

## Multipole Ewald Sums for the Fast Multipole Method

K. E. Schmidt<sup>1</sup> and Michael A. Lee<sup>2</sup>

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A generalized Ewald summation for electric multipoles in periodic arrays is presented in the form needed for multipole transformations used in the fast multipole method. In the fast multipole method the time-consuming Ewald sums are thus eliminated in favor of a simple matrix transformation with almost no computational cost. The derivation also applies to traditional electrostatic potential calculations in periodic charged systems. A summary computational prescription is provided.

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**KEY WORDS:** Fast multipole method; Ewald sum;  $N$ -body problem.

### I. INTRODUCTION

The fast multipole method (FMM), as described by Greengard,<sup>(1)</sup> can be used to calculate the energy and forces of particles interacting via coulomb or gravitational potentials in a computational time that is linear in the number of particles. In a previous paper, we showed that applying the FMM to a periodic system requires the electrostatic potential due to infinite periodic arrays of multipoles of arbitrary order and gave the result for the simple cubic lattice.<sup>(2)</sup> Here we derive the electrostatic potential of such an array for arbitrary periodic (i.e., noncubic) lattices. The special case needed in the FMM is summarized in section IV. The mathematics is the same as the classic Ewald method that is described in standard texts.<sup>(5)</sup> A different generalization for the FMM transformation equations for periodic systems was also developed by Greengard based on a renormalization method.<sup>(3)</sup>

We consider a simulation volume with an arbitrary distribution of charges (continuous and discrete, but net neutral) and its periodic replication to fill space. In applying the FMM one obtains the total electrostatic potential due to charge in the simulation volume, to which one must add the contribution from the periodic replications that fill space. As part of the

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<sup>1</sup> Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287.

<sup>2</sup> Department of Physics, Kent State University, Kent, Ohio 44242.

FMM procedure, one also gets the multipole expansion of the electrostatic potential of the simulation volume about its center. The periodic images of the simulation cell each have the same multipole expansion about their centers and these may be summed to calculate the effects of the periodic boundary conditions. (Near neighbor volumes must be treated explicitly, i.e., add the direct contribution and subtract the multipole contribution to maintain the precision of the FMM, but that implementation issue is not treated here.<sup>(2)</sup>)

## II. GENERALIZED EWALD FOR ARBITRARY MULTIPOLE

The problem reduces to finding the potential of an infinite set of multipoles distributed periodically with a lattice defined by a set of three primitive translation vectors. In spherical coordinates the electrostatic potential of one multipole, with moment  $M_{lm}$ , located at the origin is,

$$V^{lm}(\vec{r}) = \frac{4\pi M_{lm}}{2l+1} \frac{Y_{lm}(\theta, \phi)}{r^{l+1}}. \quad (1)$$

Here, and throughout, we employ the conventions and units of Jackson.<sup>(4)</sup> If we designate by  $\vec{T}$  the variable specifying translations to the lattice points, the electrostatic potential in the primitive cell due to a unit strength multipole at the origin and all periodic images is

$$\Phi_{lm}(\vec{r}) = \sum_{\vec{T}} V^{lm}(\vec{r} + \vec{T}). \quad (2)$$

The sum over infinitely many lattice sites in Eq. 2 is conditionally convergent (depends on the method of summation) for  $l=0, 1$  and  $2$ . The  $l=0$  term is absent due to charge neutrality. These particular cases were historically the motivation for the Ewald method and a discussion of Ewald-Kornfeld treatment is available in standard texts.<sup>(5)</sup> We remark that the Ewald method produces a periodic electrostatic potential for Eq. 2, whereas direct summation does not give a periodic potential for  $l=1$ . We will relate the Ewald method to other summation options later in this paper. We refer the reader to the works specifically addressing these special cases<sup>(6,7)</sup> where the effects of altering the summation order or introducing various boundary conditions are discussed.

The charge density that will give the electrostatic potential in Eq. 1, with  $M_{lm} = 1$ , is

$$\rho_{lm}(\vec{r}) = \frac{Y_{lm}(\hat{r})}{r^{l+2}} \delta(r). \quad (3)$$

The delta function in the charge density of the multipole in Eq. 3 is understood to be the limit of a unit area function extending radially an infinitesimal distance from the origin. Using the usual spherical harmonic expansion of the coulomb potential,

$$\frac{1}{|\vec{r}-\vec{r}'|} = \sum_{lm} \frac{4\pi}{2l+1} \frac{r'^l}{r^{l+1}} Y_{lm}^*(\hat{r}') Y_{lm}(\hat{r}), \quad (4)$$

it is easily verified that the charge density of Eq. 3 produces the electrostatic potential of Eq. 1.

The Ewald method replaces a delta function charge density with a delta function plus a normalized Gaussian subtracted and added. The particle electrostatic potential then has a short-range part,  $V_S(\vec{r})$ , based on the delta function with the Gaussian subtracted charge density and is used to calculate the usual real-space lattice sum. The second Gaussian term produces the long-range part,  $V_L(\vec{r})$ , which sums to produce a smoother total electrostatic potential due to all particles. This is Fourier transformed and the resulting sum done in k-space. Both sums converge much more rapidly than either a real-space or k-space sum alone.

### A. Short-Range Ewald Potential

The short-range potential,  $V_S^{lm}(\vec{r})$ , of the unit multipole at the origin is developed using the Ewald procedure with Gaussian to cancel the delta function,

$$V_S^{lm}(\vec{r}) = \int d^3r' d^3r'' \frac{1}{|\vec{r}-\vec{r}''|} \left[ \delta^3(\vec{r}'-\vec{r}'') - \left(\frac{\alpha^2}{\pi}\right)^{3/2} \exp(-\alpha^2 |\vec{r}'-\vec{r}''|^2) \right] \rho_{lm}(\vec{r}''). \quad (5)$$

The long-range potential,  $V_L^{lm}(\vec{r})$ , is the negative of this without the  $\delta^3(\vec{r}'-\vec{r}'')$  term.

Since our charge density is so simple, it is convenient to do the  $\vec{r}''$  integral in Eq. 5 first. The Gaussian is first expanded as

$$\begin{aligned} \exp(-\alpha^2 |\vec{r}'-\vec{r}''|^2) &= \exp(-\alpha^2(r'^2 + r''^2)) 4\pi \\ &\times \sum_{lm} i^l j_l(-2\alpha^2 i r' r'') Y_{lm}^*(\hat{r}') Y_{lm}(\hat{r}''). \end{aligned} \quad (6)$$

Because our  $\rho_{lm}(\vec{r}'')$  contains  $\delta(r'')$ , the integral depends on the behavior of the Bessel function around the origin. Integrating over  $\vec{r}''$  gives the effective short-range charge density,

$$Y_{lm}(\hat{r}') \left[ \frac{\delta(r')}{r'^{l+2}} - \left( \frac{\alpha^2}{\pi} \right)^{3/2} \exp(-\alpha^2 r'^2) \frac{(2\alpha^2 r')^l 4\pi}{(2l+1)!!} \right].$$

The remaining integration in Eq. 5 is performed using the expansion for the coulomb potential, Eq. 4, to give the real-space Ewald interaction

$$\begin{aligned} V_S^{lm}(\vec{r}) &= \frac{4\pi Y_{lm}(\hat{r})}{2l+1} \left( \frac{1}{r^{(l+1)}} \right. \\ &\quad \times \left[ 1 - \frac{4\pi}{(2l+1)!!} \left( \frac{\alpha^2}{\pi} \right)^{3/2} 2^l \alpha^{2l} \int_0^r dr' r'^{(2l+2)} \exp(-\alpha^2 r'^2) \right] \\ &\quad \left. - r^l \frac{4\pi}{(2l+1)!!} \left( \frac{\alpha^2}{\pi} \right)^{3/2} 2^l \alpha^{2l} \int_r^\infty dr' r' \exp(-\alpha^2 r'^2) \right). \end{aligned} \quad (7)$$

The first integral can be expressed in terms of error functions. Defining,

$$I_l(x) = \int_x^\infty dy y^{2l+2} \exp(-y^2), \quad (8)$$

permits development of a recursion relation by integration by parts,

$$I_l(x) = \frac{2l+1}{2} I_{l-1}(x) + \frac{x^{2l+1}}{2} \exp(-x^2),$$

with  $I_0(x) \equiv \sqrt{\pi}/4 \operatorname{erfc}(x) + x/2 \exp(-x^2)$ , where  $\operatorname{erfc}$  is the complimentary error function.

The short-range Ewald potential, Eq. 5, for the  $lm$ -th multipole simplifies to

$$V_S^{lm}(\vec{r}) = \frac{4\pi Y_{lm}(\hat{r})}{2l+1} \frac{2^{l+2}}{\sqrt{\pi} (2l+1)!!} \left( \frac{I_l(\alpha r)}{r^{l+1}} - \frac{\alpha^{2l+1} r^l}{2} \exp(-\alpha^2 r^2) \right). \quad (9)$$

This must be summed over all the lattice to obtain the total short-range contribution to the electrostatic potential,

$$\Phi_S^{lm}(\vec{r}) = \sum_{\vec{T}} V_S^{lm}(\vec{r} + \vec{T}), \quad (10)$$

## B. Long-Range Ewald Potential

The long-range potential,  $V_L^{lm}(\vec{r})$ , of the multipole at the origin comes from the compensating Gaussian charge distribution. (The negative Eq. 5 without the  $\delta^3(\vec{r}' - \vec{r}'')$  term.) This long-range interaction is treated using the standard Ewald approach by expanding the total long-range potential,  $\Phi_L^{lm}(\vec{r})$ , as a Fourier series in reciprocal space,

$$\Phi_L^{lm}(\vec{r}) = \left( \sum_{\vec{T}} V_L^{lm}(\vec{r} + \vec{T}) \right) = \sum_{\vec{G}} \phi_{\vec{G}}^{lm} e^{i\vec{G} \cdot \vec{r}}. \quad (11)$$

The accent above the sum over reciprocal lattice vectors,  $\vec{G}$ , indicates omission of the constant term contributed by  $\vec{G} = 0$ . The constant term has been explicitly omitted because a constant potential does not alter the energy of a neutral system. We follow the usual convention of defining the Ewald potential as a method that yields a periodic solution to Poisson's equation with this constant term set to zero. The lattice sum in Eq. 11 is conditionally convergent for  $l = 1, 2$  just as in Eq. 2. These convergence issues for  $l = 1, 2$  are well understood<sup>(6,7)</sup> as is the relationship between definitions which produce a periodic Ewald potential and nonperiodic definitions based on various methods of direct summation of the coulomb interactions.

The integrals needed to evaluate the Fourier coefficients,  $\phi_{\vec{G}}^{lm}$ , above are facilitated by the use of the convolution theorem. The Fourier transform of the charge density,  $\tilde{\rho}_{lm}(\vec{k})$ , may be calculated from Eq. 3 with the plane wave spherical harmonic expansion used in Eq. 6,

$$\tilde{\rho}_{lm}(\vec{k}) = \int d^3r \exp(-i\vec{k} \cdot \vec{r}) \rho_{lm}(\vec{r}) = 4\pi Y_{lm}(\hat{k}) \frac{(-ik)^l}{(2l+1)!!}.$$

The reciprocal-space expansion is then,

$$\Phi_L^{lm}(\vec{r}) = \frac{(4\pi)^2}{V_C} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \frac{Y_{lm}(\hat{G})}{G^2} \frac{(-iG)^l}{(2l+1)!!} e^{i\vec{G} \cdot \vec{r}}, \quad (12)$$

where  $\hat{G}$  represents the angular coordinates of  $\vec{G}$  in the original coordinate system of the simulation volume.  $V_C$  is the volume of the real-space primitive cell. The reader should observe that for  $l > 2$ , the  $\vec{G} = 0$  term in Eq. 12 would be well defined, but is indeterminate for  $l = 2$  reflecting the fact that the constant potential for a sum of quadrupole interactions is a finite value, but depends on the summation method. The undefined nature of the constant term for  $l = 1$  reflects the lack of a periodic result when direct summation is applied to dipole lattices.<sup>(6)</sup> The omission of the

constant remains correct for a neutral system. We also point out that the constant only arises from the long-range contributions from the electrostatic potential and thus can not depend on the Gaussian width parameter  $\alpha$ .

The long-range contribution,  $\Phi_L^{lm}(\vec{r})$ , is to be added to the real-space sum, to yield the total electrostatic potential at a point  $\vec{r}$  in the primitive cell. The sum of Eqs. 10 and 11 provides the desired generalization of the Ewald procedure for producing a periodic electrostatic potential due to an array of multipoles in a general Bravais lattice,

$$\Phi^{lm}(\vec{r}) = \sum_{\vec{G}} \phi_{\vec{G}}^{lm} e^{i\vec{G}\cdot\vec{r}} + \sum_{\vec{T}} V_S^{lm}(\vec{r} + \vec{T}). \quad (13)$$

Defining  $\vec{R}_T = \vec{r} + \vec{T}$ , the generalized Ewald potential can be explicitly written,

$$\begin{aligned} \Phi^{lm}(\vec{r}) = & \frac{2^{l+4} \sqrt{\pi}}{(2l+1)(2l+1)!!} \sum_{\vec{T}} Y_{lm}(\hat{R}_T) \left( \frac{I_l(\alpha R_T)}{R_T^{l+1}} - \frac{\alpha^{2l+1} R_T^l}{2} \exp(-\alpha^2 R_T^2) \right) \\ & + \frac{(4\pi)^2}{V_C} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \frac{Y_{lm}(\hat{G})}{G^2} \frac{(-iG)^l}{(2l+1)!!} e^{i\vec{G}\cdot\vec{r}}. \end{aligned} \quad (14)$$

This result will be employed to simplify transformations needed in the FMM for periodic systems.

### III. GENERALIZED EWALD FOR THE FAST MULTIPOLE METHOD.

Because the FMM calculates the multipole moments of the charge in the simulation volume as a matter of course, there is a particular economy possible in summing the electrostatic potential due to the infinite array of periodic image volumes. The FMM requires the electrostatic potential in the simulation cell due to all images expressed as a local moment expansion in spherical harmonics,

$$\Phi'(\vec{r}) = 4\pi \sum_{l,m} L_{lm} r^l Y_{lm}(\theta, \phi). \quad (15)$$

Again, the accent on the potential indicates omission of charges in the simulation cell. The FMM also provides the transformation equations<sup>(1,2)</sup> necessary to calculate the local moments,  $L_{lm}$ , about the origin due to a multipole moment expansion of an image cell centered at a translation vector  $\vec{r}_t$ ,

$$L_{l_1 m_1} = \sum_{l_2, m_2} T_{l_1 m_1, l_2 m_2}^{LM}(\vec{r}_t) M_{l_2 m_2}, \quad (16)$$

where the upper limit on the sum in a practical calculation<sup>(2)</sup> is typically  $l_2 = 16$  or 32. The transformation matrix is given by

$$T_{l_1 m_1, l_2 m_2}^{LM}(\vec{r}_i) = t_{l_1, m_1, l_2, m_2}^{LM} \frac{Y_{l_1 + l_2, m_1 - m_2}^*(\hat{r}_i)}{r_i^{l_1 + l_2 + 1}} \quad (17)$$

with

$$t_{l_1, m_1, l_2, m_2}^{LM} = \frac{(-1)^{l_2 + m_2} \sqrt{4\pi}}{\sqrt{(2l_1 + 1)(2l_2 + 1)(2l_1 + 2l_2 + 1)}} \\ \times \sqrt{\frac{(l_1 + l_2 + m_1 - m_2)! (l_1 + l_2 - m_1 + m_2)!}{(l_1 + m_1)! (l_1 - m_1)! (l_2 + m_2)! (l_2 - m_2)!}}$$

The economy of the treatment of periodic boundary conditions within the FMM is based on recognizing that the sum of all periodic images needed for the local potential is, through Eq. 16, the sum of transformation matrices for each periodic image cell since the multipole moments are the same for every cell. While the multipole moments of the simulation may change in the course of a calculation, the transformation matrix for calculating the electrostatic potential due to all periodic images requires the summation of Eq. 17 only once for the specific Bravais lattice employed. Even in simulation methods which change the lattice constants during the simulation, such as in the study of crystal structure transformation,<sup>(8)</sup> the computational cost of recalculating the transformation matrix is constant independent of particle number with a fixed maximum multipole order and the total cost is very small compared to the energy and force calculation.

### A. Relation Between Transformation Sums and Real-Space Sums

The transformation matrix sums in the FMM require, after relabeling indices in Eq. 17, the sum

$$\sum_{\vec{r}} \frac{4\pi}{2l + 1} \frac{Y_{lm}(\hat{r}_i)}{r_i^{l+1}}. \quad (18)$$

This sum is identical to the electrostatic potential at the origin due to the periodic array of multipoles (excluding the multipole at the origin). The transformation matrix sum needed in Eq. 18 must then have the same convergence characteristics as the electrostatic potential sum in Eq. 2. For  $l = 1, 2$  the sum in Eq. 18 is conditionally convergent and absolutely convergent for  $l > 2$ , while the monopole sum,  $l = 0$ , is not included for a

neutral cell. (These characteristics are also shared with the lattice sum of Eq. 11.)

Typical choices for the method of summation of Eq. 2, and hence Eq. 18, are the Ewald sum described in Sect. II and summation over spherical shells, where all translation vectors with magnitude less than the radius  $R$  of a sphere are summed and then the sphere radius is allowed to go to infinity. Alternatives include ellipsoidal shells or slab-shaped volumes as reviewed by Smith.<sup>(6)</sup> The Ewald sum of Eq. 2 produces a periodic electrostatic potential where spherical or other direct-space sums generally produce nonperiodic results which depend on the shape of the region defining the sum.

In ref. 2, we showed that for a cubic lattice, carrying out the summations for the transformation matrices, Eq. 17, using the Ewald method produces an electrostatic potential that is equivalent to doing the direct summation of the electrostatic potential, Eq. 2, with spherical shells. We then quoted the standard result<sup>(7)</sup> for converting a spherical shell sum to a periodic Ewald sum in real space. We generalize here the connection between transformation sums and the resulting real-space electrostatic potential for noncubic lattices.

## B. Ewald Sums of the Transformation Matrices

Calculating the energy by using the fast multipole method with the transformation sums calculated using our Ewald technique is not the same as calculating using the Ewald technique for the electrostatic potential. The source of the difference can be identified by considering the convergence of the transformation sums. Because our simulation cell is always taken to be neutral there is no monopole moment term entering the transformation Eq. 17. Further, an overall constant added to the electrostatic potential does not change the energy of a neutral system, therefore contributions from any multipole to the  $L_{00}$  local moment in Eq. 17 can be ignored. This eliminates the need to calculate the transformation sum in Eq. 17 for  $l_1 = 0$  or  $l_2 = 0$ . Since the transformation sum, Eq. 18, has  $l = l_1 + l_2$ , only  $l = 2$  and higher sums are needed. Since the sum is absolutely convergent for  $l > 2$ , it is only the  $l = 2$  term in the sum of transformation matrices that is affected by the summation method. Specifically, the method of summation is only relevant for the  $l_1 = l_2 = 1$  sum, or the  $T_{1, m_1, 1, m_2}^{LM}$  transformation matrix, which is used in Eq. 17 to calculate the  $L_{1, m_1}$  local moment.

Our analysis above leads us to understand that the linear term in the electrostatic potential in the simulation cell depends on the summation method applied to the FMM transformation matrices to calculate the electrostatic potential due to the dipole moments in the infinite periodic array



of image cells. This linear term, a uniform electric field, is well known<sup>(6)</sup> from analysis of direct sums of the coulomb interaction, Eq. 2, where it arises due to dependence on summation method of the  $l=1$  term. (While direct sums of Eq. 2 also include dependence of summation method on the  $l=2$  terms, the result is a method-dependent constant electrostatic potential without physical consequence.) In the FMM the constant electric field arises due to the dependence of the transformation matrix on summation method of the  $l=2$  term in Eq. 18. Because the energetics and dynamics of the particles in the simulation cell are affected by this electric field, it is necessary to identify its origin. Because the electric field is determined entirely from dipole moments, we consider now a periodic array of  $l=1$  multipoles.

### C. Periodic Array of Dipoles

We will now establish the specific relationship between the Ewald potential constructed directly, as in Sect. II, and the electrostatic potential of the periodic system constructed via the FMM. We will provide a prescription for converting between the two results when the FMM summation of the transformation matrices is done using Ewald sums. From our discussion above, we need explicitly calculate only the linear term of the local moment expansion using both methods for a dipole array with dipoles of strength  $M_{1m}$  at every lattice point.

Since our interest is only in the constant electric field, it suffices to calculate the local expansion to linear terms in  $r$ . Identifying the resulting local moments as  $L_{1m}^E$  and  $L_{1m}^{FMM}$  for the two expansion respectively, we may write, following Eq. 15, to first order in  $r$ ,

$$\Phi'_E(\vec{r}) = 4\pi \sum_{m'} L_{1m'}^E r Y_{1m'}(\theta, \phi) + C_E + \dots \quad (19)$$

$$\Phi'_{FMM}(\vec{r}) = 4\pi \sum_{m'} L_{1m'}^{FMM} r Y_{1m'}(\theta, \phi) + C_{FMM} + \dots \quad (20)$$

Here,  $C_E$  and  $C_{FMM}$  are two constants which are not of interest. The higher order terms, according to our arguments above, are the same in both cases.

Because the Ewald sum, Eq. 13, is independent of the Gaussian width parameter  $\alpha$ , it is most convenient to employ the large  $\alpha$  limit (narrow Gaussians) in calculating the linear terms in the electrostatic potentials above. With  $\alpha$  approaching infinity, we may neglect all terms in the short-range part of the Ewald sum except the term in the simulation cell itself. In the reciprocal part, we must sum all reciprocal lattice vectors. The

short-range part of the Ewald sum, Eq. 9, contains only  $V_S^{lm}(\vec{r})$ . Substituting the small argument expansion of  $I_l(\alpha r)$  from Eq. 8,

$$I_l(\alpha r) = \frac{(2l+1)!!}{2^l} \frac{\sqrt{\pi}}{4} + O((\alpha r)^{2l+3}), \quad (21)$$

yields the short-range potential for small  $r$  in the form which we will need below,

$$V_S^{lm}(\vec{r}) = \frac{4\pi}{2l+1} Y_{lm}(\hat{r}) \left( \frac{1}{r^{l+1}} - \frac{2\alpha^{2l+1} r^l}{\sqrt{\pi} (2l+1)!!} \right) + O(\alpha^{2l+3} r^{l+2}). \quad (22)$$

We first evaluate the linear terms in the FMM potential using the local moment definition, Eq. 16, summed over all translation vectors except the origin,

$$L_{1,m'}^{FMM} = \sum_{\vec{T}} T_{1,m',1,m}^{LM}(\vec{r}_t) M_{1,m}.$$

From Eq. 17, the dipole-dipole transformation matrix is a sum of  $l=2$  terms,

$$4\pi L_{1,m'}^{FMM} = 5M_{1,m} t_{1,m',1,m}^{LM} \left( \sum_{\vec{T}} \frac{4\pi}{5} \frac{Y_{2,m'-m}^*(\hat{r}_t)}{r_t^3} \right). \quad (23)$$

This sum is conditionally convergent. It will be done with the Ewald method and, apart from the bare quadrupole term at the origin, is given by the complex conjugate of the  $l=2$  sum in Eq. 13, evaluated at the origin. Since we are working in the narrow Gaussian limit, we retain only the simulation cell term, Eq. 22, in the direct space sum and Eq. 13 produces

$$\Phi^{2,m'-m}(\vec{r}) = V_S^{2,m'-m}(\vec{r}) + \sum_{\vec{G}} \phi_{\vec{G}}^{2,m'-m} e^{i\vec{G}\cdot\vec{r}} \quad (24)$$

For small  $r$ , Eq. 21, shows that  $V_S^{2,m'-m}(\vec{r})$  contributes only the pure quadrupole which is to be subtracted out as the term corresponding to  $\vec{T}=0$ ,

$$\begin{aligned} \lim_{r \rightarrow 0} (\Phi^{2,m'-m}(\vec{r}) - V_S^{2,m'-m}(\vec{r})) \\ = \frac{(4\pi)^2}{V_C} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \frac{Y_{2,m'-m}(\hat{G})}{G^2} \frac{(-iG)^2}{5!!}. \end{aligned}$$

The complex conjugate of this result is the term in parentheses in Eq. 23 which was needed for  $\Phi'_{FMM}$  in Eq. 20. The linear term in the electrostatic potential due to all image dipoles is then

$$\begin{aligned} & 4\pi \sum_{m'} L_{1m'}^{FMM} r Y_{1m'}(\theta, \phi) \\ &= -M_{1,M} \frac{(4\pi)^2}{3V_c} \sum_{m'} \sum_{\vec{G}} r Y_{1m'}(\theta, \phi) t_{1,m',1,m}^{LM} \exp\left(-\frac{G^2}{4\alpha^2}\right) Y_{2,m'-m}^*(\hat{G}). \end{aligned} \quad (25)$$

For the direct Ewald potential,  $\Phi'_E$ , we must subtract out the bare dipole from the short-range part of Eq. 9 with  $l=1$ . For large  $\alpha$  this follows from Eq. 22,

$$\Phi_S^{1m}(\vec{r}) = V_S^{1m}(\vec{r}) = \frac{4\pi}{3} M_{1m} Y_{1m}(\hat{r}) \left( \frac{1}{r^2} - \frac{4\alpha^3 r}{3\sqrt{\pi}} \right) + O(\alpha^5 r^3).$$

The long-range part of  $\Phi'_E$ , Eq. 12 for  $l=1$ , can be expanded for small  $r$  to

$$\begin{aligned} \Phi_L^{1m}(\vec{r}) &= \Phi_L^{1m}(0) + \frac{(4\pi)^2}{V_c} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \\ &\quad \times \frac{M_{1m} Y_{1m}(\hat{G})}{G^2} \frac{(-iG)}{3} \left( iGr \frac{4\pi}{5} \sum_{m'} Y_{1m'}^*(\hat{G}) Y_{1m}(\hat{r}) \right) + \dots \end{aligned}$$

The product  $Y_{1m}(\hat{G}) Y_{1m'}^*(\hat{G})$ , can be written as a linear combination of  $l=0$  and  $l=2$  spherical harmonics. The  $l=2$  terms can be written in terms of the transformation matrix with  $l_1 + l_2 = 2$ . Using the notation of Eq. 17, the reciprocal lattice sum becomes

$$\begin{aligned} \Phi_L^{1m}(\vec{r}) &= \Phi_L^{1m}(0) + M_{1m} \frac{(4\pi)^2}{V_c} \sum_{m'} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \\ &\quad \times \left[ \frac{\delta_{m,m'}}{9} - \frac{t_{1,m',1,m}^{LM}}{3} Y_{2,m'-m}^*(\hat{G}) \right] r Y_{1m}(\hat{r}). \end{aligned}$$

Extracting the linear terms from the sum,  $\Phi_S^{1m}(\vec{r}) + \Phi_L^{1m}(\vec{r})$ , and comparing to our definition of  $\Phi'_E$  in Eq. 19, yields our result,

$$\begin{aligned}
& 4\pi \sum_{m'} L_{1m'}^E r Y_{1m'}(\theta, \phi) \\
&= -\frac{4\pi}{3} M_{1m} Y_{1m}(\hat{r}) \left( \frac{4\alpha^3 r}{3\sqrt{\pi}} \right) \\
&\quad + M_{1m} \frac{(4\pi)^2}{9V_C} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \\
&\quad - M_{1m} \frac{(4\pi)^2}{V_C} \sum_{m'} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) \frac{t_{1,m',1,m}^{LM}}{3} Y_{2,m'-m}^*(\hat{G}) r Y_{1m}(\hat{r}).
\end{aligned} \tag{26}$$

The difference in the linear terms of  $\Phi'_E$  and  $\Phi'_{FMM}$ , Eqs. 25 and 26, yields

$$\begin{aligned}
& \Phi'_E(\vec{r}) - \Phi'_{FMM}(\vec{r}) \\
&= M_{1m} r Y_{1m}(\hat{r}) \left( \frac{(4\pi)^2}{9V_C} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) - \frac{16}{9} \sqrt{\pi} \alpha^3 - \frac{(4\pi)^3}{9V_C} \right), \tag{27}
\end{aligned}$$

plus a constant. Since there is no singularity at  $G=0$ , we included the  $G=0$  term in the sum and subtracted it out explicitly. The sum can be converted to an integral with an error given by the Euler–Maclaurin summation formula that goes to zero as  $\alpha$  gets large,

$$\frac{(4\pi)^3}{9V_C} \sum_{\vec{G}} \exp\left(-\frac{G^2}{4\alpha^2}\right) = \frac{16}{9} \sqrt{\pi} \alpha^3. \tag{28}$$

The sum exactly cancels the short-range contribution that also diverged like  $\alpha^3$ . Generalizing to arbitrary dipole moments yields,

$$\Phi'_E(\vec{r}) - \Phi'_{FMM}(\vec{r}) = -\frac{(4\pi)^3}{9V_C} r \sum_m Y_{1m}(\hat{r}) M_{1m}. \tag{29}$$

The difference between the two methods of determining the potential, Eq. 29, is a constant electric field proportional in magnitude and parallel in direction with the dipoles on the lattice. Thus, if the total dipole moment of the charge in the simulation volume is  $\vec{D}$ , then the electrostatic potential of the FMM gives the usual<sup>(7)</sup> extra energy,

$$PE_{ewald} = PE_{fmm} - \frac{2\pi}{3V_C} \vec{D} \cdot \vec{D}. \tag{30}$$

As described by Smith,<sup>(6)</sup> this is indeed the extra field that results from summing all interaction by spherical shells. We confirm our initial assertion, the calculation of the electrostatic potential using the Ewald sums for the transformation matrices produces a potential in the simulation cell that is the same as having directly calculated the conditionally convergent electrostatic potential, Eq. 2, by summing over spherical shells. To obtain the periodic Ewald potential one must subtract the constant electric field as specified by Eq. 29. If any method of summing transformation matrices other than the Ewald method had been employed to carry out the conditionally convergent sum of Eq. 23, then the value of the sum would change by a constant. That constant would alter the coefficient of the electric field in the simulation volume and accordingly alter the difference between the periodic Ewald potential and the FMM potential, Eq. 29, in the simulation volume.

#### IV. SUMMARY

Our principle result is an explicit procedure for calculating the infinite sum of transformation matrices, Eq. 17, needed to employ the FMM in a system with the periodicity of an arbitrary Bravais lattice; Having derived the generalization of the Ewald sum for the electrostatic potential due to a periodic array of multipoles, Eq. 14, the summation needed for the transformation matrices given in Eq. 18, can be carried out using the same Ewald summation formula and evaluating the result at the origin after removing the multipole field at the origin. To be specific, let  $\vec{a}_1, \vec{a}_2, \vec{a}_3$ , be the three translation vectors defining the period system and let  $\vec{g}_1, \vec{g}_2, \vec{g}_3$ , be the three reciprocal lattice vectors such that  $\vec{g}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$ . Then defining,  $\vec{G}_{kjp} = k\vec{g}_1 + j\vec{g}_2 + p\vec{g}_3$  and  $\vec{R}_{stu} = s\vec{a}_1 + t\vec{a}_2 + u\vec{a}_3$ , the Ewald sum can be explicitly written,

$$\begin{aligned} & \sum_{s, t, u \neq 0, 0, 0} \frac{4\pi}{2l+1} \frac{Y_{lm}(\hat{R}_{stu})}{R_{stu}^{l+1}} = \Phi^{lm'}(0) \\ & = \frac{2^{l+4} \sqrt{\pi}}{(2l+1)(2l+1)!!} \sum_{s, t, u \neq 0, 0, 0} Y_{lm}(\hat{R}_{stu}) \left( \frac{I_l(\alpha R_{stu})}{R_{stu}^{l+1}} - \frac{\alpha^{2l+1} R_{stu}^l}{2} \exp(-\alpha^2 R_{stu}^2) \right) \\ & \quad - \frac{(4\pi)^2}{V_C} \frac{1}{(2l+1)!!} \sum_{k, j, p \neq 0, 0, 0} \exp\left(-\frac{G_{kjp}^2}{4\alpha^2}\right) Y_{lm}(\hat{G}_{kjp}) (-iG_{kjp})^{l-2} \end{aligned} \quad (31)$$

When employing Eq. 31 in calculating Ewald sums of transformation matrices, the resulting electrostatic potential is not periodic. To obtain the

periodic Ewald electrostatic potential, Eq. 29 is used to remove the constant electric field.

Finally, we observe that the use of the generalized Ewald sum, Eq. 14, does not necessarily require the full FMM apparatus. It seems likely that for small or inhomogeneous systems hybrid methods for evaluating the electrostatic potential may prove efficient. One could employ direct,  $O(N^2)$ , evaluation of coulomb interactions and use the Ewald potential in terms of multipole moments to obtain the sum of distant interactions.

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