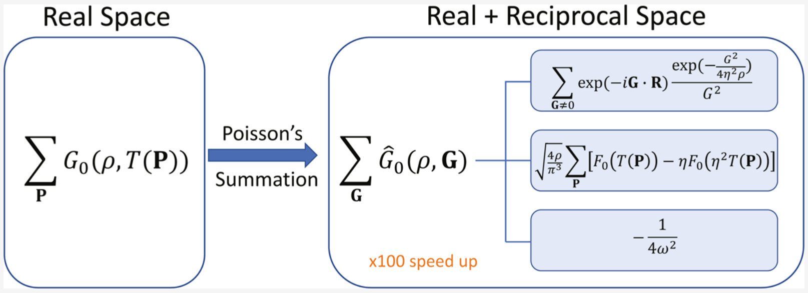
JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Efficient Evaluation of Two-Center Gaussian Integrals in Periodic Systems

Sandeep Sharma* and Gregory Beylkin

Cite This: J. Chem. Theory Comput. 2021, 17, 3916−3922 Read Online



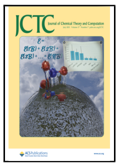
ABSTRACT: By using Poisson's summation formula, we calculate periodic integrals over Gaussian basis functions by partitioning the lattice summations between the real and reciprocal space, where both sums converge exponentially fast with a large exponent. We demonstrate that the summation can be performed efficiently to calculate two-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. The expressions for performing summation in the reciprocal space are also derived and implemented. The algorithm for reciprocal space summation allows us to reuse several terms and leads to a significant improvement in efficiency when highly contracted basis functions with large exponents are used. We find that the resulting algorithm is only between a factor of 5 and 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 three-center Coulomb integrals is also provided.

1. INTRODUCTION

Electronic structure calculations of molecular systems often use the Gaussian basis sets because they allow fast evaluation of the kinetic, overlap, and Coulomb integrals. Furthermore, they offer a compact representation of the wavefunctions both in mean-field and correlated calculations. For these reasons, there has been increasing interest in using the Gaussian basis sets for calculations on periodic systems Guidon et al.,[1] Vandevondele et al.,[2] Łazarski et al.,[3] Irmler et al.,[4] Burow et al.,[5] Sun et al.[6] In one popular approach,[7−9] 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 either avoided altogether by the use of the projector augmented wave (PAW) method[10] or are calculated explicitly. The latter approach is implemented in the PySCF software package, an algorithm that utilizes a mixture of Gaussian basis functions and plane waves to evaluate the integrals using the density fitting procedure Sun et al.[6] However, the cost of the integral evaluation remains high, especially if one uses standard basis sets containing exponents that span several orders of magnitude typical for molecular calculations.

For periodic systems, the plane waves are the most commonly used basis sets because, inter alia, 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 particularly compact representations. 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.[11−17] However, one of the major bottlenecks that has 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 altogether Tymczak et al.,[18] Challacombe et al.,[19] Kudin and Scuseria.[20,21]

Received: November 15, 2020
Published: June 1, 2021



https://doi.org/10.1021/acs.jctc.0c01195

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

$$\langle a|K|b\rangle = \iint \phi_a(\mathbf{r}_1) K(r_{12}) \phi_b(\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{1}$$

where the kernel $K(r_{12})$ is a function of the interelectron distance $r_{12} = \|\mathbf{r}_1 - \mathbf{r}_2\|$ and the associated lattice sum

$$\langle a|K|b\rangle^{\mathrm{per}} = \sum_{P} \iint \phi_a(\mathbf{r}_1) K(\|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{P}\|) \phi_b(\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{2}$$

where $\mathbf{P} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ are the lattice translation vectors. The kernel K can be the Coulomb kernel $1/r_{12}$, the attenuated Coulomb kernel $\mathrm{erf}(r_{12})/r_{12}$, and the Laplace kernel $\nabla_1\delta_{12}$ for kinetic energy operator or the overlap kernel δ_{12}, where $\delta_{12} = \delta(\mathbf{r}_1 - \mathbf{r}_2)$. 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 three-center integrals are discussed toward 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 Peels and Knizia.[22] 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 by making use of the Poisson's summation formula. A similar approach has been used in the past by Welhelm et al.[17]

2. 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

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

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

$$S_{l_a}^{m_a}(\mathbf{r} - \mathbf{A}) = \sum_{\substack{a_x, a_y, a_z \\ a_x + a_y + a_z = l_a}} S_{a_x a_y a_z}^{l_a m_a} (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} \tag{3}$$

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

A useful relation (known as Hobson's theorem Golze et al.,[23] Giese and York[24])

$$\left(\frac{1}{2a}\right)^{l_a} S_{l_a}^{m_a}(\nabla_A)\exp(-a\,\|\mathbf{r} - \mathbf{A}\|^2) = S_{l_a}^{m_a}(\mathbf{r} - \mathbf{A})\exp(-a\,\|\mathbf{r} - \mathbf{A}\|^2) \tag{4}$$

shows that a Gaussian basis function with nonzero 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 eq 1 as

$$\langle a|K|b\rangle = \left(\frac{1}{2a}\right)^{l_a} S_{l_a}^{m_a}(\nabla_A) \left(\frac{1}{2b}\right)^{l_b} S_{l_b}^{m_b}(\nabla_B) I_0(a, b, T) \tag{5}$$

$$I_0(a, b, T) = \int \exp(-a\,\|\mathbf{r}_1 - \mathbf{A}\|^2) K(r_{12}) \exp(-b\,\|\mathbf{r}_2 - \mathbf{B}\|^2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{6}$$

$$= \left(\frac{\pi}{a+b}\right)^{3/2} \int \mathrm{e}^{-\rho\|\mathbf{A}-\mathbf{B}-\mathbf{r}\|^2} K(r)\, \mathrm{d}\mathbf{r} \tag{7}$$

$$= \left(\frac{\pi}{a+b}\right)^{3/2} 2\pi\, \mathrm{e}^{-\rho\|\mathbf{A}-\mathbf{B}\|^2} \int_0^\infty \int_0^\pi \mathrm{e}^{-\rho r^2} \mathrm{e}^{2\rho\|\mathbf{A}-\mathbf{B}\| r \cos\theta} K(r) r^2\, \mathrm{d}r \sin\theta\, \mathrm{d}\theta \tag{8}$$

$$= \left(\frac{\pi}{a+b}\right)^{3/2} 2\pi\, \mathrm{e}^{-\rho\|\mathbf{A}-\mathbf{B}\|^2} \int_0^\infty \mathrm{e}^{-\rho r^2} \frac{r \sinh(2\rho\|\mathbf{A}-\mathbf{B}\| r)}{\rho\|\mathbf{A}-\mathbf{B}\|} K(r)\, \mathrm{d}r \tag{9}$$

$$= \left(\frac{\pi}{a+b}\right)^{3/2} G_0(\rho, T) \tag{10}$$

where $r = \|\mathbf{r}\| = \|\mathbf{r}_1 - \mathbf{r}_2\|$, $\rho = \frac{ab}{a+b}$, and $T = \rho\|\mathbf{A} - \mathbf{B}\|^2$ and $G_0(\rho,T)$ ends up being a 1-D integral that can be evaluated analytically for several commonly used kernels.[25,26]

It is expensive to directly evaluate all $(2l_a + 1)(2l_b + 1)$ derivatives of eq 5 to compute the integrals. Instead, we can use the MDRR motivated by the observation that

$$S_{l_a}^{m_a}(\nabla_A) = S_{l_a}^{m_a}(\nabla_R)$$
$$S_{l_a}^{m_a}(\nabla_B) = -S_{l_a}^{m_a}(\nabla_R) \tag{11}$$

where $\mathbf{R} = \mathbf{A} - \mathbf{B}$. Combining eqs 1, 3, 4, and 11, we obtain

$$(\langle a|K|b\rangle) = \left(\frac{\pi}{a+b}\right)^{3/2} \left(\frac{1}{2a}\right)^{l_a} \left(\frac{-1}{2b}\right)^{l_b} \sum_{\substack{a_x a_y a_z \\ a_x + a_y + a_z = l_a}} S_{a_x a_y a_z}^{l_a m_a} \sum_{\substack{b_x b_y b_z \\ b_x + b_y + b_z = l_b}} S_{b_x b_y b_z}^{l_b m_b} [\mathbf{c}]^{(0)} \tag{12}$$

where $\mathbf{c} = \mathbf{a} + \mathbf{b}$ and we have used the short-hand notation following Gill et al.,[27] Gill[28]

$$[\mathbf{c}]^{(m)} = (2\rho)^m \frac{\partial^{c_x}}{\partial R_x^{c_x}} \frac{\partial^{c_y}}{\partial R_y^{c_y}} \frac{\partial^{c_z}}{\partial R_z^{c_z}} \frac{\partial^m}{\partial T^m} G_0(\rho, T) \tag{13}$$

$$= (-2\rho)^m \frac{\partial^{c_x}}{\partial R_x^{c_x}} \frac{\partial^{c_y}}{\partial R_y^{c_y}} \frac{\partial^{c_z}}{\partial R_z^{c_z}} G_m(\rho, T) \tag{14}$$

where $G_m(\rho,T) = (-\partial/\partial T)^m G_0(\rho,T)$. 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 nonzero m are useful intermediates that appear in the recursion of the MDRR scheme

$$[\mathbf{c}]^{(m)} = R_i[\mathbf{c} - \mathbf{1}_i]^{(m+1)} + (r_i - 1)[\mathbf{c} - \mathbf{2}_i]^{(m+1)} \tag{15}$$

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 $m \le l_a + l_b$. Then, by using the recursion relation in eq 15, we obtain the integrals $[\mathbf{c}]^{(0)}$ for all possible vectors $\mathbf{c} = \{c_x, c_y, c_z\}$ such that $c_x + c_y + c_z = l_a + l_b$. These $[\mathbf{c}]^{(0)}$ can then be inserted in eq 12 along with the known coefficients $S_{a_x a_y a_z}^{lm}$ to evaluate the desired integrals.

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

Table 1. **Expressions for $G_m(\rho,T)$ in Eq 14 and $\hat{G}_0(\rho,\mathrm{G})$ in Eq 23 for Commonly Used Kernels to Evaluate Gaussian Integrals**[a]

Kernel $K(\mathbf{r})$	Gm(ρ,T)	Ĝ0(ρ,G)
$\delta(\mathbf{r})$	$\exp(-T)$	$\left(\frac{\pi}{\rho}\right)^{3/2}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\exp\left(-\frac{G^2}{4\rho}\right)/\Omega$
1/r	$\frac{2\pi}{\rho}F_m(T)$	$4\pi\left(\frac{\pi}{\rho}\right)^{3/2}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\exp\left(-\frac{G^2}{4\rho}\right)/(\Omega G^2)$
$\frac{\mathrm{erf}(\omega r)}{r}$	$\frac{2\pi\eta}{\rho}F_m(T\eta^2)$	$4\pi\left(\frac{\pi}{\rho}\right)^{3/2}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\exp\left(-\frac{G^2}{\eta^2 4\rho}\right)/(\Omega G^2)$

[a] Here, $\mathbf{R} = \mathbf{A} - \mathbf{B}$ is the vector connecting one Gaussian $|a\rangle$ with $|b\rangle$, $T = \rho|\mathbf{R}|^2$, $\eta = \frac{\omega}{\sqrt{\omega^2+\rho}}$, and Ω is the volume of the unit cell.

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

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

and

$$F_0(T) = \frac{1}{2}\sqrt{\frac{\pi}{T}}\,\mathrm{erf}(\sqrt{T})$$

is the Boys function.

2. We then contract these primitive quantities using the contraction coefficients to obtain the contracted $2(l_a + l_b) + 1$ quantities $[\mathbf{0}]^m$.
3. Use MDRR scheme to evaluate $(2l_a + 1)(2l_b + 1)$ integrals $[\mathbf{c}]^{(0)}$, where $c_x + c_y + c_z = l_a + l_b$.
4. Use the solid harmonic coefficients to generate the desired integral $\langle a|K|b\rangle$ from $[\mathbf{c}]^{(0)}$.

3. 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

$$\langle a|K|b\rangle^{\mathrm{per}} = \sum_{P}\iint \phi_a(\mathbf{r}_1)K(\|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{P}\|)\phi_b(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \tag{16}$$

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

$$= \sum_{\mathbf{P}}\langle a|K|b_{\mathbf{P}}\rangle \tag{17}$$

where $\mathbf{P} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ are the lattice translation vectors, n_i are the integers, $\mathbf{a}_i$ are the three primitive lattice translation 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 eq 12, only the quantity $[\mathbf{c}]^{(0)}$ depends on $\mathbf{P}$. In particular, the periodic integral can be written as

$$\langle a|K|b\rangle^{\mathrm{per}} = \left(\frac{\pi}{a+b}\right)^{3/2}\left(\frac{1}{2a}\right)^{l_a}\left(\frac{-1}{2b}\right)^{l_b}\sum_{\substack{a_xa_ya_z\\ a_x+a_y+a_z=l_a}} S^{l_am_a}_{a_xa_ya_z}\sum_{\substack{b_xb_yb_z\\ b_x+b_y+b_z=l_b}} S^{l_bm_b}_{b_xb_yb_z}\sum_{\mathbf{P}}[\mathbf{c}(\mathbf{P})]^{(0)} \tag{18}$$

where

$$[\mathbf{c}(\mathbf{P})]^{(0)} = \frac{\partial^{c_x}}{\partial R_x^{c_x}}\frac{\partial^{c_y}}{\partial R_y^{c_y}}\frac{\partial^{c_z}}{\partial R_z^{c_z}}G_0(\rho, T(\mathbf{P}))$$

$T(\mathbf{P}) = \rho\|\mathbf{A} - \mathbf{B} - \mathbf{P}\|^2$ and three Cartesian coordinates of $\mathbf{R}$ are $R_i = A_i - B_i - P_i$. It is also useful to observe that

$$\sum_{\mathbf{P}}[\mathbf{c}(\mathbf{P})]^{(0)} = \frac{\partial^{c_x}}{\partial R_x^{c_x}}\frac{\partial^{c_y}}{\partial R_y^{c_y}}\frac{\partial^{c_z}}{\partial R_z^{c_z}}\sum_{\mathbf{P}}[0(\mathbf{P})] \tag{19}$$

$$= \frac{\partial^{c_x}}{\partial R_x^{c_x}}\frac{\partial^{c_y}}{\partial R_y^{c_y}}\frac{\partial^{c_z}}{\partial R_z^{c_z}}\sum_{P}G_0(\rho, T(P)) \tag{20}$$

which means that the summation and the derivatives commute. We will make use of this property when performing summation in reciprocal space (see Section 3.1).

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 the previous section) for each value of $\mathbf{P}$ to accumulate $[\mathbf{c}(\mathbf{P})]^{(0)}$ for increasing values of P until the sum $\sum_{\mathbf{P}}[\mathbf{c}(\mathbf{P})](0)$ converges. Finally, step 3 to obtain the desired integrals is performed only once after the results of the lattice summation are available.

3.1. Summation in Reciprocal Space. Although spatial summation can be carried out for all kernels (the Coulomb kernel required special considerations because, as written, the sum diverges; see the next section), the sum converges slowly when either a or b is 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

$$\sum_{\mathbf{P}} f(\mathbf{P}) = \sum_{\mathbf{G}}\hat{f}(\mathbf{G}) \tag{21}$$

where $\hat{f}$ is the Fourier transform of f and is given by

$$\hat{f}(\mathbf{G}) = \int \exp(-\mathrm{i}2\pi\mathbf{G}\cdot\mathbf{P})f(\mathbf{P})\,\mathrm{d}\mathbf{P} \tag{22}$$

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 eqs 20 and 18, we obtain

$$\langle a|K|b\rangle^{\mathrm{per}} = \left(\frac{\pi}{a+b}\right)^{3/2}\left(\frac{1}{2a}\right)^{l_a}\left(\frac{-1}{2b}\right)^{l_b}\sum_{\substack{a_xa_ya_z\\ a_x+a_y+a_z=l_a}} S^{l_am_a}_{a_xa_ya_z}\sum_{\substack{b_xb_yb_z\\ b_x+b_y+b_z=l_b}} S^{l_bm_b}_{b_xb_yb_z}\sum_{\mathbf{P}}[\mathbf{c}(\mathbf{P})]^{(0)} \tag{23}$$

https://doi.org/10.1021/acs.jctc.0c01195
J. Chem. Theory Comput. 2021, 17, 3916−3922

$$= \left(\frac{\pi}{a+b}\right)^{3/2}\left(\frac{1}{2a}\right)^{l_a}\left(\frac{-1}{2b}\right)^{l_b}\sum_{\substack{a_xa_ya_z\\ a_x+a_y+a_z=l_a}} S^{l_am_a}_{a_xa_ya_z}\sum_{\substack{b_xb_yb_z\\ b_x+b_y+b_z=l_b}} S^{l_bm_b}_{b_xb_yb_z}\,\frac{\partial^{c_x}}{\partial R_x^{c_x}}\frac{\partial^{c_y}}{\partial R_y^{c_y}}\frac{\partial^{c_z}}{\partial R_z^{c_z}}\sum_{\mathbf{P}} G_0(\rho, T(\mathbf{P})) \tag{24}$$

$$= \left(\frac{\pi}{a+b}\right)^{3/2}\left(\frac{1}{2a}\right)^{l_a}\left(\frac{-1}{2b}\right)^{l_b}\sum_{\substack{a_xa_ya_z\\ a_x+a_y+a_z=l_a}} S^{l_am_a}_{a_xa_ya_z}\sum_{\substack{b_xb_yb_z\\ b_x+b_y+b_z=l_b}} S^{l_bm_b}_{b_xb_yb_z}\,\frac{\partial^{c_x}}{\partial R_x^{c_x}}\frac{\partial^{c_y}}{\partial R_y^{c_y}}\frac{\partial^{c_z}}{\partial R_z^{c_z}}\sum_{G} \hat{G}_0(\rho, \mathbf{G}) \tag{25}$$

here, $\hat{G}_0$ is the Fourier transform of G_0; the expressions for a few kernels are given in Table 1. Notice that when ρ 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

$$\sum_{\mathbf{P}} [\mathbf{c}(\mathbf{P})]^{(0)} = \frac{\partial^{c_x}}{\partial R_x^{c_x}}\frac{\partial^{c_y}}{\partial R_y^{c_y}}\frac{\partial^{c_z}}{\partial R_z^{c_z}}\sum_{P} G_0(\rho, \mathbf{P}) \tag{26}$$

$$= \sum_{\mathbf{G}} (-iG_x)^{c_x}(-iG_y)^{c_y}(-iG_z)^{c_z}\hat{G}_0(\rho, \mathbf{G}) \tag{27}$$

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

1. First, we calculate the primitive $(l_a + l_b + 1)(l_a + l_b + 2)/2$ integrals, where $c_x + c_y + c_z = l_a + l_b$ by summing over the reciprocal vectors in eq 27.
2. These primitive integrals are now contracted to obtain the contracted integrals.
3. These contracted integrals are then substituted in eq 23 to obtain the necessary integrals containing solid harmonics.

3.2. 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 Table 1 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 ρ, the sum does not converge rapidly. Therefore, we use the approach of Ewald's summation[29] and introduce a parameter η, 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 1.

$$\begin{aligned}
\sum_{\mathbf{G}\neq 0} \hat{G}_0(\rho, \mathbf{G}) &= 4\pi\left(\frac{\pi}{\rho}\right)^{3/2}\sum_{\mathbf{G}\neq 0}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\frac{\exp(-G^2/4\rho)}{\Omega G^2}\\
&= \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\sum_{\mathbf{G}\neq 0}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\left(\frac{\exp(-G^2/4\eta^2\rho)}{G^2} - \frac{\exp(-G^2/4\eta^2\rho)}{G^2}\right.\\
&\quad\left. + \frac{\exp(-G^2/4\rho)}{G^2}\right) = \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\sum_{\mathbf{G}\neq 0}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\frac{\exp(-G^2/4\eta^2\rho)}{G^2}\\
&\quad + \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\sum_{\mathbf{G}}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\frac{\exp(-G^2/4\rho) - \exp(-G^2/4\eta^2\rho)}{G^2}\\
&\quad - \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\lim_{\delta\to 0}\frac{\exp(-\delta^2/4\rho) - \exp(-\delta^2/4\eta^2\rho)}{\delta^2}\\
&= \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\sum_{\mathbf{G}\neq 0}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\frac{\exp(-G^2/4\eta^2\rho)}{G^2}\\
&\quad + 4\pi\left(\frac{\pi}{\rho}\right)^{3/2}\sqrt{\frac{\rho}{4\pi^3}}\sum_{\mathbf{P}}(F_0(T(\mathbf{P})) - \eta F_0(\eta^2 T(\mathbf{P}))) - \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\frac{1}{4\omega^2}
\end{aligned} \tag{28}$$

$$\begin{aligned}
&= \frac{4\pi}{\Omega}\left(\frac{\pi}{\rho}\right)^{3/2}\sum_{\mathbf{G}\neq 0}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\frac{\exp(-G^2/4\eta^2\rho)}{G^2}\\
&\quad + \frac{2\pi}{\rho}\sum_{\mathbf{P}}(F_0(T(\mathbf{P})) - \eta F_0(\eta^2 T(\mathbf{P}))) - \left(\frac{\pi^{5/2}}{\Omega\rho^{3/2}\omega^2}\right)
\end{aligned} \tag{29}$$

where $G = \|\mathbf{G}\|$ and $\omega = \frac{\eta\sqrt{\rho}}{\sqrt{1-\eta^2}}$ (which is the same relation between ω and η in Table 1). 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 η, we can ensure the fast convergence in both real and reciprocal spaces Kolafa and Perram.[30] The real space summation follows closely the algorithm at the end of Section 2 and the reciprocal space summation is identical to the one in Section 3.1. The constant background term $1/4\omega^2$ is only present for s-type Gaussians because it gets eliminated when one takes derivatives to obtain integrals for higher angular momentum Gaussians (see eq 27).

3.3. Selecting the Screening Parameter and Reusing Reciprocal Summations.

Here, we focus on the Coulomb kernel not only because it is most expensive to evaluate but, also, because the cost of performing mean-field calculations is determined to a large extent by the efficiency with which three-/four-center integrals over Coulomb kernel are evaluated. (While this is outside the scope of current work, we give an outline of an algorithm in Section 5 to be implemented in a future publication.) For calculation of the Coulomb integrals, we may need to perform summations in both the real and reciprocal space. The summation in the reciprocal space consists of evaluating

$$\sum_{\mathbf{G}\neq 0}(-\mathrm{i}G_x)^{c_x}(-\mathrm{i}G_y)^{c_y}(-\mathrm{i}G_z)^{c_z}\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{R})\frac{\exp(-G^2/4\eta^2\rho)}{G^2} \tag{30}$$

where $c_x + c_y + c_z = l_a + l_b$ and $\mathbf{R} = \mathbf{A} - \mathbf{B}$. The sum in eq 30 depends only on $\mathbf{R}$ and $\eta^2\rho$; for a fixed value of $\eta^2\rho$, there are only as many distinct values of $\mathbf{R}$ as the number of unique atom pairs. This allows us to reuse summations as follows:

Table 2. Cost of Calculating the Two-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)[a]

			time elapsed (s)								
			molecule			custom periodic			standard periodic		
system	basis	Nbas	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
$Ir_4Ba_4O_{10}$											
	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	1.01	4.11	7.81	576.55	590.31	316.89

[a] For all kernels, the cost of calculating the integrals in periodic systems using the custom algorithm is between a factor of 5 and 10 more expensive than in molecules. This is a significant improvement over the standard PySCF algorithm.

1. We begin by choosing a threshold value of $\eta^2\rho$, which, for the purposes of this paper, is always chosen to be $T/8$, where T is the smallest of the three dimensions of the unit cell.
2. If the pair of basis functions is diffuse enough such that the value of ρ is smaller than $T/8$, then the value of the integral is calculated entirely in the reciprocal space and no part of the summation is done in real space, that is, $\eta = 1$ is used for these pairs of basis functions.
3. If the pair of basis functions is sharp such that the value of ρ is greater than $T/8$, then we chose $\eta = \sqrt{\frac{T}{8\rho}}$. This ensures that the summation in the reciprocal space is given in eq 30. However, instead of performing this summation for each pair of sharp basis functions, that is, $O(N_{\text{basis}}^2)$ times, we perform this summation once at the beginning of the calculation for each unique value of $\mathbf{R}$ of which there are only $O(N_{\text{atom}}^2)$ terms, usually 1 or 2 order of magnitude fewer than the total number $O(N_{\text{basis}}^2)$. The real space summation is performed as usual with the attenuated Coulomb kernel, which converges quickly (usually within less than a unit cell to numerical accuracy). Effectively, we only need to perform summation in the real space.

The above illustrates the fact that one only needs to perform either real or reciprocal space summations to calculate the Coulomb integrals. For the purposes of this paper, we have always used a value of $T/8$ as the threshold of $\eta^2\rho$, which gives reasonable timing for all the systems studied here, but we do find that for some calculations shown below the cost can be reduced further by choosing a threshold other than $T/8$. This will be investigated more thoroughly in a future publication.

4. RESULTS

The algorithm outlined above has been implemented in a custom branch of PySCF Sun et al.[31,32] 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 Supporting Information. All calculations were performed on a single core of the Intel Xeon CPU E5-2680 v4 @ 2.40 GHz processor (Table 2).

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 is subtracted that makes the overall Gaussian function charge-neutral Sun et al.[6] The contribution of the background charge is then calculated in the reciprocal space. 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 three-center integrals, which are used to approximate the four-center coulomb integrals in the density fitting procedure Whitten,[33] Dunlap.[34]

5. DENSITIES AND THREE-CENTER INTEGRALS

The approach outlined in this article can be extended to evaluate electron densities and three-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

$$\rho_a(\mathbf{r}) = \sum_{\mathbf{P}} \phi_a(\mathbf{r} + \mathbf{P})$$

where ϕ_a is a Gaussian basis function and ρ_a is the contribution to density due to this basis function. The density can be evaluated, as usual, by summation in real space for sharp Gaussians and in reciprocal space for diffuse Gaussians by using the Poisson's summation formula.

For molecules, the three-center integrals of the s-type Gaussians can be evaluated as follows Ahlrichs[25,26]

$$\left\langle ab\left|\frac{1}{r}\right|c\right\rangle = \left(\frac{\pi}{a+b+c}\right)^{3/2} S_{ab}G_0(\rho, T) \tag{31}$$

where $S_{ab} = \exp(-\alpha\|\mathbf{A}-\mathbf{B}\|^2)$, $\alpha = \frac{ab}{a+b}$, $\rho = \frac{(a+b)c}{a+b+c}$, and $T = \rho\left\|\frac{a\mathbf{A}}{a+b}+\frac{b\mathbf{B}}{a+b}-\mathbf{C}\right\|^2$.

In the periodic case, the three-center integrals acquire two additional summations

$$\sum_{\mathbf{P},\mathbf{Q}}\left\langle ab_{\mathbf{Q}}\left|\frac{1}{r}\right|c_{\mathbf{P}}\right\rangle = \left(\frac{\pi}{a+b+c}\right)^{3/2} \sum_{\mathbf{P},\mathbf{Q}} \exp\left(-\frac{ab}{a+b}\|\mathbf{A}-\mathbf{B}-\mathbf{Q}\|^2\right)G_0(\rho, T(\mathbf{P},\mathbf{Q})) \tag{32}$$

or

$$\sum_{\mathbf{P},\mathbf{Q}}\left\langle ab_{\mathbf{Q}}\left|\frac{1}{r}\right|c_{\mathbf{P}}\right\rangle = \left(\frac{\pi}{a+b+c}\right)^{3/2} \sum_{\mathbf{Q}} \exp\left(-\frac{ab}{a+b}\|\mathbf{A}-\mathbf{B}-\mathbf{Q}\|^2\right)\sum_{\mathbf{P}} G_0(\rho, T(\mathbf{P},\mathbf{Q})) \tag{33}$$

where $T(\mathbf{P},\mathbf{Q}) = \rho\left\|\frac{a\mathbf{A}}{a+b}+\frac{b\mathbf{B}}{a+b}-\mathbf{C}+\frac{b\mathbf{Q}}{a+b}-\mathbf{P}\right\|^2$.

We have already shown that the summation over $\mathbf{P}$ can be treated efficiently by splitting it between the real and reciprocal spaces. The inner summation over $\mathbf{P}$ can be split up into three terms (T_G, T_P, and a constant) using eq 29; we then treat each of these terms separately starting with the term that is calculated by performing summation in the reciprocal space (T_G). We obtain

$$\begin{aligned} T_G &= \frac{4\pi^4}{(a+b)^{3/2}c^{3/2}}\sum_{\mathbf{Q}}\exp\left(-\frac{ab}{a+b}\|\mathbf{A}-\mathbf{B}-\mathbf{Q}\|^2\right) \\ &\quad \sum_{G\neq 0}\frac{\exp(-G^2/4\eta^2\rho)}{\Omega G^2}\exp\left(-\mathrm{i}\mathbf{G}\cdot\left(\frac{a\mathbf{A}}{a+b}+\frac{b\mathbf{B}}{a+b}-\mathbf{C}+\frac{b\mathbf{Q}}{a+b}\right)\right) \\ &= \frac{4\pi^4}{(a+b)^{3/2}c^{3/2}}\sum_{G\neq 0}\frac{\exp(-G^2/4\eta^2\rho)}{\Omega G^2} \\ &\quad \left(\sum_{\mathbf{Q}}\exp\left(-\frac{ab}{a+b}\|\mathbf{A}-\mathbf{B}-\mathbf{Q}\|^2\right)\right. \\ &\quad \left.\exp\left(-\mathrm{i}\mathbf{G}\cdot\left(\frac{a\mathbf{A}}{a+b}+\frac{b\mathbf{B}}{a+b}-\mathbf{C}+\frac{b\mathbf{Q}}{a+b}\right)\right)\right) \end{aligned} \tag{34}$$

In the second line, we have rearranged terms so that the inner summation can be readily converted to summation in Fourier space using the Poisson's summation formula. The second term (T_P) that is calculated by performing summation in the real space is

$$T_P = \frac{2\pi}{\rho}\left(\frac{\pi}{a+b+c}\right)^{3/2}\sum_{\mathbf{Q}}\exp\left(-\frac{ab}{a+b}\|\mathbf{A}-\mathbf{B}-\mathbf{Q}\|^2\right) \sum_{\mathbf{P}}(F_0(T(\mathbf{P},\mathbf{Q})) - \eta F_0(\eta^2 T(\mathbf{P},\mathbf{Q}))) \tag{35}$$

$$= \frac{2\pi^{5/2}}{(a+b)c\sqrt{a+b+c}}\sum_{\mathbf{Q}}\exp\left(-\frac{ab}{a+b}\|\mathbf{A}-\mathbf{B}-\mathbf{Q}\|^2\right) \sum_{\mathbf{P}}(F_0(T(\mathbf{P},\mathbf{Q})) - \eta F_0(\eta^2 T(\mathbf{P},\mathbf{Q}))) \tag{36}$$

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

Work is currently under way for implementing these integrals.

6. CONCLUSIONS

In this article, we have outlined an algorithm to efficiently calculate two-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 to with overlap, kinetic, and Coulomb kernels. Furthermore, we have outlined an algorithm for calculating electron densities and three-center integrals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.0c01195.

PySCF input files with geometries of the systems (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Sandeep Sharma − *Department of Chemistry, University of Colorado, Boulder, Boulder, Colorado 80302, United States;* orcid.org/0000-0002-6598-8887; Email: sanshar@gmail.com

Author

Gregory Beylkin − *Department of Applied Mathematics, University of Colorado, Boulder, Boulder, Colorado 80309, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.0c01195

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.S. was supported by NSF through the grant CHE-1800584. S.S. was also partly supported through the Sloan Research Fellowship. We also acknowledge Minyan Wang for help with the TOC graphic.

■ REFERENCES

(1) Guidon, M.; Hutter, J.; VandeVondele, J. Robust periodic Hartree-Fock exchange for large-scale simulations using Gaussian basis sets. *J. Chem. Theory Comput.* **2009**, *5*, 3010−3021.

(2) Vandevondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **2005**, *167*, 103−128.

(3) Łazarski, R.; Burow, A. M.; Grajciar, L.; Sierka, M. Density functional theory for molecular and periodic systems using density fitting and continuous fast multipole method: Analytical gradients. *J. Comput. Chem.* **2016**, *37*, 2518−2526.

(4) Irmler, A.; Burow, A. M.; Pauly, F. Robust Periodic Fock Exchange with Atom-Centered Gaussian Basis Sets. *J. Chem. Theory Comput.* **2018**, *14*, 4567−4580.

(5) Burow, A. M.; Sierka, M.; Mohamed, F. Resolution of identity approximation for the Coulomb term in molecular and periodic systems. *J. Chem. Phys.* **2009**, *131*, 214101.

(6) Sun, Q.; Berkelbach, T. C.; McClain, J. D.; Chan, G. K. L. Gaussian and plane-wave mixed density fitting for periodic systems. *J. Chem. Phys.* **2017**, *147*, 164119.

(7) Füsti-Molnár, L.; Pulay, P. The Fourier transform Coulomb method: Efficient and accurate calculation of the Coulomb operator in a Gaussian basis. *J. Chem. Phys.* **2002**, *117*, 7827−7835.

(8) Füsti-Molnar, L.; Pulay, P. Accurate molecular integrals and energies using combined plane wave and Gaussian basis sets in molecular electronic structure theory. *J. Chem. Phys.* **2002**, *116*, 7795−7805.

(9) Krack, M.; Parrinello, M. All-electron ab-initio molecular dynamics. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2105−2112.

(10) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953−17979.

(11) Pisani, C.; Dovesi, R.; Roetti, C. *Hartree−Fock Ab Initio Treatment of Crystalline Systems*; Springer Science & Business Media, 2012; Vol. *48*.

(12) Usvyat, D.; Civalleri, B.; Maschio, L.; Dovesi, R.; Pisani, C.; Schütz, M. Approaching the theoretical limit in periodic local MP2 calculations with atomic-orbital basis sets: The case of LiH. *J. Chem. Phys.* **2011**, *134*, 214105.

(13) Paier, J.; Diaconu, C. V.; Scuseria, G. E.; Guidon, M.; VandeVondele, J.; Hutter, J. Accurate Hartree-Fock energy of extended systems using large Gaussian basis sets. *Phys. Rev. B* **2009**, *80*, 174114.

(14) Del Ben, M.; Hutter, J.; VandeVondele, J. Electron Correlation in the Condensed Phase from a Resolution of Identity Approach Based on the Gaussian and Plane Waves Scheme. *J. Chem. Theory Comput.* **2013**, *9*, 2654−2671.

(15) Booth, G. H.; Tsatsoulis, T.; Chan, G. K.-L.; Grüneis, A. From plane waves to local Gaussians for the simulation of correlated periodic systems. *J. Chem. Phys.* **2016**, *145*, 084111.

(16) McClain, J.; Sun, Q.; Chan, G. K.-L.; Berkelbach, T. C. Gaussian-based coupled-cluster theory for the ground-state and band structure of solids. *J. Chem. Theory Comput.* **2017**, *13*, 1209−1218.

(17) Wilhelm, J.; Seewald, P.; Del Ben, M.; Hutter, J. Large-Scale Cubic-Scaling Random Phase Approximation Correlation Energy Calculations Using a Gaussian Basis. *J. Chem. Theory Comput.* **2016**, *12*, 5851−5859.

(18) Tymczak, C. J.; Weber, V. T.; Schwegler, E.; Challacombe, M. Linear scaling computation of the Fock matrix. VIII. Periodic boundaries for exact exchange at the Gamma point. *J. Chem. Phys.* **2005**, *122*, 124105.

(19) Challacombe, M.; White, C.; Head-Gordon, M. Periodic boundary conditions and the fast multipole method. *J. Chem. Phys.* **1997**, *107*, 10131−10140.

(20) Kudin, K. N.; Scuseria, G. E. A fast multipole method for periodic systems with arbitrary unit cell geometries. *Chem. Phys. Lett.* **1998**, *283*, 61−68.

(21) Kudin, K. N.; Scuseria, G. E. Revisiting infinite lattice sums with the periodic fast multipole method. *J. Chem. Phys.* **2004**, *121*, 2886−2890.

(22) Peels, M.; Knizia, G. Fast Evaluation of Two-Center Integrals over Gaussian Charge Distributions and Gaussian Orbitals with General Interaction Kernels. *J. Chem. Theory Comput.* **2020**, *16*, 2570−2583.

(23) Golze, D.; Benedikter, N.; Iannuzzi, M.; Wilhelm, J.; Hutter, J. Fast evaluation of solid harmonic Gaussian integrals for local resolution-of-the-identity methods and range-separated hybrid functionals. *J. Chem. Phys.* **2017**, *146*, 034105.

(24) Giese, T. J.; York, D. M. Contracted auxiliary Gaussian basis integral and derivative evaluation. *J. Chem. Phys.* **2008**, *128*, 064104.

(25) Ahlrichs, R. Efficient evaluation of three-center two-electron integrals over Gaussian functions. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5119−5121.

(26) Ahlrichs, R. A simple algebraic derivation of the Obara-Saika scheme for general two-electron interaction potentials. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3072−3077.

(27) Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. An efficient algorithm for the generation of two-electron repulsion integrals over gaussian basis functions. *Int. J. Quantum Chem.* **1989**, *36*, 269−280.

(28) Gill, P. M. W. *Molecular Integrals over Gaussian Basis Functions*; Sabin, J. R., Zerner, M. C., Eds.; Advances in Quantum Chemistry; Academic Press, 1994; Vol. *25*, pp 141−205.

(29) Ewald, P. P. Die Berechnung optischer und elektrostatischer Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253.

(30) Kolafa, J.; Perram, J. W. Cutoff Errors in the Ewald Summation Formulae for Point Charge Systems. *Mol. Simul.* **1992**, *9*, 351−368.

(31) Sun, Q.; Berkelbach, T. C.; Blunt, N. S.; Booth, G. H.; Guo, S.; Li, Z.; Liu, J.; McClain, J. D.; Sayfutyarova, E. R.; Sharma, S.; Wouters, S.; Chan, G. K. L. PySCF: the Python-based simulations of chemistry framework. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, *8*, No. e1340.

(32) Sun, Q.; et al. Recent developments in the PySCF program package. *J. Chem. Phys.* **2020**, *153*, 024109.

(33) Whitten, J. L. Coulombic potential energy integrals and approximations. *J. Chem. Phys.* **1973**, *58*, 4496−4501.

(34) Dunlap, B. I. Robust and variational fitting. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2113−2116.

https://doi.org/10.1021/acs.jctc.0c01195
J. Chem. Theory Comput. 2021, 17, 3916−3922