accumulates \( [c(\mathbf{P})]^{(0)} \) for increasing values of \( \mathbf{P} \) until the sum \( \sum_{\mathbf{P}} [c(\mathbf{P})]^{(0)} \) converges. Finally step 3 to obtain the
desired integrals is performed only once after the results of the lattice summation are available.

### A. Summation in reciprocal space

Although spatial summation can be carried out for all kernels (the Coulomb kernel required special considerations
since, as written, the sum diverges; see next section) the sum converge slowly when either \( a \) or \( b \) are small. A
straightforward technique for avoiding this is to perform the summation in reciprocal space by making use of the
Poisson’s summation formula which states that
\[
\sum_{\mathbf{P}} f(\mathbf{P}) = \sum_{\mathbf{G}} \hat{f}(\mathbf{G}),
\]
where \( \hat{f} \) is the Fourier transform of \( f \) and is given by
\[
\hat{f}(\mathbf{G}) = \int \exp(-i2\pi \mathbf{G} \cdot \mathbf{P}) f(\mathbf{P}) d\mathbf{P}.
\]

In these equations \( \mathbf{G} = m_1 \mathbf{A}_1 + m_2 \mathbf{A}_2 + m_3 \mathbf{A}_3 \) are the reciprocal lattice vectors, \( m_i \) are integers and \( \mathbf{A}_i \) are the
primitive lattice vectors of the reciprocal lattice such that \( \mathbf{A}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \).
Now by making use of the Poisson’s summation formula in Equation 20 and Equation 18 we obtain

\[ \langle a | K | b \rangle_{per} = \left( \frac{\pi}{a + b} \right)^{3/2} \left( \frac{1}{2a} \right)^{l_a} \left( -\frac{1}{2b} \right)^{l_b} \sum_{\alpha \beta} S_{\alpha \beta}^{a m a} \sum_{\gamma \delta} S_{\gamma \delta}^{b m b} \sum_{\beta \gamma} \mathbf{c}(\mathbf{P})^{(0)} \]  

(23)

\[ = \left( \frac{\pi}{a + b} \right)^{3/2} \left( \frac{1}{2a} \right)^{l_a} \left( -\frac{1}{2b} \right)^{l_b} \sum_{\alpha \beta} S_{\alpha \beta}^{a m a} \sum_{\gamma \delta} S_{\gamma \delta}^{b m b} \frac{\partial^x}{\partial R_x} \frac{\partial^y}{\partial R_y} \frac{\partial^z}{\partial R_z} \sum_{\mathbf{P}} G_0(\rho, T(\mathbf{P})) \]  

(24)

\[ = \left( \frac{\pi}{a + b} \right)^{3/2} \left( \frac{1}{2a} \right)^{l_a} \left( -\frac{1}{2b} \right)^{l_b} \sum_{\alpha \beta} S_{\alpha \beta}^{a m a} \sum_{\gamma \delta} S_{\gamma \delta}^{b m b} \frac{\partial^x}{\partial R_x} \frac{\partial^y}{\partial R_y} \frac{\partial^z}{\partial R_z} \sum_{\mathbf{G}} \hat{G}_0(\rho, \mathbf{G}). \]  

(25)

Here \( \hat{G}_0 \) is the Fourier transform of \( G_0 \); the expressions for a few kernels are given in Table I. Notice that when \( \rho \) is small it is advantageous to perform the summation in reciprocal space (and vice versa). The derivatives with respect to \( R_i \) are easily evaluated

\[ \sum_{\mathbf{P}} \mathbf{c}(\mathbf{P})^{(0)} = \frac{\partial^x}{\partial R_x} \frac{\partial^y}{\partial R_y} \frac{\partial^z}{\partial R_z} \sum_{\mathbf{P}} G_0(\rho, \mathbf{P}) \]  

(26)

\[ = \sum_{\mathbf{G}} (iG_x)^{c_x} (iG_y)^{c_y} (iG_z)^{c_z} \hat{G}_0(\rho, \mathbf{G}) \]  

(27)

The algorithm for calculating the integrals by reciprocal summation then consists of two steps:

1. First we calculate \( (2l_a + 1)(2l_b + 1) \sum_{\mathbf{P}} \mathbf{c}(\mathbf{P})^{(0)} \) using Equation 27 with \( c_x + c_y + c_z \leq l_a + l_b \).

2. The result is then substituted in Equation 23 to obtain the necessary integrals.

B. Coulomb kernel

The summation over Coulomb kernel requires special care because if one uses the bare Coulomb kernel \( 1/r \) then \( \sum_{\mathbf{P}} G_0(\rho, T(\mathbf{P})) \) is divergent. Here we will derive the relevant expressions by starting from the summation in the reciprocal space, \( \sum_{\mathbf{G}} \hat{G}_0(\rho, \mathbf{G}) \) which is also divergent but only due to the \( G = 0 \) term when \( \rho \neq 0 \) (see the Table I for the expression). The standard procedure for obtaining convergent Coulomb integrals calls for performing the summation in reciprocal space and eliminating the \( G = 0 \) term. This makes the total system charge-neutral by removing a constant background charge and imposes conducting boundary conditions which ensure that the surface term disappears. Performing the summation entirely in reciprocal space leads to acceptable results except for the fact that for large \( \rho \) the sum does not converge rapidly. Therefore, we use the approach of Ewald’s summation and introduce a parameter \( \eta \) which allows us to perform part of the summation in real space and the remaining in reciprocal space so that both sums converge rapidly. Below we derive the appropriate expression by starting with \( \hat{G}_0(\rho, \mathbf{G}) \) from Table I (we have removed the constant prefactors to avoid clutter).
The constant background term $\sum_{G \neq 0} \tilde{G}_0 (\rho, \mathbf{G}) = \sum_{G \neq 0} \exp (-i \mathbf{G} \cdot \mathbf{R}) \frac{\exp \left(-\frac{G^2}{4\rho} \right)}{G^2}$

$= \sum_{G \neq 0} \exp (-i \mathbf{G} \cdot \mathbf{R}) \left( \frac{\exp \left(-\frac{G^2}{4\rho} \right)}{G^2} - \frac{\exp \left(-\frac{G^2}{4\eta\rho} \right)}{G^2} + \frac{\exp \left(-\frac{G^2}{4\eta\rho} \right)}{G^2} \right)$

$= \sum_{G \neq 0} \exp (-i \mathbf{G} \cdot \mathbf{R}) \frac{\exp \left(-\frac{G^2}{4\rho} \right)}{G^2} + \sum_{G \neq 0} \exp (-i \mathbf{G} \cdot \mathbf{R}) \frac{\exp \left(-\frac{G^2}{4\rho} \right)}{G^2} - \lim_{\delta \to 0} \frac{\exp \left(-\frac{\delta^2}{4\rho} \right)}{\delta^2}$

$= \sum_{G \neq 0} \exp (-i \mathbf{G} \cdot \mathbf{R}) \frac{\exp \left(-\frac{G^2}{4\rho} \right)}{G^2} + \sqrt{\frac{4\rho}{\pi^3}} \sum_{\mathbf{P}} F_0 (T (\mathbf{P})) - \eta F_0 \left( \eta^2 T (\mathbf{P}) \right) - \frac{1}{4\omega^2}, \tag{28}$

where $G = \| \mathbf{G} \|$ and $\omega = \frac{\exp (\eta)}{\sqrt{1-\eta^2}}$ (which is the same relation between $\omega$ and $\eta$ in Table I). In the second step above, we have added and subtracted the $\mathbf{G} = 0$ contribution to the summation and, in the third step, we have used the Poisson summation to convert from the reciprocal space to the real space summation. By picking an appropriate value of $\eta$, we can ensure the fast convergence in both real and reciprocal spaces. The real space summation follows closely the algorithm at the end of Section III A and the reciprocal space summation is identical to the one in Section III A. The constant background term $\frac{1}{4\omega^2}$ is only present for $s$-type Gaussians because it gets eliminated when one takes derivatives to obtain integrals for higher angular momentum Gaussians (see Equation 27).

IV. RESULTS

The algorithm outlined above has been implemented in a custom branch of PySCF. Here we show the performance of some typical periodic systems with large auxiliary Gaussian basis sets. The choice of the basis is partly motivated by the fact that these basis sets are available for elements of the entire periodic table and we expect that high accuracy all-electron calculations can be performed with these. The pyscf input files with geometries of the systems are given in the supplementary information. All calculations were performed on a single core of the Intel® Xeon® CPU E5-2680 v4 @ 2.40GHz processor.

| System    | Basis | Nbas | Molecule (Time Elapsed (s)) | Custom periodic (Time Elapsed (s)) | Standard periodic (Time Elapsed (s)) |
|-----------|-------|------|----------------------------|-----------------------------------|-------------------------------------|
|           |       |      | Ovlp | Kin | Coul | Ovlp | Kin | Coul | Ovlp | Kin | Coul |
| Diamond   |       |      |      |     |      |      |     |      |      |     |      |
| univ-JKFIT 600 | 0.02 | 0.02 | 0.01 | 0.14 | 0.15 | 0.19 | 5.73 | 6.45 | 5.32 |
| ANO-RCC 728 | 0.02 | 0.02 | 0.02 | 0.15 | 0.20 | 0.24 | 21.73 | 24.94 | 9.85 |
| Silicon    |       |      |      |     |      |      |     |      |      |     |      |
| univ-JKFIT 1024 | 0.04 | 0.05 | 0.03 | 0.18 | 0.21 | 0.34 | 6.54 | 7.17 | 4.46 |
| ANO-RCC 800 | 0.02 | 0.03 | 0.02 | 0.13 | 0.17 | 0.28 | 9.55 | 11.17 | 5.22 |
| Ir3Ba4O10   |       |      |      |     |      |      |     |      |      |     |      |
| univ-JKFIT 3942 | 0.58 | 0.73 | 0.58 | 1.93 | 1.83 | 4.60 | 78.58 | 81.60 | 65.01 |
| ANO-RCC 3870 | 0.52 | 0.70 | 0.73 | 1.04 | 1.11 | 7.81 | 576.55 | 590.31 | 316.89 |

TABLE II. The table shows the cost of calculating the 2-center integrals with overlap, kinetic, and Coulomb kernels in molecules (using PySCF) and in periodic systems using the algorithm outlined in this paper (Custom periodic) and the standard algorithm currently implemented in PySCF (Standard periodic). For all kernels, the cost of calculating the integrals in periodic systems using the custom algorithm is between a factor of 5 and 10 times more expensive than in molecules. This is a significant improvement over the standard PySCF algorithm.

The algorithm outlined in the current work is about a factor of 10 slower than molecular integral evaluation. This is to be contrasted with the standard algorithm which is in some cases a factor of up to 1000 slower than the molecular integral evaluation. In the standard algorithm, the overlap and kinetic integrals are evaluated using summation in
the direct space and this becomes expensive when diffuse functions are included in the basis set. It is interesting to note that, in the standard algorithm the coulomb integral evaluation is cheaper than overlap and kinetic integrals. This is because, for coulomb kernel, a background density in subtracted that makes the overall Gaussian function charge-neutral is subtracted. The contribution of the background charge is then calculated in the reciprocal space using fast-Fourier transform (FFT). This is similar in spirit to what we have proposed here, with the conceptual difference that we split the kernel into the real and reciprocal space and the practical difference that we use analytic Fourier transform of the Gaussian basis functions instead of FFT. In the following, we show that the present algorithm can be extended to calculate electron densities that are needed in density functional theory calculations and also for 3-center integrals which are used to approximate the 4-center coulomb integrals in the density fitting procedure.

V. DENSITIES AND 3-CENTER INTEGRALS

The approach outlined in this article can be extended to evaluate electron densities and 3-electron integrals for periodic systems. To evaluate the Gaussian densities one needs to be able to calculate the value of a periodized Gaussian function at a grid point

$$\rho_a(r) = \sum_P \phi_a(r + P)$$

where, $\phi_a$ is a Gaussian basis function and $\rho_a$ is the contribution to density due to this basis function. The density can be evaluated straightforwardly by summation in real space for sharp Gaussians and in reciprocal space, using the Poisson's summation formula, for diffuse Gaussians.

In molecules, the three center integrals of the $s$–type Gaussians can be evaluated as follows:

$$\langle ab|\frac{1}{r}|c \rangle = \left(\frac{\pi}{\alpha + c}\right)^{3/2} S_{ab} G_0(\rho, T)$$

where $\alpha = \frac{ab}{a+b}$, $S_{ab} = \exp\left(\frac{ab}{\alpha} ||A - B||^2\right)$, and $T = \rho ||2A_B + 2B - C||^2$. We have already shown how the summation over $P$ can be treated efficiently by splitting it between the real and reciprocal spaces. We have

$$\sum_P \langle ab|\frac{1}{r}|c_P \rangle = \left(\frac{\pi}{\alpha + c}\right)^{3/2} \sum_P \exp\left(\frac{ab}{\alpha} ||A - B - Q||^2\right) G_0(\rho, T(P, Q)),$$

where $T(P, Q) = \rho \left(||\frac{2A}{\alpha} + \frac{2B}{\alpha} - C + \frac{2D}{\alpha} - P||^2\right)$. We have already shown how the summation over $P$ can be treated efficiently by splitting it between the real and reciprocal spaces. We have

$$\sum_P \langle ab|\frac{1}{r}|c_P \rangle = \left(\frac{\pi}{\alpha + c}\right)^{3/2} \sum_P \exp\left(\frac{ab}{\alpha} ||A - B - Q||^2\right) G_0(\rho, T(P, Q)).$$

The inner summation over $P$ can be split up into three terms using Equation we then treat each of these terms separately starting with the reciprocal summation. We obtain

$$\left(\frac{\pi}{\alpha + c}\right)^{3/2} \sum_P \exp\left(\frac{ab}{\alpha} ||A - B - Q||^2\right) \sum_P \exp\left(-iG \cdot (A - B - Q)\right) \frac{\exp\left(-\frac{G^2}{4\pi^2\rho}\right)}{G^2}$$

$$= \left(\frac{\pi}{\alpha + c}\right)^{3/2} \sum_P \sum_{G \neq 0} \exp\left(\frac{ab}{\alpha} ||A - B - Q||^2\right) \exp\left(-iG \cdot (A - B - Q)\right) \frac{\exp\left(-\frac{G^2}{4\pi^2\rho}\right)}{G^2}. $$

In the second line we have rearranged terms so that the inner summation just represents the Fourier transform of the 3D Gaussian which can be readily evaluated. The real space contribution

$$\sqrt{\frac{4\rho}{\pi^3}} \left(\frac{\pi}{\alpha + c}\right)^{3/2} \sum_P \exp\left(\frac{ab}{\alpha} ||A - B - Q||^2\right) \sum_P F_0(T(P, Q)) - \eta F_0(\eta^2T(P, Q))$$

$$F_0(T(P, Q)) = \frac{\exp\left(-\frac{G^2}{4\pi^2\rho}\right)}{G^2}$$

can also be evaluated efficiently by choosing $\eta$ such that the difference $F_0(T(P, Q)) - \eta F_0(\eta^2T(P, Q))$ is sufficiently small. By making use of the property that $F_0(T) \approx \sqrt{\frac{4\rho}{\pi^3}T}$ for $T > 30$ (to better than 14 decimal places), we can ensure that both the $P$ and $Q$ summations converge rapidly even when $\frac{ab}{\alpha}$ is small.

Work is currently under way for implementing these integrals.
VI. CONCLUSIONS

In this article we have outlined an algorithm to efficiently calculate 2-center integrals for periodic systems. The algorithm partitions the lattice summation between real and reciprocal space by making use of the Poisson’s summation formula. The real space summation can be performed with any of the standard algorithms using the molecular codes. We provide details on how the reciprocal space summation can be performed efficiently. The technique is quite general and we have shown that it can be used with overlap, kinetic and Coulomb kernels. Further, we have outlined an algorithm for calculating electron densities and 3-center integrals.

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