Extended Ewald Summation Technique

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We present a technique to efficiently compute long-range interactions in systems with periodic boundary conditions. We extend the well-known Ewald method by using a linear combination of screening Gaussian charge distributions instead of only one as in the standard Ewald scheme. The combined simplicity and efficiency of our method is demonstrated, and the scheme is readily applicable to large-scale periodic simulations, classical as well as quantum.

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In computer simulations with periodic boundary conditions the long-range potentials are usually expressed in rapidly converging sums in both real and reciprocal space according to the Ewald method of images [1, 2]. The method is in extensive use in various fields of condensed matter, material, and biological physics, to properly account for the long-range interactions, e.g., the electrostatic Coulomb interaction. In practice, however, the Ewald scheme is subject to real-space cut-off for the desired accuracy. Overall, our efforts in the optimization and implementation.

In this Letter, we show how to straightforwardly implement the extended Ewald scheme by using a linear combination of screening Gaussian charge distributions instead of only one as in the standard Ewald scheme.

$$V(r) = Z_1 Z_2 \sum_{n} W(|r+nL|),$$

which includes all the interactions between a particle and the replicas of the other particle in periodically repeated space, and $Z_1$ and $Z_2$ are the charges of the particles. In terms of a short-range part (SR) and a long-range part (LR), $V_p(r)$ can be written as

$$V_p(r) = \sum_{n} V_{SR}(|r+nL|) + \sum_{n} V_{LR}(|r+nL|),$$

where

$$V_{SR}(|r+nL|) = W(|r+nL|) - V_{LR}(|r+nL|).$$

Assuming that the long-range part is Fourier transformable, as it is in the case of a Gaussian charge distribution, the potential can be further modified to

$$V_p(r) = \sum_{n} V_{SR}(|r+nL|) + \sum_{k} V_{k} e^{ikr}.$$

In a more practical form, i.e., in the presence of a neutralizing background, or under the assumption of charge neutrality, we can write

$$V_p(r) = \sum_{n} V_{SR}(|r+nL|) + \sum_{k \neq 0} V_{k} e^{ikr} + C_V.$$
where

\[ C_V = -\frac{1}{\Omega} \int dr \left[ W(r) - V_{LR}(r) \right]. \]

This term represents contributions from a neutralizing background, and in the total energy these \( C_V \) terms will cancel out for charge neutral systems. In the calculation of the total energy the Madelung constant \( V_M = \frac{1}{\Omega} \lim_{r \to 0} [V_p(r) - W(r)] \) is also needed, the energy term being \( \sum_i Z_i^2 V_M \).

In the case of a single screening Gaussian term, the long-range potential, or screening potential, is given in real space as

\[ V_{LR}(r) = \frac{\text{erf}(\alpha r)}{r}, \quad (8) \]

and in reciprocal space the Fourier coefficients are

\[ V_k = V_k = \frac{4\pi e^{-k^2/4\alpha^2}}{\Omega k^2}. \quad (9) \]

As mentioned earlier, in the case of a linear combination of screening Gaussian charge distributions with zero mean, the potentials are given as

\[ V_{LR}(r) = \sum_i c_i V_{LR,i}(r) = \sum_i c_i \frac{\text{erf}(\alpha r)}{r}, \quad (10) \]

and

\[ V_k = \sum_i c_i V_{k,i}(r) = \frac{4\pi}{\Omega} \sum_i c_i e^{-k^2/4\alpha^2} / k^2, \quad (11) \]

where index \( i \) refers to different \( \alpha \)-parameters, i.e., Gaussian functions with different variances.

At this point we have introduced all the equations that are needed in performing either the standard Ewald summation or the extended Ewald technique. In theory, both cases are exact in the presented form for any given set of \( \alpha \)-parameters and \( c_i \) coefficients (for which \( \sum_i c_i = 1 \)). In practice, however, it is critical to choose proper values for the cut-offs \( r_c \) and \( k_c \) in order to obtain good accuracy and reasonable computation time.

Here we choose the real-space cut-off to be \( r_c = L/2 \), which restricts the potential to be a function of the minimum distance of a particle to any image. Thus, the set of \( \alpha \)-parameters needs to ensure that

\[ \sum_{n \neq 0} V_{SR}(|r + nL|) \approx 0, \quad (12) \]

that is, \( W(|r|) \approx V_{LR}(|r|) \) for all \( r > r_c \). Now the image potential of Eq. \((12)\) can be written as

\[ V_p(r) \approx V_{SR}(r) \Theta(r_c - r) + \sum_{|k| \leq k_c} V_k e^{i k \cdot r} + \sum_{|k| > k_c} V_k e^{i k \cdot r}, \quad (13) \]

where we also included the cut-off in the reciprocal space, and \( \Theta(x) \) is the Heaviside step function. If the short-range part is truncated accurately according to Eq. \((12)\), the k-space cut-off will be the source for the accuracy in the image potential. Therefore, if \( \Delta \) represents the error due to the k-space cut-off, we have

\[ \Delta = \sum_{|k| > k_c} V_k e^{i k \cdot r}. \quad (14) \]

Here it should be pointed out that for the optimized breakup of Natoli and Ceperley the constraint of Eq. \((12)\) is exact, since the screening charge distribution is equal to zero for \( r \geq r_c \). For Gaussian distributions this will become exact only in the limit \( \alpha \to \infty \), but highly accurate approximations can be made with reasonable values of \( \alpha \).

In the case of the conventional Ewald method, if the condition in Eq. \((12)\) is fulfilled accurately, the k-space part will usually end up being slowly convergent, and the convergence is solely determined by the Gaussian parameter \( \alpha \), see Eq. \((9)\). However, in the case of multiple Gaussian distributions, the \( V_k \) is given by Eq. \((11)\), and thus, we have

\[ \Delta = \sum_n \sum_{|k| > k_c} c_n V_{k,n} e^{i k \cdot r}. \quad (15) \]

Now the convergence in k-space is affected by the coefficients \( c_i \) as well as the Gaussian parameters \( \alpha_i \). Since \( V_k = V_{-k} = V_k \), the above expression can be written in terms of a cosine function, and also the summation order can be changed:

\[ \Delta = \sum_n \sum_{|k| > k_c} V_{k,n} \cos(k \cdot r). \quad (16) \]

This expression can be already used to obtain the coefficients \( c_i \) for a predefined set of \( \alpha_i \)-parameters. First, we define a three-dimensional grid, \( x = -L/2 \ldots L/2 \), \( y = -L/2 \ldots L/2 \) and \( z = -L/2 \ldots L/2 \). Secondly, we construct a matrix equation from the equation above and use also the fact that \( \sum c_i = 1 \). Solving this overdetermined set of linear equations results in the least-squares solution for the integrand in

\[ \chi^2 = \frac{1}{\Omega} \int \Omega dr \Delta^2. \quad (17) \]

Thirdly, we can compute the integral with the obtained coefficients in order to estimate the \( \chi^2 \) error.

Another, improved way \( \mathbb{E} \) to achieve the coefficients
\( c_i \) is to start from Eqs. (15) and (17), i.e.,

\[
\chi^2 = \frac{1}{\Omega} \int d\mathbf{r} \left( \sum_{|k| > k_c} \sum c_n V_{k,n} e^{i k \cdot \mathbf{r}} \right)^2
\]

\[
= \frac{1}{\Omega} \int d\mathbf{r} \sum_{|k| > k_c} \sum_{|k'| > k_c} \sum_{n} \sum_{m} c_n c_m V_{k,n} V_{k',m} e^{i (k + k') \cdot \mathbf{r}}
\]

\[
= \sum_{|k| > k_c} \sum_{|k'| > k_c} \sum_{n} \sum_{m} c_n c_m V_{k,n} V_{k',m} \delta_{k, -k'}
\]

\[
= \sum_{|k| > k_c} \sum_{n} c_n c_m V_{k,n} V_{k,m}. \quad \text{(18)}
\]

Next, let us take the derivative of this expression with respect to \( c_n \) and set it be equal to zero, that is,

\[
\frac{\partial \chi^2}{\partial c_n} = 0,
\]

which for each \(|k| > k_c\) leads to

\[
\sum_{m} c_m V_{k,m} = 0. \quad \text{(20)}
\]

For each \( k \) we have a linear equation, and therefore, together with the constraint \( \sum c_i = 1 \), we have an overdetermined set of linear equations, which minimizes the \( \chi^2 \). After having determined the coefficients, \( \chi^2 \) can be computed from

\[
\chi^2 = \sum_{|k| > k_c} \left( \sum c_i V_{k,i} \right)^2. \quad \text{(21)}
\]

In finding the coefficients \( c_i \) for the Gaussian functions above we assumed that Eq. (12) holds accurately. This is a valid assumption for sufficiently large values of \( \alpha \). However, it restricts the degrees of freedom in the optimization, which can be released by a new term

\[
\tilde{\Delta} = \sum_{|k| > k_c} V_k e^{i k \cdot \mathbf{r}} + \sum_{k} V_k e^{i k \cdot \mathbf{r}},
\]

where

\[
\tilde{V}_k = \frac{1}{\Omega} \int d\mathbf{r} V_{SR}(r) \left[ 1 - \Theta(r_c - r) \right] e^{i k \cdot \mathbf{r}}.
\]

In this work the potentials were chosen to be spherically symmetric, and therefore, \( \tilde{V}_k \) can also be written as

\[
\tilde{V}_k = \frac{4 \pi}{\Omega k} \int_{0}^{r_c} dr W(r) \sin(k r),
\]

With this \( \tilde{\Delta} \) term the exact equality in Eq. (13) is restored, i.e.,

\[
V_{\tilde{\nu}}(\mathbf{r}) = V_{SR}(\mathbf{r}) \Theta(r_c - r) + \sum_{|k| \leq k_c} V_k e^{i k \cdot \mathbf{r}} + \tilde{\Delta}. \quad \text{(25)}
\]

Figure 1: (Color online) Natural logarithm of \( \tilde{\chi}L \) for the Coulomb potential as a function of the dimensionless parameter \( k_c r_c \). For our extended Ewald scheme (red symbols), the optimized break-up by Natoli and Ceperley \( \tilde{\Delta} \) (solid line), and the optimized standard Ewald method (dashed line).

Now, \( \tilde{\chi}^2 \) may be expressed as

\[
\tilde{\chi}^2 = \frac{1}{\Omega} \int d\mathbf{r} \tilde{\Delta}^2
\]

\[
= \sum_{k} \left( A_k + \sum_{n} c_n B_{k,n} \right) \left( A_k + \sum_{m} c_m B_{k,m} \right),
\]

where \( A_k \) and \( B_{k,i} \) are defined as

\[
A_k = W_k - \frac{4 \pi}{\Omega k} \int_{0}^{r_c} dr W(r) \sin(k r),
\]

\[
B_{k,i} = \frac{4 \pi}{\Omega k} \int_{0}^{r_c} dr V_{LR,i}(r) \sin(k r) - V_{k,i} \Theta(k_c - k),
\]

where \( W_k \) is the Fourier coefficient of \( W(|r|) \). Setting the derivative of \( \tilde{\chi}^2 \) with respect to \( c_n \) to zero leads to a set of linear equations for each \( k \):

\[
\sum_{m} c_m B_{k,m} = -A_k,
\]

which for \( k = 0 \) reduces to \( \sum_{m} c_m = 1 \), and the accuracy can be estimated by

\[
\tilde{\chi}^2 = \sum_{k} \left( A_k + \sum_{i} c_i B_{k,i} \right)^2.
\]
As an example, let us consider the commonly-used Coulomb potential with the standard Ewald method in comparison with our extended scheme. The potential is given by $W(r) = 1/r$ and its Fourier coefficients are $W_k = 4\pi/\Omega k^2$. The product of charges, $Z_1 Z_2$, is set equal to one. Here we use Newton’s method for finding a minimum for the function $g(\{c_i\}, \{\alpha_i\}) = \chi^2 + \lambda \left(\sum_i c_i - 1\right)^2$, where $\lambda$ is a Lagrange multiplier.

Fig. 1 shows the error $\ln(\chi L)$ as a function of $k_r r_c$ for both the conventional Ewald method (dashed line) and our extended scheme for various $k_r$ and $r_c$ values (symbols), together with the the fit by Natoli and Ceperley (solid line). Remarkably, the extended Ewald approach improves the accuracy by more than an order of magnitude over the conventional Ewald case. On the other hand, the “optimized break-up” acts as a lower bound estimate for our values. It should be pointed out that the results of our scheme can be improved further by enhanced optimization. This could involve a combination of the three schemes introduced here along with optimizing the Gaussian $\alpha_i$-parameters, for example.

The screening charge distribution for $k_r r_c \approx 12.11$ is shown in Fig. 2a. For the extended Ewald scheme the distribution is spread out more than in the standard Ewald case. Both distributions converge close to zero before the real-space cut-off $r_c$. With these optimized coefficients the effect seems to be more pronounced here than in the optimized break-up case, see Fig. 4 in Ref. [3].

In Fig. 2b) we show the long-range potentials of Eqs. (8) and (10) corresponding to the distributions shown in Fig. 2a). The potentials are different from origin to roughly $0.3L$, after which (in the scale of the figure) the potentials coincide well before the real-space cut-off ($r_c = L/2$). In the differing range the changes in the potential are smoother in the extended scheme, and thus, the Fourier coefficients converge considerably faster than in the standard approach, which is demonstrated in Fig. 2c).

In addition to the improved accuracy, another clear advantage of the extended Ewald scheme is the fact that it is easily adaptable to numerical codes already having the standard Ewald method. Moreover, in the extended scheme the analytical form is preserved, which is advantageous when calculating accurate derivatives of the potentials to obtain forces, for example. It is also important to note that, regardless of the number of terms in the extended scheme, computations will not be more time consuming, since in any case a radial potential (with an error function) should be interpolated from a radial grid during the simulation. Therefore, the linear combination coefficients are needed only in the beginning of the simulation.

In this Letter we have demonstrated that a linear combination of Gaussian functions as the screening charge distribution can be used to considerably improve the standard Ewald method of images. The modified charge distribution enables smaller reciprocal space cut-off than only a single Gaussian function for a higher level of accuracy. The extended scheme leads to reduced computer time in simulations of periodic systems and it can be easily implemented in any numerical package using periodic boundary conditions within, e.g., density-functional methods, molecular dynamics, and classical or quantum Monte Carlo calculations. The full potential of the present technique can be achieved by a further developed optimization procedure.

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