Lattice Sum Calculations for $1/r^p$ Interactions via Multipole Expansions and Euler Summation

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ABSTRACT: A method is developed here for doing multiple calculations of lattice sums when the lattice structure is kept fixed, while the molecular orientations or the molecules within the unit cells are altered. The approach involves a two-step process. In the first step, a multipole expansion is factored in such a way as to separate the geometry from the multipole moments. This factorization produces a formula for generating geometry constants that uniquely define the lattice structure. A direct calculation of these geometry constants, for all but the very smallest of crystals, is computationally impractical. In the second step, an Euler summation method is introduced that allows for efficient calculation of the geometry constants. This method has a worst case computational complexity of $O((\log N)^2/N)$, where N is the number of unit cells. If the lattice sum is rapidly converging, then the computational complexity can be significantly less than N. Once the geometry constants have been calculated, calculating a lattice sum for a given molecule becomes computationally very fast. Millions of different molecular orientations or molecules can quickly be evaluated for the given lattice structure.
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Introduction

Consider a hypothetical crystal with square unit cells and one atom at the center of each unit cell. We would like to compute the sum, of some $1/r^p$ interaction, between the central unit cell and all other unit cells. If the crystal has one shell, then 26 interactions need to be computed. With two shells, 124 interactions need to be computed. As can be seen from Table I, the number of interaction grows very rapidly.

Clearly, calculating a finite lattice sum can be computationally very expensive. If one is to perform such a calculation for a crystal of any tangible size, some method other than direct calculation needs to be employed.

In recent years, multipole expansion methods that take advantage of periodicity (e.g., refs. 1, 2, and 3) have been developed for crystal modeling. The basic multipole expansion that is used in refs. 1, 2, and 3, is a one center expansion. By this, we mean that when computing the interaction of two charge distributions, the multipole moments of the two distributions are all relative to the same coordinate system. If instead of having the two distributions share a common coordinate system each distribution is assigned its own coordinate system, then a greater degree of computational separation can be achieved. In this article we will examine the use of a Cartesian dual coordinate system (or two-center) expansion, in lattice sums. A spherical harmonic analog of the expansion in this paper can be found in ref. 4.

TABLE I.
Increase of the Number of Interactions with the Number of Shells.

Number of Shells	Number of Interactions
1	26
2	124
5	1330
10	9260
20	68,920
50	1,030,300
100	8,120,601
500	1,003,003,000
1000	8,012,006,000
5000	10^{12} (approx.)

Using a two-center expansion, we first derive the following approximation:

$$\sum_{\omega\in\Omega} f_{\omega_0}(\omega) \approx \sum_{m=0}^{M} \langle C_{p,m}(\Omega), f_{m,\omega_0} \rangle. \qquad (1)$$

In the above formula, Ω represents the periodic placement of a multipole moment in a crystal, while, ω represents a specific location, of the multipole moment, within the crystal. The term $f_{\omega_0}(\omega)$ represents $1/r^p$ interaction between a multipole moment in the central unit cell represented by ω_0, and the multipole moment of Ω at location ω. The $\langle \cdot, \cdot \rangle$, is the inner product operator. The f_{m,ω_0} are mth order multipole moments of the expansion. And finally, the $C_{p,m}(\Omega)$ are geometry constants that are uniquely defined by the shape of the unit cell and the size of the crystal.

The interesting and useful feature of formula (1) is that, unlike lattice summation approaches based on more standard methods, the geometry and the multipole moments are essentially independent of each other. It is therefore possible to modify either the geometry or the charge distribution without having to recalculate the other quantity. This method does not require that Ω has a lattice structure. However, its greatest usefulness is probably in the systematic studies of the energies of multipole lattices as a function of the number, the type, the orientation, and the magnitudes of the multipoles contained in a certain unit cell. In a first step in this direction, we have implemented formula (1), with $M = 2$. In this study we explored the rotational variance of the potential interaction between the central unit cell and all other unit cells in a crystal composed of cubic unit cells containing a single dipole. The results showed, unexpectedly and somewhat counterintuitively, that the lattice energy is invariant under such rotation.[5] In another example,[6] we used the geometry constant method to search for the potential energy minima of a crystal composed of unit cells containing two dipolar molecules. The study revealed that an energy well exists when the dipoles are parallel aligned. This is a very counter intuitive result because two dipoles, by themselves, will not form a stable structure. This study points out the importance of the surrounding environment, and the need for performing minimizations on structures that are of substantial size.

In separating the geometry from the multipole moments, we have effectively taken the computational complexity that is depicted in Table I and moved it into the $C_{p,m}$. Our problem is now how

to perform the lattice sum calculations that produce the $C_{p,m}$. In ref. 7, Kukhtin and Shramko have come up with a rather elegant idea for performing lattice sum calculations. They approach this problem using a method known as Euler summation. This method is essentially a method for converting discrete sums into continuous sums (i.e., integrals). From a mathematical point of view, but not necessarily from an intuitive point of view, Euler sums are closely related to the widely used Ewald sums.[8] Euler sums have been around for a long time. They even predate Ewald summation. The reason that they have not caught on in the past is that the integrals they produced could not be evaluated with existing methods. Recent advances in symbolic, and numerical integration have changed this situation. Symbolic integration packages such as Reduce, Maple, or Mathematica when combined with recently developed numerical integration methods, can now be applied to obtain highly accurate estimates of integrals that are produced from the Euler summation process.

This article is organized as follows. In the following section a two-center multipole expansion is derived for $1/r^p$; then, formula (1) is derived. Then, we show how to use formula (1) to calculate potential energy. And finally, then we derive the Euler summation integrals for calculating the $C_{p,m}$.

Multipole–Multipole Interaction Formula Derived for Lattice Sums

Because a complete derivation of the $1/r^p$ multipole–multipole interactions formulas, of arbitrary order, are difficult to find, these formulas are derived below. The general formula is then factored in such a way as to separate the geometry from the actual multipole moments. This allows for certain efficiencies when dealing with the sums of multipole–multipole interactions when the geometry is kept fixed. At the end of this section, p is set to 1, and two formulas for the multipole–multipole components of potential energy is presented.

THE MULTIPOLE EXPANSION

Using the coordinate system depicted in Figure 1, we have $R = (R_1, R_2, R_3)$, $r = (r_1, r_2, r_3)$, $s = (s_1, s_2, s_3)$, and $z = (z_1, z_2, z_3) = r - s$.

Let $\otimes^n$ denote the n-fold tensor (Kronecker) product. If A, B are nth order tensors, then denote the inner product of A and B by $\langle A, B\rangle_n$ or just $\langle A, B\rangle$. Let $\{e_j\}_{j=1}^3$ be the standard basis for $\mathbb{R}^3$ and let I be the 3

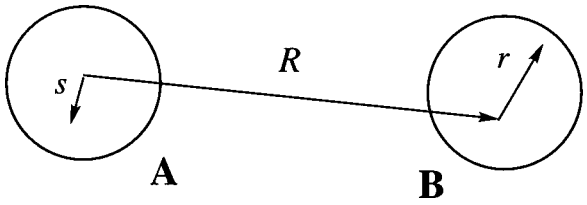

FIGURE 1. Coordinate system.

by 3 identity matrix. We will use "$\cdot$" to represent the standard inner product on $\mathbb{R}^n$. Define

$$a_{n,p} = \frac{\frac{-p}{2}\left(\frac{-p}{2}-1\right)\left(\frac{-p}{2}-2\right)\cdots\left(\frac{-p}{2}-n+1\right)}{n!}.$$

With a slight abuse of notation, the p subscript will be dropped and a_n will be written instead of $a_{n,p}$.

Theorem 1. *Define*

$$b_{n,k} = |R|^{-2n-p} a_n 2^{n-k}\binom{n}{k},$$

$$A_{n,k} = \left(\overset{n-k}{\otimes} R\right) \otimes \left(\overset{k}{\otimes} I\right).$$

Then the expression

$$\frac{1}{|R|^p} + \sum_{m=1}^{\infty}\left\langle \sum_{k=0}^{\lfloor m/2\rfloor} b_{m-k,k} A_{m-k,k}, \overset{m}{\otimes} z \right\rangle$$

converges absolutely whenever the condition

$$\left|\frac{2z\cdot R}{|R|^2} + \frac{|z|^2}{|R|^2}\right| < 1 \tag{2}$$

is satisfied. Whenever (2) *is satisfied, we have the following expansion.*

$$\frac{1}{|R+z|^p} = \frac{1}{|R|^p} + \sum_{m=1}^{\infty}\left\langle \sum_{k=0}^{\lfloor m/2\rfloor} b_{m-k,k} A_{m-k,k}, \overset{m}{\otimes} z \right\rangle. \tag{3}$$

Proof. If we set

$$x = \frac{2z\cdot R}{|R|^2} + \frac{|z|^2}{|R|^2},$$

then $1/|R+z|^p$ can be expressed as

$$\begin{aligned}\frac{1}{|R+z|^p} &= \frac{1}{((R+z)\cdot(R+z))^{p/2}} \\ &= \frac{1}{(R\cdot R + 2z\cdot R + z\cdot z)^{p/2}} \\ &= \frac{1}{|R|^p}\left(1 + \frac{2z\cdot R}{|R|^2} + \frac{|z|^2}{|R|^2}\right)^{-p/2} \\ &= \frac{1}{|R|^p}(1+x)^{-p/2}\end{aligned}$$

and, whenever $|x| < 1$, $1/|R+z|^p$ has the absolutely convergent expansion

$$\frac{1}{|R+z|^p} = \frac{1}{|R|^p}\left(1 + \sum_{n=1}^{\infty} a_n x^n\right). \tag{4}$$

By the binomial theorem, we have the following

$$\begin{aligned}
|R|^{2n}x^n &= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\langle R,z\rangle^{n-k}\left(|z|^2\right)^k \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\langle R,z\rangle^{n-k}\left(z_1^2+z_2^2+z_3^2\right)^k \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\langle R,z\rangle^{n-k}\left(\sum_{j=1}^{3}\langle e_j,z\rangle^2\right)^k \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\left\langle \overset{n-k}{\otimes} R, \overset{n-k}{\otimes} z\right\rangle\left(\sum_{j=1}^{3}\left\langle \overset{2}{\otimes} e_j, \overset{2}{\otimes} z\right\rangle\right)^k \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\left\langle \overset{n-k}{\otimes} R, \overset{n-k}{\otimes} z\right\rangle\left(\left\langle \sum_{j=1}^{3}\overset{2}{\otimes} e_j, \overset{2}{\otimes} z\right\rangle\right)^k \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\left\langle \overset{n-k}{\otimes} R, \overset{n-k}{\otimes} z\right\rangle\left\langle I, \overset{2}{\otimes} z\right\rangle^k \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\left\langle \overset{n-k}{\otimes} R, \overset{n-k}{\otimes} z\right\rangle\left\langle \overset{k}{\otimes} I, \overset{2k}{\otimes} z\right\rangle \\
&= \sum_{k=0}^{n}\binom{n}{k}2^{n-k}\left\langle \left(\overset{n-k}{\otimes} R\right)\otimes\left(\overset{k}{\otimes} I\right), \overset{n+k}{\otimes} z\right\rangle.
\end{aligned}$$

Thus, we obtain

$$\frac{1}{|R+z|^p} = \frac{1}{|R|^p}\left(1 + \sum_{n=1}^{\infty} a_n\left[|R|^{-2n}\sum_{k=0}^{n}\binom{n}{k}2^{n-k} \times\left\langle\left(\overset{n-k}{\otimes} R\right)\otimes\left(\overset{k}{\otimes} I\right), \overset{n+k}{\otimes} z\right\rangle\right]\right). \tag{5}$$

Set $m = n+k$. Because $k = 0,\ldots,n$, we must have that $k = 0,\ldots,\lfloor m/2\rfloor$. Reindexing the left hand side of eq. (5) we arrive at eq. (3):

$$\frac{1}{|R+z|^p} = \frac{1}{|R|^p} + \sum_{m=1}^{\infty}\left\langle\sum_{k=0}^{\lfloor m/2\rfloor} b_{m-k,k}A_{m-k,k}, \overset{m}{\otimes} z\right\rangle. \quad \blacksquare$$

Numerical studies have shown that eq. (3) converges very slowly whenever

$$\left|\frac{2z\cdot R}{|R|^2} + \frac{|z|^2}{|R|^2}\right|$$

is near 1. A possible method to improve the convergence rate would be to use nonlinear convergence acceleration methods of the type used in ref. 9.

Recalling that $z = r - s$, where z, r, s are vectors, the $(i_1, i_2, \ldots, i_m)$ tensorial component of $\otimes^m z = \otimes^m(r-s)$ is the term $(r_{i_1} - s_{i_1})(r_{i_2} - s_{i_2})\cdots(r_{i_m} - s_{i_m})$, $i_k = 1,2,3$. For reason that will become clear later in the paper, we would like to be able to write $\otimes^m z$, in eq. (3), in terms of the multipole moments whose $(i_1, i_2, \ldots, i_m)$ tensorial components are $(r_{i_1}r_{i_2}\cdots r_{i_m})$, and $(s_{i_1}s_{i_2}\cdots s_{i_m})$, $i_k = 1,2,3$. This can be accomplished with the following.

For nonnegative integers t and m with $t \le m$, define

$$\begin{aligned}
\mathcal{S}_{t,m} = \big\{&(k_1,k_2,\ldots,k_t) \mid k_i \in \{\text{positve integers}\},\\
&1 \le k_i \le m, \quad \text{and} \quad k_i < k_j \text{ whenever } i < j\big\}.
\end{aligned}$$

If $\eta \in \mathcal{S}_{t,m}$, define $\tilde{\eta} = (k_1, k_2, \ldots, k_{m-t})$ where the $k_i < k_j$ whenever $i < j$, $k_i \in \{1,2,\ldots,m\}$, and any k_i that appears in η does not appear in $\tilde{\eta}$. For $\eta \in \mathcal{S}_{t,m}$ define $\iota(j)$, $\eta(j)$, and $\tilde{\eta}(j)$ as jth components of ι, η, and $\tilde{\eta}$. If $\eta \in \mathcal{S}_{0,m}$ then η is the null sequence; and if $\eta \in \mathcal{S}_{m,m}$ then $\tilde{\eta}$ is the null sequence. Using the preceding notation we have the following lemma.

Lemma 2. *For a fixed* $\iota = (i_1, i_2, \ldots, i_m)$,

$$\prod_{j=1}^{m}(r_{\iota_j} - s_{\iota_j}) = \sum_{t=0}^{m}(-1)^{m-t}\sum_{\eta\in\mathcal{S}_{t,m}}\prod_{q=1}^{t} r_{\iota(\eta(q))}\prod_{q=1}^{m-t} s_{\iota(\tilde{\eta}(q))}. \tag{6}$$

Proof. The proof is by induction on m. ■

Equation (6) can now be used to turn expression (3) into an expression of multipole moments.

SEPARATION OF GEOMETRY FROM THE CHARGE DISTRIBUTIONS

Let Ω be a finite collection of nodes (points) in $\mathbb{R}^3$, whose elements are denoted by $\omega_0, \omega_1, \ldots, \omega_M$. Define R_{ω_i} as the vector from ω_0 to ω_i, and define

$$\begin{aligned}
b(\omega_i)_{n,k} &= |R_{\omega_i}|^{-2n-p}a_n 2^{n-k}\binom{n}{k},\\
A(\omega_i)_{n,k} &= \left(\overset{k}{\otimes} I\right)\otimes\left(\overset{n-k}{\otimes} R_{\omega_i}\right).
\end{aligned}$$

Let $f_{\omega_0}(\omega_i)$ be some $1/r^n$ interaction (e.g., potential energy or Lennard–Jones) between the atoms/molecules located at ω_0 and ω_i, such that

$$f_{\omega_0}(\omega_i) = \frac{1}{|R_{\omega_i}|^p}f_{0,\omega_0}(\omega_i) + \sum_{m=1}^{\infty}\left\langle\sum_{k=0}^{\lfloor m/2\rfloor} b(\omega_i)_{m-k,k} \times A(\omega_i)_{m-k,k}, f_{m,\omega_0}(\omega_i)\right\rangle, \tag{7}$$

where $f_{m,\omega_0}(\omega_i)$ is some presently unspecified tensor of rank m, that is a function of the atoms/molecules located at ω_0, and ω_i.

We would like to be able to calculate $\sum_{\omega\in\Omega} f_{\omega_0}(\omega)$ in a manner that separates geometric aspects from the $f_{m,\omega_0}(\omega)$, as much as possible. The approach that we use is described below.

From eq. (7), we have

$$\sum_{\omega\in\Omega} f_{\omega_0}(\omega) = \sum_{\omega\in\Omega} \frac{1}{|R_\omega|^p} f_{0,\omega_0}(\omega) + \sum_{\omega\in\Omega}\sum_{m=1}^{\infty}\left\langle \sum_{k=0}^{\lfloor m/2\rfloor} b(\omega)_{m-k,k} A(\omega)_{m-k,k},\ f_{m,\omega_0}(\omega)\right\rangle. \quad (8)$$

Interchanging the order of summation, and setting $C_{p,0}(\Omega) = \sum_{\omega\in\Omega} 1/|R_\omega|^p$ and $C_{p,m}(\Omega) = \sum_{\omega\in\Omega}\sum_{k=0}^{\lfloor m/2\rfloor} b(\omega)_{m-k,k}A(\omega)_{m-k,k}$ we can write

$$\sum_{\omega\in\Omega} f_{\omega_0}(\omega) = C_{p,0}(\Omega) f_{0,\omega_0} + \sum_{m=1}^{\infty}\langle C_{p,m}(\Omega), f_{m,\omega_0}\rangle. \quad (9)$$

POTENTIAL ENERGY

When p is set to 1, eq. (9) can be used for potential energy calculations. The specifics follow. Let $r = (r_1, r_2, r_3)_\alpha$ be a local coordinate system. If $\rho_e(r)$ is an electron density distribution that occupies some finite region of space A_0, then the "charge distribution," $\rho(r)$, is defined as follows. Let q_i be the charge of the ith nucleus located at position P_i. Then

$$\rho(r) = \rho_e(r) + \sum_i q_i \delta_{P_i}(r),$$

where the Dirac delta function, δ, has the following property:

$$\int_A \delta_{P_i}(r) = \begin{cases} 1 & \text{if } P_i \in A, \\ 0 & \text{if } P_i \notin A. \end{cases}$$

Letting $\rho(r)$ be a continuous charge distribution, we define the nth multipole moment as the tensor whose $\iota = (i_1, i_2, \ldots, i_n)$, $i_k = 1, 2, 3$, component is

$$\iiint \rho(r_1, r_2, r_3) r_{i_1} r_{i_2} \cdots r_{i_n}\, dr_1\, dr_2\, dr_3.$$

Using Theorem 1, and the above notation, the potential,

$$\int_{\mathbf{A}}\int_{\mathbf{B}} \frac{\boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)}{|R + (r-s)|}\, dr\, ds,$$

can be expanded as follows:

$$\int_{\mathbf{A}}\int_{\mathbf{B}} \frac{\boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)}{|R+(r-s)|}\, dr\, ds = \frac{1}{|R|}\int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)\, dr\, ds + \sum_{m=1}^{\infty}\left\langle \sum_{k=0}^{\lfloor m/2\rfloor} b_{m-k,k} A_{m-k,k},\ \int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)\Big(\overset{m}{\otimes}(r-s)\Big)\, dr\, ds\right\rangle, \quad (10)$$

where the $\iota = (\iota_1, \iota_2, \ldots, \iota_m)$, $\iota_k = 1, 2, 3$, tensorial component

$$\int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)(r_{\iota_1} - s_{\iota_1})(r_{\iota_2} - s_{\iota_2})\cdots(r_{\iota_m} - s_{\iota_m})\, dr\, ds$$

of

$$\int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)\big(\otimes^m(r-s)\big)\, dr\, ds$$

is

$$\sum_{t=0}^{m}(-1)^{m-t}\sum_{\eta\in\mathcal{S}_{t,m}}\left(\int_{\mathbf{B}}\boldsymbol{\rho}(r)\prod_{q=1}^{t} r_{\iota(\eta(q))}\, dr\right) \times\left(\int_{\mathbf{A}}\boldsymbol{\sigma}(s)\prod_{q=1}^{m-t} s_{\iota(\tilde{\eta}(q))}\, ds\right). \quad (11)$$

The following example demonstrates how to apply these formulas to the $m = 2$ term.

Example 3. The (a, b), $a = 1, 2, 3$ and $b = 1, 2, 3$, tensorial component of

$$\int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)\big(\otimes^2(r-s)\big)\, dr\, ds$$

is

$$\int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)(r_a - s_a)(r_b - s_b)\, dr\, ds.$$

One can expand this expression as follows:

$$\begin{aligned}
&\int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s)\big[(r_a - s_a)(r_b - s_b)\big]\, dr\, ds \\
&\quad= \int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s) r_a r_b\, dr\, ds \\
&\qquad - \int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s) r_a s_b\, dr\, ds \\
&\qquad - \int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s) s_a r_b\, dr\, ds \\
&\qquad + \int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}(r)\boldsymbol{\sigma}(s) s_a s_b\, dr\, ds \\
&\quad= \left(\int_{\mathbf{B}}\boldsymbol{\sigma}(s)\, ds\right)\left(\int_{\mathbf{A}}\boldsymbol{\rho}(r) r_a r_b\, dr\right) \\
&\qquad - \left(\int_{\mathbf{B}}\boldsymbol{\sigma}(s) s_b\, ds\right)\left(\int_{\mathbf{A}}\boldsymbol{\rho}(r) r_a\, dr\right) \\
&\qquad - \left(\int_{\mathbf{B}}\boldsymbol{\sigma}(s) s_a\, ds\right)\left(\int_{\mathbf{A}}\boldsymbol{\rho}(r) r_b\, dr\right) \\
&\qquad + \left(\int_{\mathbf{B}}\boldsymbol{\sigma}(s) s_a s_b\, ds\right)\left(\int_{\mathbf{A}}\boldsymbol{\rho}(r)\, dr\right). \quad (12)
\end{aligned}$$

Note that the right-hand side of eq. (12) is strictly a function of the monopole, dipole, and quadrupole terms of the charge distributions.

Setting

$$f_{m,\omega_0}(\omega) = \int_{\mathbf{A}}\int_{\mathbf{B}} \boldsymbol{\rho}\big(r(\omega)\big)\boldsymbol{\sigma}\big(s(\omega)\big)\Big(\overset{m}{\otimes}\big(r(\omega)-s(\omega)\big)\Big),$$

we can know apply eq. (9) to find the potential energy of the central unit cell of a crystal.

To implement eqs. (10) and (11), $\boldsymbol{\rho}_e$ and $\boldsymbol{\sigma}_e$ need to be determined. For molecules with fewer than 300 atoms Hartree–Fock methods can be used to estimate $\boldsymbol{\rho}_e$ and $\boldsymbol{\sigma}_e$.[10] The latest developments even allow for perturbation treatments of very large systems, such as polyglycine chains and water clusters with over 3000 basis functions.[11] Still, even with modern hardware and software, the computational demand of *ab initio* computation of very large molecules remains substantial and perhaps unnecessary in studies of large series of large molecules. There exist several alternatives to obtain useful electron density distributions in more efficient ways and these approaches fall into two categories. One can either treat the entire large system and employ approximations in the theoretical level, or one can choose to treat the large system as a composite. Semiempirical molecular orbital theory is based on an approximative Hartree–Fock formalism, and several empirical parameters are introduced and fit to experimental data. There are various implementations, and their performances have been reviewed.[12]

The alternative approach is based on the assumption of the transferability of fragments of molecules[13] and employs this strategy to construct approximations to the electron density of a very large molecule using the electron densities and properties of much smaller molecules.[14] Density composition methods differ from each other primarily in the way the fragments are defined and in the way the properties of the fragments are determined. The various approaches to additive fuzzy electron density fragmentation methods have recently been reviewed.[15]

Euler Sums on Periodic Ω

To facilitate the use of eq. (9), an efficient method for determining the $C_{p,m}(\Omega)$ needs to be developed. Because we are primarily interested in $\sum_{\omega\in\Omega} f_{\omega_0}(\omega)$ when Ω has a lattice structure, the discussion below will be limited to calculating the $C_{p,m}(\Omega)$ of periodic structures.

In the following two theorems

$$P(t) = -\sum_{k=1}^{\infty} \frac{\sin 2k\pi t}{k\pi},$$

which is the Fourier series for $t - \lfloor t\rfloor - \frac{1}{2}$.

Theorem 4 *(Euler Summation). If $f(x)$ has a continuous derivative on $\frac{1}{2} < x < N + \frac{1}{2}$ then*

$$\sum_{n=1}^{N} f(n) = \int_{\frac{1}{2}}^{N+\frac{1}{2}} f(x)\,dx + \int_{\frac{1}{2}}^{N+\frac{1}{2}} f_x(x)P(x)\,dx. \quad (13)$$

Proof. If the Riemann–Stieltjes integral $\int_{1/2}^{N+1/2} f(x)\,d\lfloor x\rfloor$ (where $\lfloor\ \rfloor$ is the greatest integer function) exists, then

$$\sum_{n=1}^{N} f(n) = \int_{\frac{1}{2}}^{N+\frac{1}{2}} f(x)\,d\lfloor x\rfloor.$$

We, thus, have that

$$\int_{\frac{1}{2}}^{N+\frac{1}{2}} f(x)\,dx - \sum_{n=1}^{N} f(n) = \int_{\frac{1}{2}}^{N+\frac{1}{2}} f(x)\,d\left(x - \lfloor x\rfloor - \frac{1}{2}\right). \quad (14)$$

Integrating the right-hand side by parts gives

$$\int_{\frac{1}{2}}^{N+\frac{1}{2}} f(x)\,d\left(x - \lfloor x\rfloor - \frac{1}{2}\right) = -\int_{\frac{1}{2}}^{N+\frac{1}{2}} P(x)f_x(x)\,dx. \quad (15)$$

Equation (13) is now immediate from eqs. (14) and (15). ■

Theorem 5. *If $f_{xyz}(x,y,z)$ exists and is continuous on all open sets contained in*

$$\left[\tfrac{1}{2}, N+\tfrac{1}{2}\right]\times\left[\tfrac{1}{2}, M+\tfrac{1}{2}\right]\times\left[\tfrac{1}{2}, L+\tfrac{1}{2}\right]$$

then

(1)

$$\begin{aligned}\sum_{m=1}^{M}\sum_{n=1}^{N} f(n,m) &= \int_{\frac{1}{2}}^{M+\frac{1}{2}}\int_{\frac{1}{2}}^{N+\frac{1}{2}} f(x,y)\,dx\,dy \\ &+ \int_{\frac{1}{2}}^{M+\frac{1}{2}} P(y)\int_{\frac{1}{2}}^{N+\frac{1}{2}} f_y(x,y)\,dx\,dy \\ &+ \int_{\frac{1}{2}}^{M+\frac{1}{2}}\left(\int_{\frac{1}{2}}^{N+\frac{1}{2}} f_x(x,y)P(x)\,dx\right)dy \\ &+ \int_{\frac{1}{2}}^{M+\frac{1}{2}} P(y)\left(\int_{\frac{1}{2}}^{N+\frac{1}{2}} f_{xy}(x,y)P(x)\,dx\right)dy\end{aligned}$$

(2)

$$\begin{aligned}
&\sum_{l=1}^{L}\sum_{m=1}^{M}\sum_{n=1}^{N} f(n,m,l)\\
&\quad=\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y,z)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_z(x,y,z)P(z)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_x(x,y,z)P(x)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_{xz}(x,y,z)P(x)P(z)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_y(x,y,z)P(y)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_{yz}(x,y,z)P(y)P(z)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_{xy}(x,y,z)P(x)P(y)\,dx\,dy\,dz\\
&\qquad+\int_{\frac12}^{L+\frac12}\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_{xyz}(x,y,z)\\
&\qquad\qquad\times P(x)P(y)P(z)\,dx\,dy\,dz.
\end{aligned}$$

Proof. Using eq. (13) we have that

$$\begin{aligned}
\sum_{m=1}^{M}\sum_{n=1}^{N} f(n,m) &= \int_{\frac12}^{M+\frac12}\sum_{n=1}^{N} f(n,m)\,d\lfloor y\rfloor\\
&= \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\\
&\quad + f_x(x,y)P(x)\,dx\,d\lfloor y\rfloor.
\end{aligned}$$

Thus,

$$\begin{aligned}
&\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,dy - \sum_{m=1}^{M}\sum_{n=1}^{N} f(n,m)\\
&\quad= \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,dy\\
&\qquad- \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y) + f_x(x,y)P(x)\,dx\,d\lfloor y\rfloor\\
&\quad= \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,dy\\
&\qquad- \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,d\lfloor y\rfloor\\
&\qquad- \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_x(x,y)P(x)\,dx\,d\lfloor y\rfloor\\
&\quad= \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,d\big(y-\lfloor y\rfloor\big)\\
&\qquad- \int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f_x(x,y)P(x)\,dx\,d\lfloor y\rfloor. \qquad (16)
\end{aligned}$$

Setting $u=\int_{1/2}^{N+1/2} f(x,y)\,dx$ and $dv=d(y-\lfloor y\rfloor)$ (with $v=y-\lfloor y\rfloor-\frac12$), the term

$$\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,d\big(y-\lfloor y\rfloor\big)$$

can be integrated by parts:

$$\begin{aligned}
&\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,d\big(y-\lfloor y\rfloor\big)\\
&\qquad= -\int_{\frac12}^{M+\frac12} P(y)\int_{\frac12}^{N+\frac12} f_y(x,y)\,dx\,dy. \qquad (17)
\end{aligned}$$

Now using eq. (13) to sum over y

$$\begin{aligned}
&\int_{\frac12}^{M+\frac12}\left(\int_{\frac12}^{N+\frac12} f_x(x,y)P(x)\,dx\right)d\lfloor y\rfloor\\
&\quad=\sum_{m=1}^{M}\int_{\frac12}^{N+\frac12} f_x(x,m)P(x)\,dx\\
&\quad=\int_{\frac12}^{M+\frac12}\left(\int_{\frac12}^{N+\frac12} f_x(x,y)P(x)\,dx\right)dy\\
&\qquad+\int_{\frac12}^{M+\frac12} P(y)\left(\int_{\frac12}^{N+\frac12} f_{xy}(x,y)P(x)\,dx\right)dy. \qquad (18)
\end{aligned}$$

Combining eqs. (16), (17), and (18), we have that

$$\begin{aligned}
&\int_{\frac12}^{M+\frac12}\int_{\frac12}^{N+\frac12} f(x,y)\,dx\,dy - \sum_{m=1}^{M}\sum_{n=1}^{N} f(n,m)\\
&\quad= -\int_{\frac12}^{M+\frac12} P(y)\int_{\frac12}^{N+\frac12} f_y(x,y)\,dx\,dy\\
&\qquad-\int_{\frac12}^{M+\frac12}\left(\int_{\frac12}^{N+\frac12} f_x(x,y)P(x)\,dx\right)dy\\
&\qquad-\int_{\frac12}^{M+\frac12} P(y)\left(\int_{\frac12}^{N+\frac12} f_{xy}(x,y)P(x)\,dx\right)dy
\end{aligned}$$

Statement (1) now follows immediately. The proof of statement (2) is similar. ■

Formula (2) of Theorem 5 is the three-dimensional Euler summation formula that we need to evaluate. The first triple integral, which is also the

dominant term, can be completely integrated with a symbolic integrator for quadrupole or higher components. For monopole or dipole components, the first triple integral can be integrated by combining symbolic integration (e.g., Reduce, Maple, Macsyma, Mathematica) with newly developed deterministic analogs of Monte–Carlo methods, often referred to as quasi-Monte Carlo.[16, 17] The remaining triple integrals need to be integrated with a quasi-Monte Carlo method.

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