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An Optimized Ewald Method for Long-Ranged Potentials

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A modified Ewald method is described for calculating the potential and its gradient for systems with long-ranged interactions and periodic boundary conditions (PBC). Following the work of Natoli and Ceperley, the division between the direct- and reciprocal-space terms is optimized by minimizing the squared deviation of the approximate representation from the exact form. In simulations using this method most of the computational effort is required in performing the reciprocal-space summation. For comparable accuracy, this method requires between one half and one third of the number of reciprocal-space lattice vectors of the standard Ewald technique. In addition our technique requires the choice of only a single parameter which controls the accuracy achieved, rather than the three parameters required in the standard Ewald technique. We give formulae (for the face-centered cubic (*fcc*), body-centered cubic (*bcc*) and simple cubic (*sc*) lattices), which allow for efficient evaluation of the terms in the reciprocal-space summation. © 1994 Academic Press, Inc.

I. INTRODUCTION

In molecular dynamics and Monte Carlo simulations the evaluation of the interactions between the particles is normally a costly part of the computation. PBC are often used in simulations of condensed matter systems and, if the interactions between the particles are long-ranged, then the summation over the periodic images may converge very slowly. The most popular method for dealing with this problem is the Ewald method [1], in which the expression for the interaction energy or potential is written in the form of two summations, one in direct-space and the other in reciprocal-space, which both converge fairly rapidly. Although Ewald's method was invented before the age of computers it is still in widespread use today.

Our particular interest is in quantum Monte Carlo calculations for condensed matter systems, which involve on the order of hundreds of electrons and nuclei interacting via the Coulomb potential. Normally the repeated evaluation of the interaction terms, and similar terms in the wavefunction, for different particle configurations is the most costly part of the calculation. Compared with classical simulations the number of particles is not large, but the accuracy required is comparatively high. In Monte Carlo methods the particles are normally moved one at a time and consequently the potential is evaluated at a point in space, rather than evaluating the total potential energy of the particles. This methodology makes the use of the so-called particle–particle and particle–mesh methods [3] and the multipole algorithm developed by Greengard [4] less effective. In addition, Greengard's method is restricted to Coulomb potentials, and although it is $O(N)$, it is inefficient unless the simulation involves at least several thousands of particles. Consequently the Ewald method and variants thereof have normally been used. Although the optimized Ewald method was developed for use in quantum Monte Carlo calculations it may well find applications in other areas such as classical Monte Carlo and molecular dynamics methods. We have considered simulation cells with high symmetry, but we do not assume any symmetry for the arrangement of the particles within the simulation cell, so that our method can be used in supercell studies of perfect crystalline solids, defective solids, surfaces, and liquids, etc.

In this paper we describe our derivation and evaluation of a modified Ewald formula, which we have found to be both accurate and efficient. We will discuss the evaluation of both the potential and its gradient. These methods are suitable for any long-ranged pairwise interaction potential, although we will concentrate on the case of the Coulomb potential. Our method for dividing the potential between the direct- and reciprocal-space summations is based on the ideas of Natoli and Ceperley [2], although our formulation differs from theirs in some important respects. When applying these methods, most of the computational effort is spent in evaluating the reciprocal-space sum. To facilitate efficient evaluation of the reciprocal-space sum we have manipulated the various terms into convenient forms which we tabulate for the *sc*, *bcc*, and *fcc* lattices.

II. OPTIMIZED DIVISION BETWEEN DIRECT AND RECIPROCAL SPACE

The Ewald formula for the Coulomb potential at a point $\mathbf{r}$ due to a periodic array of point charges is, in atomic units,

$$V_c(\mathbf{r}) = \sum_{\mathbf{R}} \frac{\operatorname{erfc}(\kappa|\mathbf{r}-\mathbf{R}|)}{|\mathbf{r}-\mathbf{R}|} - \frac{\pi}{\kappa^2\Omega} + \frac{4\pi}{\Omega}\sum_{\mathbf{G}\neq 0}\frac{\exp(-\mathbf{G}^2/4\kappa^2)}{\mathbf{G}^2}\cos(\mathbf{G}\cdot\mathbf{r}), \tag{1}$$

where $\{\mathbf{R}\}$ is the set of direct-space translation vectors of the supercell lattice, $\{\mathbf{G}\}$ is the corresponding set of reciprocal-space translation vectors, and Ω is the volume of the simulation cell. The potential $V_c(\mathbf{r})$ is independent of the value of the parameter κ, which is chosen to give reasonable convergence of both the direct- and reciprocal-space summations. The Ewald formula is one example of a type of expression for arbitrary potentials which can be written in terms of direct- and reciprocal-space summations

$$V(\mathbf{r}) = \sum_{\mathbf{R}} f(|\mathbf{r} - \mathbf{R}|) + \sum_{\mathbf{G}} a_{\mathbf{G}} \cos(\mathbf{G} \cdot \mathbf{r}), \tag{2}$$

where there are infinitely many pairs of functions $f(r)$ and Fourier coefficients $a_{\mathbf{G}}$ which reproduce the correct potential [6]. If the direct-space summation is truncated then the resulting formula is not periodic and the standard procedure is to reduce the displacement vector $\mathbf{r}$ into the Wigner–Seitz (WS) cell, so that the effect of the truncation is minimized. With this convention $V(\mathbf{r})$ can be represented exactly by Eq. (2), even when the direct-space summation is truncated, because the cosines form a complete set (for potentials with inversion symmetry). In practice the reciprocal-space summation must be truncated after a certain number of vectors, N_G, and often one truncates the direct-space summation so that it includes only the $\mathbf{R} = \mathbf{0}$ vector, giving

$$V(\mathbf{r}) \simeq f(r) + \sum_{n=1}^{N_G} a_{\mathbf{G}_n} \cos(\mathbf{G}_n \cdot \mathbf{r}). \tag{3}$$

We will use this form of approximation for $V(\mathbf{r})$, and we now require the form of the radial function $f(r)$ and Fourier coefficients $a_{\mathbf{G}_n}$ which give the best approximation to the potential $V(\mathbf{r})$. Recently, Natoli and Ceperley [2] have developed a method for determining the optimized functions $f(r)$ and Fourier coefficients $a_{\mathbf{G}_n}$, based on minimizing the squared deviation from the exact potential, i.e., minimizing A_N, where

$$A_N = \frac{1}{\Omega} \int \left[V(\mathbf{r}) - f(r) - \sum_{n=1}^{N_G} a_{\mathbf{G}_n} \cos(\mathbf{G}_n \cdot \mathbf{r}) \right]^2 g(\mathbf{r})\, d\mathbf{r}, \tag{4}$$

where the weight function $g(\mathbf{r})$ is taken to be equal to unity inside the WS cell and zero outside. In the next two sections we will describe our implementation of these ideas for obtaining good approximations to the potential and its gradient, which differs from that of Natoli and Ceperley in several significant respects.

III. CALCULATION OF THE OPTIMIZED FUNCTIONS FOR THE POTENTIAL

It will be convenient to rewrite the reciprocal-space sum in Eq. (4) in terms of shells of reciprocal-space lattice vectors. Noting that the Fourier coefficients $a_{\mathbf{G}_n}$ depend only on the shell of reciprocal-space lattice vectors to which $\mathbf{G}_n$ belongs, we have

$$\sum_{n=1}^{N_G} a_{\mathbf{G}_n} \cos(\mathbf{G}_n \cdot \mathbf{r}) = \sum_{s=1}^{N_s} a_s \sum_{\alpha=1}^{n_s} \cos(\mathbf{G}_\alpha \cdot \mathbf{r}) \tag{5}$$

$$= \sum_{s=1}^{N_s} a_s H_s(\mathbf{r}), \tag{6}$$

where s labels the N_s shells of reciprocal-space lattice vectors and α labels the n_s vectors in shell s. The determination of the functions $f(r)$ and a_s which minimize A_N is simple if one notes that, whatever the function $f(r)$ is, the coefficients a_s are *always* given by

$$a_s = \frac{1}{n_s \Omega} \int [V(\mathbf{r}) - f(r)] H_s(\mathbf{r}) g(\mathbf{r})\, d\mathbf{r}. \tag{7}$$

This result follows directly from the orthogonality of the cosine functions. Substituting a_s into Eq. (4) and setting the differential with respect to the radial function $f(r)$ equal to zero gives

$$\begin{aligned} f(r) \frac{r^2}{\Omega} \int g(\mathbf{r}) \sin\theta\, d\theta\, d\phi &= \frac{r^2}{\Omega} \int V(\mathbf{r}) g(\mathbf{r}) \sin\theta\, d\theta\, d\phi \\ &\quad - \sum_{s=1}^{N_s} \frac{1}{n_s} \left\{ \frac{1}{\Omega} \int [V(\mathbf{r}) - f(r)] H_s(\mathbf{r}) g(\mathbf{r})\, d\mathbf{r} \right\} \\ &\quad \times \left\{ \frac{1}{\Omega} \int H_s(\mathbf{r}) g(\mathbf{r}) \sin\theta\, d\theta\, d\phi \right\}. \end{aligned} \tag{8}$$

Equation (8) is a Fredholm integral equation of the second kind for $f(r)$. There is some interest in isotropic approximations to the Ewald potential [5], although such approximations are not accurate enough for our purposes. Equation (8) shows that the best isotropic approximation (in the least-squares sense) at radius r is given by the average of $V(\mathbf{r})$ over that portion of the surface of the sphere of radius r which lies inside the WS cell. We have solved Eq. (8) using a basis of Chebyshev polynomials. We expand $f(r)$ as a sum of Chebyshev polynomials, T_i, up to degree M,

$$f(r) = \sum_{i=0}^{M} b_i T_i(\tilde{r}), \tag{9}$$

where $\tilde{r}$ is a scaled variable given by

$$\tilde{r} = \frac{(2r - r_{\max})}{r_{\max}} \tag{10}$$

and where $r_{\max}$ is the maximum distance from the origin to the boundary of the WS cell. Multiplying Eq. (8) by $T_j(\tilde{r})$ and integrating with respect to r gives the matrix equation

$$\begin{aligned}
\sum_{i=0}^{M} \left\{ \frac{1}{\Omega} \int T_j(\tilde{r}) T_i(\tilde{r}) g(\mathbf{r})\, d\mathbf{r} \right\} b_i
&= \frac{1}{\Omega} \int V(\mathbf{r}) T_j(\tilde{r}) g(\mathbf{r})\, d\mathbf{r} \\
&\quad - \sum_{s=1}^{N_s} \frac{1}{n_s} \left\{ \frac{1}{\Omega} \int V(\mathbf{r}) H_s(\mathbf{r}) g(\mathbf{r})\, d\mathbf{r} \right\} \\
&\quad \times \left\{ \frac{1}{\Omega} \int H_s(\mathbf{r}) T_j(\tilde{r}) g(\mathbf{r})\, d\mathbf{r} \} \\
&\quad + \sum_{s=1}^{N_s} \sum_{i=0}^{M} \frac{1}{n_s} \left\{ \frac{1}{\Omega} \int T_i(\tilde{r}) H_s(\mathbf{r}) g(\mathbf{r})\, d\mathbf{r} \right\} \\
&\quad \times \left\{ \frac{1}{\Omega} \int H_s(\mathbf{r}) T_j(\tilde{r}) g(\mathbf{r})\, d\mathbf{r} \right\} b_i .
\end{aligned} \tag{11}$$

Simple manipulations show that Eq. (11) is equivalent to Eq. (12) of Ref. [2]. Equation (11) must be solved to obtain the coefficients b_i, which can then be used, in conjunction with Eqs. (7) and (9), to obtain the Fourier coefficients a_s. The maximum degree of the Chebyshev polynomials, M, used in the expansion of $f(r)$ and the maximum value, N, of the index j in Eq. (11), need not be related. We use $N > M$, which results in an overdetermined set of linear equations which are solved by singular value decomposition [8], giving the best approximate solution in the least-squares sense.

Each of the integrals in Eq. (11) can be evaluated by integrating over only the irreducible wedge of the WS cell and multiplying by the number of equivalent wedges. For the cubic cases considered in this paper there are 48 equivalent wedges and, therefore, the saving is considerable. The integrals of products of Chebyshev polynomials may be evaluated efficiently using the product formula

$$T_i(x) T_j(x) = \tfrac{1}{2}[T_{i+j}(x) + T_{|i-j|}(x)]. \tag{12}$$

Natoli and Ceperley [2] used a basis of quintic splines for the radial basis functions, and the radial function $f(r)$ was constrained to vanish smoothly at a radius $r_{\min}$, where $r_{\min}$ is the minimum distance from the origin to the surface of the WS cell. If $f(r)$ does not tend smoothly to a constant at (or inside of) $r_{\min}$ then the resulting approximation to $V(\mathbf{r})$ will have a discontinuous first derivative at the surface of the WS cell, which the exact $V(\mathbf{r})$ does not have. However, the minimization procedure used to determine $f(r)$ and a_s tends to give a function $f(r)$ which very nearly goes smoothly to a constant at $r_{\min}$ and we do not believe that it is advantageous to impose that $f(r)$ obeys this condition exactly.

TABLE I

The RMS and Maximum Errors in the Potential for Different Numbers, N_s of Shells of Reciprocal-Lattice Vectors, Using the Optimized Ewald Formula (Eq. (3)) for the *fcc* Lattice

N_s	N_G	RMS error	Max. error
3	26	8.1×10^{-3}	1.0×10^{-2}
8	112	2.5×10^{-5}	9.8×10^{-4}
13	258	1.0×10^{-6}	3.4×10^{-6}

Note. N_G is the number of reciprocal-lattice vectors in N_s shells.

The Coulomb potential, $V_c(\mathbf{r})$, diverges like $1/r$ at the origin. We find it convenient to remove this divergence, and the potential $V(\mathbf{r})$ that we use in Eq. 11 is

$$V(\mathbf{r}) = V_c(\mathbf{r}) - 1/r. \tag{13}$$

After solution of Eq. (11) the $1/r$ term may be added back into the function $f(r)$. The maximum degrees, N and M, of the Chebyshev polynomials in Eq. (11) control the accuracy of the solution of Eq. (8). Appropriate values will depend on the problem at hand, but for the *fcc* lattice we have used $M = 30 - 50$ and $N = 60 - 250$. The number, N_s, of shells of reciprocal-space lattice vectors used controls the accuracy of the approximation (Eq. (3)) to the exact potential (Eq. (1)). Appropriate values of N_s will depend on the requirements of accuracy and computational speed. A convenient measure of the error in the approximate representation of the potential is the dimensionless root-mean square (RMS) deviation, defined as $LA_N^{1/2}$, where L is the lattice constant and A_N is given by Eq. (4). Also of interest is the maximum error, defined as the square root of the maximum value of the integrand in Eq. (4), multiplied by L. In Table I we give the RMS and maximum errors for the optimized Ewald sum for three values of the numbers of shells of reciprocal-space lattice vectors, N_s, for the *fcc* lattice. For comparison we give in Table II the RMS and maximum errors for the standard Ewald formula of Eq. (1) for seven values of N_s, summing only over the $\mathbf{R} = \mathbf{0}$ term and with the value of κ chosen to minimize the RMS error at each N_s. From these tables one can see that the number of shells of reciprocal-lattice vectors required for a given accuracy is between two and three times less for the optimized Ewald sum.

IV. CALCULATION OF THE GRADIENT OF THE POTENTIAL

Although the algorithm described in the previous section works very well for approximating the potential, $V(\mathbf{r})$, some difficulties arise when calculating the gradient of the potential, $\nabla V(\mathbf{r})$. In many quantum Monte Carlo calculations one uses an approximate wavefunction which correlates the particles in pairs. For electronic systems a typical form of the pair part of the wavefunction is

$$u(r) = \frac{1}{r} - \frac{e^{-r/F}}{r} \tag{14}$$

which is the sum of a long-ranged and a short-ranged term. In addition to the (Ewald) sum of u over all pairs of electrons, we also require the sums of ∇u and $\nabla^2 u$. In our implementation we sum the short-ranged term in direct-space and perform Ewald sums for the contribution of the long-ranged term to the sum over all pairs of electrons of u and ∇u. An Ewald sum is not required for the $\nabla^2 u$ contribution because it is short-ranged.

If we use the gradient of Eq. (3) and the functions $f(r)$ and a_s determined as in Section III, we find that the relative errors in the gradient are large close to the surface of the WS cell. In this region the magnitude of the gradient is small and the oscillations arising from the reciprocal-space sum give large relative errors in the gradient. Close to the origin the error in the gradient is also significant (although the relative error is small because the gradient is very large in this region). These problems also arise with the standard Ewald formula of Eq. (1), but are less pronounced because one normally uses many more terms in the reciprocal-space summation. Natoli and Ceperley [2] also noted a similar problem in the calculation of second derivatives, which they overcame by minimizing the error in the representation of the second derivative of the potential instead of the potential itself. We have not followed this procedure because in our simulations we use Ewald sums for the potential and its first derivative only.

One idea might be to use the function $g(\mathbf{r})$ in Eq. (4) to give a larger weight to the regions close to the surface of the WS cell, where the gradient is poorly described. However, this has the disadvantage that the cosine functions are no longer orthogonal with respect to the weight function, and the minimization of Eq. (4) becomes more difficult, so we have not followed this approach. Our approach is to minimize the squared deviation from the exact gradient, i.e., to minimize B_N, where

$$B_N = \frac{1}{\Omega}\int \left[\nabla V(\mathbf{r}) - \nabla f(r) - \sum_{s=1}^{N_s} a_s \nabla H_s\right]^2 g(\mathbf{r})\, d\mathbf{r}. \tag{15}$$

TABLE II

The RMS and Maximum Errors in the Potential for Different Numbers, N_s of Shells of Reciprocal-Lattice Vectors, Using the Standard Ewald Formula (Eq. (1)) for the *fcc* Lattice

N_s	N_G	κL	RMS error	Max. error
3	26	5.0	1.3×10^{-2}	4.6×10^{-2}
8	112	6.3	9.4×10^{-4}	5.6×10^{-3}
13	258	7.3	1.5×10^{-4}	1.1×10^{-3}
18	386	7.8	4.0×10^{-5}	3.7×10^{-4}
23	560	8.3	1.3×10^{-5}	1.1×10^{-4}
28	748	8.7	5.1×10^{-6}	4.5×10^{-5}
33	964	9.1	1.5×10^{-6}	1.7×10^{-5}

Note. Only the $\mathbf{R} = \mathbf{0}$ term is used in the direct-space summation and the value of κL is chosen to minimize the RMS error. N_G is the number of reciprocal-lattice vectors in N_s shells.

The minimization of B_N is carried out in a manner analogous to that of A_N. The radial derivative, df/dr is expanded as a sum of Chebyshev polynomials,

$$\frac{df}{dr} = \sum_{i=0}^{M} c_i T_i(\tilde{r}), \tag{16}$$

and the resulting matrix equation is

$$\begin{aligned}
&\sum_{i=0}^{M} \left\{\frac{1}{\Omega}\int T_j(\tilde{r})T_i(\tilde{r})g(\mathbf{r})\, d\mathbf{r}\right\} c_i \\
&\quad = \frac{1}{\Omega}\int \left[\frac{xV_x + yV_y + zV_z}{r}\right] T_j(\tilde{r})g(\mathbf{r})\, d\mathbf{r} \\
&\qquad - \sum_{s=1}^{N_s} \frac{1}{G_s^2 n_s}\left\{\frac{1}{\Omega}\int \left[V_x H_{xs} + V_y H_{ys} + V_z H_{zs}\right] g(\mathbf{r})\, d\mathbf{r}\right\} \\
&\qquad \times \left\{\frac{1}{\Omega}\int \left[\frac{xH_{xs} + yH_{ys} + zH_{zs}}{r}\right] T_j(\tilde{r})g(\mathbf{r})\, d\mathbf{r}\right\} \\
&\qquad + \sum_{s=1}^{N_s} \frac{1}{G_s^2 n_s}\sum_{i=0}^{M} \left\{\frac{1}{\Omega}\int \left[\frac{xH_{xs} + yH_{ys} + zH_{zs}}{r}\right] T_i(\tilde{r})g(\mathbf{r})\, d\mathbf{r}\right\} \\
&\qquad \times \left\{\frac{1}{\Omega}\int \left[\frac{xH_{xs} + yH_{ys} + zH_{zs}}{r}\right] T_j(\tilde{r})g(\mathbf{r})\, d\mathbf{r}\right\} c_i,
\end{aligned} \tag{17}$$

where V_x and H_{xs} denote the x-derivatives of the potential $V(\mathbf{r})$ and the reciprocal-space basis functions H_s (Eq. (6)), and G_s^2 is the squared length of the reciprocal-space lattice vectors in shell s. Equation (17) is written in a form in which each of the integrals may be evaluated by integrating over the irreducible wedge of the WS cell and multiplying by the number of such wedges. For solution of Eq. (17) we remove the divergence in the gradient of the Coulomb potential at the origin, as in Eq. (13).

We solve Eq. (17) using the same singular value decomposition method used for Eq. (11). Appropriate values of the maximum degrees of the Chebyshev polynomials, N and M, are similar to those used for Eq. (11). The Fourier coefficients, a_s, are then calculated from

$$a_s = \frac{1}{n_s G_s^2 \Omega} \int \left\{ \left[V_x - \frac{x}{r}\frac{df}{dr} \right] H_{xs} + \left[V_y - \frac{y}{r}\frac{df}{dr} \right] H_{ys} + \left[V_z - \frac{z}{r}\frac{df}{dr} \right] H_{zs} \right\} g(\mathbf{r})\, d\mathbf{r}. \tag{18}$$

Using the method of this section we find that the accuracy of the representation of the gradient of the potential near the origin and at the surface of the WS cell is significantly better than that given by the gradient of the potential obtained from the method of Section III.

For some applications it may be desirable that the approximation used for the gradient of the potential is precisely equal to the gradient of the approximation used for the potential itself. This would not be the case if Eq. (11) was used to obtain the approximation for the potential while Eq. (17) was used to obtain the gradient. This problem may be circumvented by using Eq. (17) for the gradient and integrating the radial function df/dr to obtain an expression for the potential itself. This is best done by integrating the Chebyshev representation of Eq. (16); the constant of integration must be determined by a separate calculation.

V. EVALUATION OF THE RECIPROCAL-SPACE SUM

Evaluation of the potential at a point in space arising from a particle and its periodic images proceeds as follows:

1. Reduce the displacement vector into the WS cell, giving the reduced vector **r**.
2. Evaluate the contribution to the potential from the radial function $f(r)$.
3. Evaluate the contribution to the potential from the reciprocal-space sum.

Evaluation of the gradient is performed in an entirely analogous manner. Efficient algorithms for carrying out operation (1) are known for a number of shapes of simulation cell. For the *sc* lattice the operation is trivial, while for the *fcc* lattice (for which the WS cell is a truncated octahedron) and the *bcc* lattice (where the WS cell is a regular dodecahedron) efficient algorithms are given in Appendix F of [7].

To perform operation (2) we tabulate $f(r)$ on a fine radial grid and use a simple interpolation procedure, which is very efficient. Operation (3) is the most computationally expensive part of the algorithm, even when using the optimized Fourier coefficients described in Sections III and IV. In order to reduce this cost we have developed a method in which the reciprocal-space basis functions $H_s(\mathbf{r})$ are manipulated into forms which allow rapid evaluation. When evaluating Fourier series it is standard practice to use recurrence relations to calculate the trigonometric functions, so as to avoid repeated calls to the computer's intrinsic trigonometric functions. Modern computers generally have very fast intrinsic trigonometrical functions, which reduce the benefits of recurrence relations, but it is still generally more efficient to use recurrence relations.

TABLE III

Formulae for the Reciprocal-Space Basis Functions, H_s (Eq. (19)), for the *sc* Lattice

s	n_s	G_s^2	H_s
1	6	1	$2[\alpha_1 + \beta_1 + \gamma_1]$
2	12	2	$4[\alpha_1\beta_1 + \alpha_1\gamma_1 + \beta_1\gamma_1]$
3	8	3	$8[\alpha_1\beta_1\gamma_1]$
4	6	4	$2[\alpha_2 + \beta_2 + \gamma_2]$
5	24	5	$4[\alpha_1\gamma_2 + \beta_1\gamma_2 + \beta_2\gamma_1 + \alpha_2\gamma_1 + \alpha_1\beta_2 + \alpha_2\beta_1]$
6	24	6	$8[\alpha_1\beta_1\gamma_2 + \alpha_1\beta_2\gamma_1 + \alpha_2\beta_1\gamma_1]$
7	12	8	$4[\alpha_2\beta_2 + \alpha_2\gamma_2 + \beta_2\gamma_2]$
8	30	9	$8[\alpha_2\beta_2\gamma_1 + \alpha_2\beta_1\gamma_2 + \alpha_1\beta_2\gamma_2] + 2[\alpha_3 + \beta_3 + \gamma_3]$
9	24	10	$4[\alpha_3\beta_1 + \alpha_3\gamma_1 + \alpha_1\beta_3 + \alpha_1\gamma_3 + \beta_3\gamma_1 + \beta_1\gamma_3]$
10	24	11	$8[\alpha_3\beta_1\gamma_1 + \alpha_1\beta_3\gamma_1 + \alpha_1\beta_1\gamma_3]$
11	8	12	$8[\alpha_2\beta_2\gamma_2]$
12	24	13	$4[\alpha_2\gamma_3 + \alpha_2\beta_3 + \beta_2\gamma_3 + \beta_3\gamma_2 + \alpha_3\beta_2 + \alpha_3\gamma_2]$
13	48	14	$8[\alpha_3\beta_2\gamma_1 + \alpha_3\beta_1\gamma_2 + \alpha_2\beta_1\gamma_3 + \alpha_2\beta_3\gamma_1 + \alpha_1\beta_2\gamma_3 + \alpha_1\beta_3\gamma_2]$
14	6	16	$2[\alpha_4 + \beta_4 + \gamma_4]$
15	48	17	$8[\alpha_3\beta_2\gamma_2 + \alpha_2\beta_3\gamma_2 + \alpha_2\beta_2\gamma_3] +$ $4[\beta_1\gamma_4 + \beta_4\gamma_1 + \alpha_1\beta_4 + \alpha_4\beta_1 + \alpha_1\gamma_4 + \alpha_4\gamma_1]$
16	36	18	$4[\beta_3\gamma_3 + \alpha_3\gamma_3 + \alpha_3\beta_3] + 8[\alpha_4\beta_1\gamma_1 + \alpha_1\beta_4\gamma_1 + \alpha_1\beta_1\gamma_4]$
17	24	19	$8[\alpha_1\beta_3\gamma_3 + \alpha_3\beta_1\gamma_3 + \alpha_3\beta_3\gamma_1]$
18	24	20	$4[\beta_2\gamma_4 + \beta_4\gamma_2 + \alpha_4\beta_2 + \alpha_2\beta_4 + \alpha_4\gamma_2 + \alpha_2\gamma_4]$
19	48	21	$8[\alpha_1\beta_2\gamma_4 + \alpha_1\beta_4\gamma_2 + \alpha_4\beta_2\gamma_1 + \alpha_2\beta_4\gamma_1 + \alpha_4\beta_1\gamma_2 + \alpha_2\beta_1\gamma_4]$
20	24	22	$8[\alpha_2\beta_3\gamma_3 + \alpha_3\beta_2\gamma_3 + \alpha_3\beta_3\gamma_2]$

Note. n_s is the number of reciprocal-lattice vectors in shell s and G_s^2 is the squared length of the vectors in shell s in units of $(2\pi/L)^2$. The notation α_n, β_n, and γ_n is defined in Eq. (20).

We have developed a method which combines the efficiency of the recurrence relations with particularly convenient formulae for the basis functions H_s. We write the basis functions in the form

$$H_s(\mathbf{r}) = \sum_{n_1,n_2,n_3} \cos\left[\left(\frac{2\pi x n_1}{L}\right) + \left(\frac{2\pi y n_2}{L}\right) + \left(\frac{2\pi z n_3}{L}\right) \right], \tag{19}$$

where $\mathbf{r} = (x, y, z)$, L is the lattice constant, and the integers n_1, n_2, and n_3 define the appropriate reciprocal-space lattice vectors for shell s. We have manipulated these formulae into convenient forms for the first 20 shells of reciprocal-space lattice vectors of the *sc*, *fcc*, and *bcc* lattices and have tabulated the results in Tables III–V, where our notation is

$$\begin{aligned} \alpha_n &= \cos\left(\frac{2\pi x n}{L}\right) \\ \beta_n &= \cos\left(\frac{2\pi y n}{L}\right) \\ \gamma_n &= \cos\left(\frac{2\pi z n}{L}\right). \end{aligned} \tag{20}$$

The reduction in operation count from using the expressions in these tables is significant. Further savings can be obtained by noting that various combinations of the α_n, β_n, and γ_n defined above occur in more than one shell, e.g., for the *fcc* case the combination $\alpha_1\beta_1$ occurs in shells 1, 4, 10, and 18. These combinations may be calculated once and used in the different shells as required. The gradients of the basis functions are easily evaluated by differentiating the formulae given in the tables. We also make use of the recurrence relation between cosines

$$\alpha_n = 2\alpha_1\alpha_{n-1} - \alpha_{n-2} \qquad (21)$$

(a similar recurrence relation holds for the sines). These recurrence relations are highly efficient, but may become unstable for small values of x. Alternative recurrence relations are known to be more stable (and more costly to evaluate) [8]; however, in practice we do not require values of n greater than about 6, and we have found that Eq. (21) is perfectly adequate for our purposes.

TABLE IV

Formulae for the Reciprocal-Space Basis Functions, H_s (Eq. (19), for the *bcc* Lattice

s	n_s	G_s^2	H_s
1	12	2	$4[\alpha_1\beta_1 + \beta_1\gamma_1 + \alpha_1\gamma_1]$
2	6	4	$2[\alpha_2 + \beta_2 + \gamma_2]$
3	24	6	$8[\alpha_1\beta_1\gamma_2 + \alpha_1\beta_2\gamma_1 + \alpha_2\beta_1\gamma_1]$
4	12	8	$4[\alpha_2\beta_2 + \beta_2\gamma_2 + \alpha_2\gamma_2]$
5	24	10	$4[\alpha_1\gamma_3 + \beta_1\gamma_3 + \beta_3\gamma_1 + \alpha_3\gamma_1 + \alpha_1\beta_3 + \alpha_3\beta_1]$
6	8	12	$8[\alpha_2\beta_2\gamma_2]$
7	48	14	$8[\alpha_1\beta_2\gamma_3 + \alpha_1\beta_3\gamma_2 + \alpha_2\beta_1\gamma_3 + \alpha_2\beta_3\gamma_1 + \alpha_3\beta_1\gamma_2 + \alpha_3\beta_2\gamma_1]$
8	6	16	$2[\alpha_4 + \beta_4 + \gamma_4]$
9	36	18	$8[\alpha_1\beta_1\gamma_4 + \alpha_1\beta_4\gamma_1 + \alpha_4\beta_1\gamma_1] + 4[\alpha_3\gamma_3 + \beta_3\gamma_3 + \alpha_3\beta_3]$
10	24	20	$4[\beta_2\gamma_4 + \alpha_2\gamma_4 + \beta_4\gamma_2 + \alpha_4\gamma_2 + \alpha_2\beta_4 + \alpha_4\beta_2]$
11	24	22	$8[\alpha_3\beta_3\gamma_2 + \alpha_3\beta_2\gamma_3 + \alpha_2\beta_3\gamma_3]$
12	24	24	$8[\alpha_4\beta_2\gamma_2 + \alpha_2\beta_4\gamma_2 + \alpha_2\beta_2\gamma_4]$
13	72	26	$4[\alpha_5\gamma_1 + \beta_5\gamma_1 + \alpha_1\gamma_5 + \beta_1\gamma_5 + \alpha_5\beta_1 + \alpha_1\beta_5] +$ $8[\alpha_1\beta_4\gamma_3 + \alpha_1\beta_3\gamma_4 + \alpha_3\beta_1\gamma_4 + \alpha_3\beta_4\gamma_1 + \alpha_4\beta_1\gamma_3 +$ $\alpha_4\beta_3\gamma_1]$
14	48	30	$8[\alpha_1\beta_5\gamma_2 + \alpha_1\beta_2\gamma_5 + \alpha_2\beta_1\gamma_5 + \alpha_2\beta_5\gamma_1 + \alpha_5\beta_1\gamma_2 + \alpha_5\beta_2\gamma_1]$
15	12	32	$4[\beta_4\gamma_4 + \alpha_4\gamma_4 + \alpha_4\beta_4]$
16	48	34	$4[\alpha_5\gamma_3 + \alpha_5\beta_3 + \beta_5\gamma_3 + \beta_3\gamma_5 + \alpha_3\beta_5 + \alpha_3\gamma_5] +$ $8[\alpha_4\beta_3\gamma_3 + \alpha_3\beta_4\gamma_3 + \alpha_3\beta_3\gamma_4]$
17	30	36	$2[\alpha_6 + \beta_6 + \gamma_6] + 8[\alpha_2\beta_4\gamma_4 + \alpha_4\beta_2\gamma_4 + \alpha_4\beta_4\gamma_2]$
18	72	38	$8[\alpha_2\beta_3\gamma_5 + \alpha_2\beta_5\gamma_3 + \alpha_5\beta_2\gamma_3 + \alpha_5\beta_3\gamma_2 + \alpha_3\beta_2\gamma_5$ $+ \alpha_3\beta_5\gamma_2] + 8[\alpha_6\beta_1\gamma_1 + \alpha_1\beta_6\gamma_1 + \alpha_1\beta_1\gamma_6]$
19	24	40	$4[\alpha_2\beta_6 + \alpha_2\gamma_6 + \beta_6\gamma_2 + \beta_2\gamma_6 + \alpha_6\gamma_2 + \alpha_6\beta_2]$
20	48	42	$8[\alpha_1\beta_5\gamma_4 + \alpha_1\beta_4\gamma_5 + \alpha_4\beta_1\gamma_5 + \alpha_4\beta_5\gamma_1 + \alpha_5\beta_1\gamma_4 + \alpha_5\beta_4\gamma_1]$

Note. n_s is the number of reciprocal-lattice vectors in shell s and G_s^2 is the squared length of the vectors in shell s in units of $(2\pi/L)^2$. The notation α_n, β_n, and γ_n is defined in Eq. (20).

TABLE V

Formulae for the Reciprocal-Space Basis Functions, H_s (Eq. (19), for the *fcc* Lattice

s	n_s	G_s^2	H_s
1	8	3	$8[\alpha_1\beta_1\gamma_1]$
2	6	4	$2[\alpha_2 + \beta_2 + \gamma_2]$
3	12	8	$4[\beta_2\gamma_2 + \alpha_2\gamma_2 + \alpha_2\beta_2]$
4	24	11	$8[\alpha_3\beta_1\gamma_1 + \alpha_1\beta_3\gamma_1 + \alpha_1\beta_1\gamma_3]$
5	8	12	$8[\alpha_2\beta_2\gamma_2]$
6	6	16	$2[\alpha_4 + \beta_4 + \gamma_4]$
7	24	19	$8[\alpha_1\beta_3\gamma_3 + \alpha_3\beta_1\gamma_3 + \alpha_3\beta_3\gamma_1]$
8	24	20	$4[\alpha_4\beta_2 + \alpha_4\gamma_2 + \alpha_2\gamma_4 + \alpha_2\beta_4 + \beta_4\gamma_2 + \beta_2\gamma_4]$
9	24	24	$8[\alpha_4\beta_2\gamma_2 + \alpha_2\beta_4\gamma_2 + \alpha_2\beta_2\gamma_4]$
10	32	27	$8[\alpha_5\beta_1\gamma_1 + \alpha_1\beta_5\gamma_1 + \alpha_1\beta_1\gamma_5 + \alpha_3\beta_3\gamma_3]$
11	12	32	$4[\beta_4\gamma_4 + \alpha_4\gamma_4 + \alpha_4\beta_4]$
12	48	35	$8[\alpha_3\beta_1\gamma_5 + \alpha_1\beta_3\gamma_5 + \alpha_3\beta_5\gamma_1 + \alpha_5\beta_3\gamma_1 + \alpha_1\beta_5\gamma_3 + \alpha_5\beta_1\gamma_3]$
13	30	36	$8[\alpha_2\beta_4\gamma_4 + \alpha_4\beta_2\gamma_4 + \alpha_4\beta_4\gamma_2] + 2[\alpha_6 + \beta_6 + \gamma_6]$
14	24	40	$4[\beta_6\gamma_2 + \beta_2\gamma_6 + \alpha_6\beta_2 + \alpha_6\gamma_2 + \alpha_2\gamma_6 + \alpha_2\beta_6]$
15	24	43	$8[\alpha_5\beta_3\gamma_3 + \alpha_3\beta_5\gamma_3 + \alpha_3\beta_3\gamma_5]$
16	24	44	$8[\alpha_2\beta_2\gamma_6 + \alpha_2\beta_6\gamma_2 + \alpha_6\beta_2\gamma_2]$
17	8	48	$8[\alpha_4\beta_4\gamma_4]$
18	48	51	$8[\alpha_1\beta_1\gamma_7 + \alpha_7\beta_1\gamma_1 + \alpha_1\beta_7\gamma_1] + 8[\alpha_1\beta_5\gamma_5 + \alpha_5\beta_1\gamma_5$ $+ \alpha_5\beta_5\gamma_1]$
19	24	52	$4[\beta_4\gamma_6 + \beta_6\gamma_4 + \alpha_6\gamma_4 + \alpha_6\beta_4 + \alpha_4\gamma_6 + \alpha_4\beta_6]$
20	48	56	$8[\alpha_2\beta_4\gamma_6 + \alpha_2\beta_6\gamma_4 + \alpha_6\beta_2\gamma_4 + \alpha_6\beta_4\gamma_2 + \alpha_4\beta_2\gamma_6 + \alpha_4\beta_6\gamma_2]$

Note. n_s is the number of reciprocal-lattice vectors in shell s and G_s^2 is the squared length of the vectors in shell s in units of $(2\pi/L)^2$. The notation α_n, β_n, and γ_n is defined in Eq. (20).

VI. CONCLUSIONS

We have described a modified Ewald method for calculating the total potential and its gradient arising from a periodic array of particles with arbitrary long-ranged potentials. The method is based on an optimized division between the direct- and reciprocal-space terms, which minimizes the squared error in the representation. The method requires the choice of a single parameter, N_s, the number of shells of reciprocal-lattice vectors included in the sum, which controls both the accuracy and the computational expense. This compares favorably with the standard Ewald method (Eq. (1)), which requires up to three parameters to be chosen (the number of direct- and reciprocal-space lattice vectors and the parameter κ).

Between one-half and one-third of the number of shells of reciprocal-space lattice vectors are required to give an accuracy equivalent to the standard Ewald formula, (Eq. (1) including only the $\mathbf{R} = \mathbf{0}$ term from the direct-space sum and with the parameter κ optimized for convergence of the reciprocal-space sum). In simulations using the optimized Ewald method most of the computational effort is required in the evaluation of the reciprocal-space sum. We have provided formulae for the terms in the reciprocal-space sum for the *sc*, *bcc*, and *fcc* lattices, which allow efficient evaluation.

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