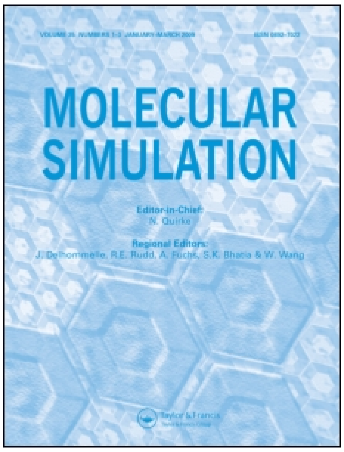

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Modified Wolf electrostatic summation: Incorporating an empirical charge overlap

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Modified Wolf electrostatic summation: Incorporating an empirical charge overlap

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The original Wolf sum [D. Wolf *et al.*, *J. Chem. Phys.* **110** (1999) 8254–8282] was modified to account for the effect of charge overlap in an empirical manner in order to correct the direct $1/r$ coulomb interaction in covalent systems. The resulting modified Wolf sum takes a form that is similar to the original one. More importantly, the inclusion of the charge overlap effect does not introduce any additional systematic error. Thus, the error analysis can be evaluated either analytically for 3D periodic systems or estimated numerically for general cases, which is the same as in the original Wolf sum. Application of this modified Wolf sum to covalent or partially covalent systems such as SiC and SiO_2 shows that it gives a more realistic description of the electrostatic interactions in those systems. Although the Wolf method does not conserve energy in principle, in practice the energy is conserved very well. Thus this method is particular suitable in molecular dynamics simulations.

Keywords: Wolf sum; Covalent systems; Molecular simulations; Electrostatic interactions

1. Introduction

In molecular simulations, the most important task is probably to find an appropriate interatomic potential. When the simulated systems contain charged species, Coulomb interactions will inevitably appear in the potential and have to be evaluated accurately. For a system of N ions with charges q_i, the total Coulomb energy can be expressed as:

$$E^{\text{ele}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_i q_j}{r_{ij}} \tag{1}$$

The difficulty in evaluating the summation given in equation (1) is that such a summation is conditionally convergent, which is well known as the Madelung problem [1]. The standard technique in dealing with this problem is the so called Ewald sum [2], in which the conditionally convergent sum in equation (1) is transformed mathematically into two rapid convergent series in both real and reciprocal spaces, as well as a self correction term. Despite its popularity, the use of the Ewald sum is problematic, especially for disordered systems where the artificially imposed periodicity in the Ewald sum is absent [3,4]. Computationally, this method is also very costly.

Recently, Wolf *et al.* [3] analyzed the origin of the poor convergence of summation (1) and recognized the importance of local charge neutrality. By ensuring that the net charge within the cutoff sphere equals zero, the convergence behavior of summation (1) improved remarkably. Further, by applying a damping function and analyzing the associated systematic error, Wolf *et al.* [3] concluded that as long as the damping factor was chosen such that the systematic error thus introduced was negligible, the total electrostatic energy could be evaluated accurately by a spherically truncated, pairwise $1/r$ summation. This method, referred to as the Wolf sum, provided new physical insight into the nature of Coulomb interaction. Compared to the traditional Ewald sum, it is computationally more efficient, conceptually more transparent and easier to implement in practice. Also, its extension to disordered systems such as melts, free surfaces and interfaces is straightforward [3].

One should note that there is an underlying assumption behind both Wolf and Ewald sum. That is, all the charges are treated as point charges and their interactions can be modeled by the Coulomb $1/r$ interaction. Such a point charge model is of course accurate enough for the description of highly ionic system. Unfortunately, however, due to the diffuse character of charge distribution, the point charge model is at least theoretically invalid. The remedy to this problem is to evaluate the Coulomb integral between two charge densities [5]. It is theoretically more well-founded but computationally more demanding. Empirical

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methods also exist where the overlap integral was mimicked by a simple function with adjustable parameter [6,7]. By an appropriate choice of the adjustable parameter, one can reproduce the overlap integral with reasonable accuracy. Because of its low computational cost and high accuracy (compared to the direct $1/r$ interaction), it is well suited for molecular dynamics simulations. Incorporating such an empirical overlap integral into the Wolf sum is thus the major purpose of this paper.

In the simulation of highly or partially covalent systems like SiC, SiO_2, etc., such an extension is of great importance. Unlike ionic systems, the diffuse character of the 2p and 3p orbitals in these systems certainly invalidates the use of point charge approximation, especially at or less than bonding distances. Thus for an appropriate description of the electrostatic interactions, one should take the effect of charge overlap into account explicitly, at least in an empirical manner, which is the key driving force in deriving the modified Wolf sum containing the effect of charge overlap. In the following section, emphasis will be put on the theoretical derivation of the modified Wolf sum. In section III, the results for model calculations on SiC/SiO_2 systems will be reported which proved the validity of our approach.

2. Theory

2.1 Original Wolf sum

In practice, the electrostatic summation given in equation (1) can only be evaluated within a finite cutoff distance R_c. To ensure convergence within R_c, the complementary error function is used and equation (1) transforms into:

$$E^{\mathrm{ele}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_iq_j erfc(r_{ij}/\beta)}{r_{ij}} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_iq_j erf(r_{ij}/\beta)}{r_{ij}} \tag{2}$$

where β is the damping parameter which determines the speed of convergence for the first summation in equation (2). Following Wolf *et al.* [3], by adding and subtracting the self term for the second summation in equation (2), the total electrostatic energy is then subdivided into two parts:

$$E^{\mathrm{ele}} = E^{\mathrm{ele}}_{(1)} + E^{\mathrm{ele}}_{(2)} \tag{3}$$

where

$$E^{\mathrm{ele}}_{(1)} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_iq_j erfc(r_{ij}/\beta)}{r_{ij}} - \lim_{r_{ij}\to 0}\left\{\frac{1}{2}\sum_{i=1}^{N}\frac{q_i^2 erf(r_{ij}/\beta)}{r_{ij}}\right\} \tag{4}$$

$$E^{\mathrm{ele}}_{(2)} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{\infty}\frac{q_iq_j erf(r_{ij}/\beta)}{r_{ij}} \tag{5}$$

Evaluating the limit in equation (4) explicitly gives:

$$E^{\mathrm{ele}}_{(1)} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_iq_j erfc(r_{ij}/\beta)}{r_{ij}} - \frac{1}{\beta\pi^{1/2}}\sum_{i=1}^{N} q_i^2 \tag{6}$$

Because of the fast decay of the complementary error function, it is now possible to evaluate summation (6) within a finite cutoff distance R_c. Applying local charge neutrality [3], equation (6) can then be written as:

$$E^{\mathrm{ele}}_{(1)} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j\neq i\\ r_{ij}<R_c}}\left(\frac{q_iq_j erfc(r_{ij}/\beta)}{r_{ij}} - \lim_{r_{ij}\to R_c}\left\{\frac{q_iq_j erfc(r_{ij}/\beta)}{r_{ij}}\right\}\right) - \left(\frac{erfc(R_c/\beta)}{2R_c} + \frac{1}{\beta\pi^{1/2}}\right)\sum_{i=1}^{N} q_i^2 \tag{7}$$

On the other hand, as argued by Wolf *et al.*, $E^{\mathrm{ele}}_{(2)}$ is the systematic error introduced by damping [3]. By a judicious choice of damping parameter β and cutoff distance R_c, the systematic error is negligible thus:

$$E^{\mathrm{ele}} \approx E^{\mathrm{ele}}_{(1)} \tag{8}$$

The formal relationship between this method and the traditional Ewald sum has also been established by Wolf *et al.* [3]. The systematic error represented by equation (5) is just the reciprocal space energy in the Ewald sum, while the real space energy given by the Ewald sum corresponds to the charge neutralized, or equivalently shifted potential given in equation (7). The drastic effect of charge neutralization is thus obvious: the reciprocal space energy can be discarded completely.

The choice of damping parameter β and cutoff distance R_c merits further discussion. In general, one wishes to use a smaller R_c to speed up calculation, which in turn requires a smaller β so that the damping is larger. On the other hand, a larger damping corresponds to a larger systematic error that is inevitably introduced by damping. Hence the optimal compromise has to be found between the speed of convergence and the magnitude of systematic error associated with it. One should also be aware that the systematic error is related to structural disorder. Thus a set of β and R_c values that works for a perfect crystal may fail for the same crystal melted, since the thermal disorder in the melt may introduce large systematic error. To overcome this problem, additional terms have to be added [3].

To test the validity of this approach, Wolf *et al.* applied it to some simple ionic crystals and their melt [3]. In this paper, similar tests have been carried out for partially to highly covalent systems: α-quartz and β-SiC. Note that the partial charge instead of full valence charge has been used in those systems. For example, the charge of Si atom in α-quartz is 1.6, while in β-SiC is 1.0. The actual value of these charges are determined empirically, falling in the range which is consistent with *ab initio* results [8,9].

Figures 1 and 2 plot the total electrostatic energy (given in equation 7) as a function of cutoff distance for α-quartz and β-SiC perfect crystals, respectively. Four different β values have been used for the purpose of comparison. Clearly, the converged value of the total electrostatic energy does not depend on the specific choice of damping factor β; but different β values do give different speeds of convergence. For example, for the largest β value used in both systems, the total energies are never really converged. For the smallest β value, the total energies converge quickly and it is possible to use a relatively small cutoff around 10 Å. The convergence behavior of the other β values falls in between. The fact that all β values give the same total energy suggests that the reciprocal space contribution, or the systematic error, is indeed negligible for the cases shown in figures 1 and 2.

Following Wolf *et al.*, the force between a pair of atoms corresponding to total energy given in equation (7) can be written as [3]:

$$f_{ij} = \sum_{\substack{j\neq i\\(r_{ij}<R_c)}} q_i q_j \left\{ \left(\frac{erfc(r_{ij}/\beta)}{r_{ij}^2} + \frac{2}{\beta\pi^{1/2}} \frac{\exp(-r_{ij}^2/\beta^2)}{r_{ij}} \right) - \left(\frac{erfc(R_c/\beta)}{R_c^2} + \frac{2}{\beta\pi^{1/2}} \frac{\exp(-R_c^2/\beta^2)}{R_c} \right) \right\} \qquad (9)$$

The force given in equation (9), as pointed out by Wolf *et al.* [3], is not consistent with the energy given in equation (7). This can be easily seen by explicitly taking the derivative of the energy. Since the second term in the energy expression (which represents the neutralization potential) is a constant after taking the limit, it will not appear in the forces, stresses, or any higher derivatives. Thus a system described by equations (7) and (9) will not necessarily conserve energy. Although the energy conservation is broken, the advantage is that all the forces, stresses and higher derivatives defined this way will vanish at R_c continuously, thus avoiding any truncation error. It is also more physically meaningful. Since the neutralization potential describes the contribution from the image charge on the truncation surface, they should also contribute to forces and stresses, as discussed by Wolf *et al.* [3].

Equations (7) and (9) form the basis of Wolf sum in the context of molecular dynamics simulation. The advantage of switching from traditional Ewald summation to the Wolf summation should now be obvious. Instead of evaluating both real space and reciprocal space energies, only the charge-neutralized real space energy needs to be considered in the Wolf sum. The computational cost is thus reduced. For a detailed comparison of the computational efficiency of these two methods, see the paper by Demontis *et al.* [4].

2.2 *Empirical overlap integral*

As pointed out previously, the Wolf approach is also based on $1/r$ summation, while the validity of such a summation is questionable. As can be seen from figures 1 and 2, the electrostatic energy per atom calculated by original Wolf sum is −8.5 and −6.3 eV for α-quartz and β-SiC,

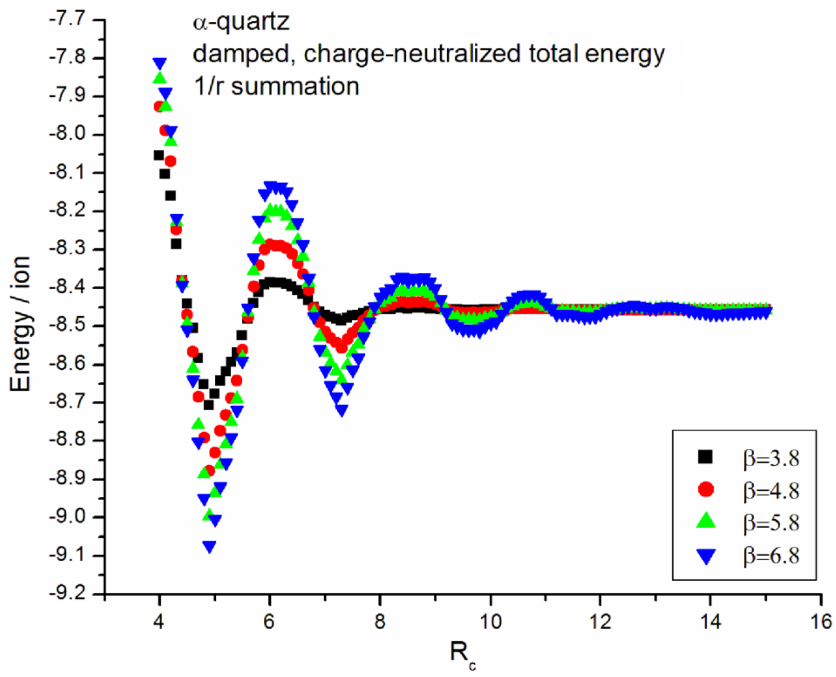

Figure 1. Total electrostatic calculated for α-quartz by original Wolf summation. Different damping parameters show different convergence behavior, while all of them converge to the same value.

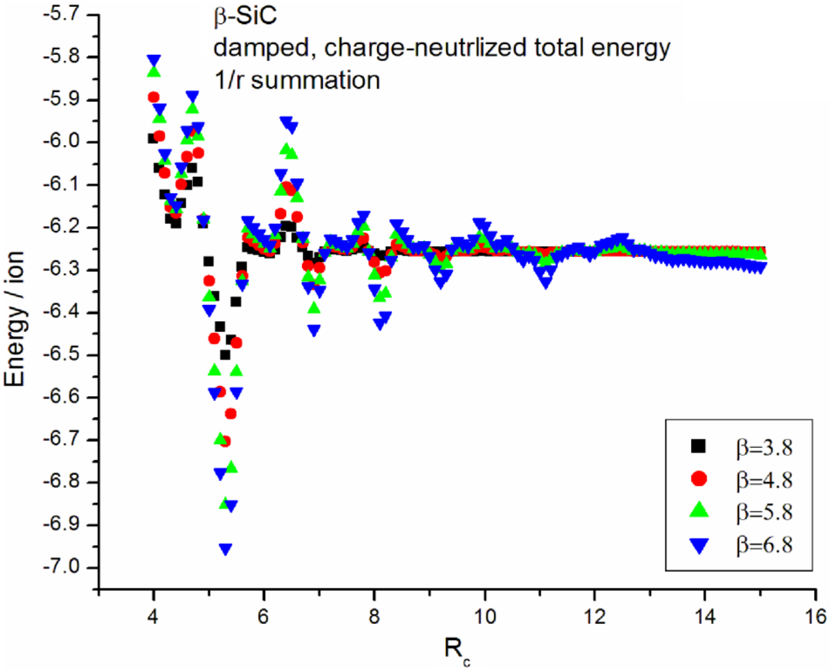

Figure 2. Total electrostatic calculated for β-SiC by original Wolf summation. Results are similar to those obtained in the case of α-quartz.

respectively. Considering the fact that the electrostatic energy for most of the ionic crystals falls in the range of $-5 \sim -10\,\mathrm{eV}$ [1], systems such as SiO_2 and SiC should not have such a large electrostatic energy. The underlying assumption behind the $1/r$ summation is that all the charges in the system can be modeled by point charges while in fact, charges do distribute themselves in some way in space. The diffuse character of charge distribution certainly invalidates the use of point charge, especially for neighboring atoms, where the interatomic distance is relatively small. On the other hand, if two atoms are separated enough far away from each other, the charge overlap effect can be neglected and their interaction energy can be effectively modeled by point charges. Thus when applying the Wolf summation, corrections have to be made to account for the short range charge overlap.

Different ways exist to explicitly take this effect into account. The most rigorous one is to obtain charge densities from quantum mechanical calculations and then evaluate the Coulomb integral between the charge densities. Such a method is, of course, computationally demanding although simplifications can be made such as choosing a simple basis set. Point charges can be modified using Gaussian Distributions [10], which affect charges over the short range. Empirical methods also exist in literature where the Coulomb integral was calculated by simple empirical functions. One such function takes the following form [6]:

$$\frac{q_i q_j}{r_{ij}} \longrightarrow \frac{q_i q_j}{\left(r_{ij}^3 + \left(\frac{1}{\gamma_{ij}}\right)^3\right)^{\frac{1}{3}}} = \frac{q_i q_j}{r_{\mathrm{eff}}} \tag{10}$$

where the $1/r$ summation is substituted by $1/r_{\mathrm{eff}}$ summation which is referred to as "effective R" approach in this paper. This method, by appropriately choosing the parameter γ, can describe the Coulomb interaction between two charge densities with good accuracy. The problem now is to incorporate equation (10) into the Wolf summation. In other words, one needs to use Wolf approach to evaluate the following total energy:

$$E^{\mathrm{ele}'} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_i q_j}{r_{\mathrm{eff}}} \tag{11}$$

Intuitively, this can be done by changing all the r_{ij} in equation (7) to r_{eff}, since it is the only difference between equations (1) and (11). Thus equation (7) is then written as:

$$\begin{aligned} E^{\mathrm{ele}'}_{(1)} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j\neq i \\ r_{ij}<R_c}} & \left(\frac{q_i q_j erfc(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}} \right. \\ & \left. - \lim_{r_{ij}\to R_c}\left\{\frac{q_i q_j erfc(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}}\right\}\right) \\ & - \left(\frac{erfc(R_c/\beta)}{2R_c} + \frac{1}{\beta\pi^{1/2}}\right)\sum_{i=1}^{N} q_i^2 \end{aligned} \tag{12}$$

Unfortunately, it is not the case. Following the route taken by Wolf *et al.*, the problems with equation (12) can be easily seen. First, the self energy should be given by taking the appropriate limit for $r_{ij} \longrightarrow 0$, as shown in equation (4). Thus

$$\begin{aligned} \lim_{r_{ij}\to 0}\left\{\frac{1}{2}\sum_{i=1}^{N}\frac{q_i^2 erf(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}}\right\} &= \frac{1}{2}\sum_{r=1}^{N}\frac{q_i^2 erf(1/\gamma_i\beta)}{1/\gamma_i} \\ &\neq \frac{1}{\beta\pi^{1/2}}\sum_{i=1}^{N} q_i^2 \end{aligned} \tag{13}$$

Second, the error term is now different from equation (5). Instead, it is given by:

$$E_{(2)}^{\mathrm{ele}'} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{\infty}\frac{q_i q_j erf(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}} \tag{14}$$

Equation (12) is then corrected by equation (13) and the total electrostatic energy is now:

$$\begin{aligned} E^{\mathrm{ele}'} &= E_{(1)}^{\mathrm{ele}'} + E_{(2)}^{\mathrm{ele}'} \\ &= \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j\neq i \\ r_{ij}<R_c}}\left(\frac{q_i q_j erfc(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}}\right. \\ &\quad \left. - \lim_{r_{ij}\to R_c}\left\{\frac{q_i q_j erfc(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}}\right\}\right) \\ &\quad - \left(\frac{erfc(R_c/\beta)}{2R_c} + \frac{erf(1/\gamma_i\beta)}{2/\gamma_i}\right)\sum_{i=1}^{N} q_i^2 \\ &\quad + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{\infty}\frac{q_i q_j erf(r_{\mathrm{eff}}/\beta)}{r_{\mathrm{eff}}} \end{aligned} \tag{15}$$

If the error term thus defined in equation (14) represents only a small correction to the total electrostatic energy, which is the case in original Wolf sum, then the total energy can be calculated using only $E_{(1)}^{\mathrm{ele}'}$. Unfortunately, however, $E_{(2)}^{\mathrm{ele}'}$ given in equation (14) are no longer negligible. This can be seen from figure 3 where $E_{(1)}^{\mathrm{ele}'}$ in equation (15) has been applied to calculate the total electrostatic energy for α-quartz perfect crystal. The obvious difference in energies obtained by different β values clearly suggests the existence of large systematic error.

2.3 Incorporating charge overlap into Wolf sum

Considering the above discussion, the challenges brought out by introducing effective R to the Wolf sum are:

1. Calculate the total electrostatic energy given in equation (11) in a way similar to the Wolf sum.
2. The systematic error thus introduced can be controlled by the choice of the damping parameter. By an appropriate selection of the damping parameter, one should be able to neglect the systematic error completely.

To achieve the above two goals, a simple modification has to be made to equation (11). Considering the fact that when $r_{ij} \to \infty$, $r_{\mathrm{eff}} \to r_{ij}$, hence for long interatomic distances, r_{eff} can be substituted directly by r_{ij}, for practical purposes. We thus assert that for $r_{ij} > R_c$ and the appropriate γ, the $1/r_{\mathrm{eff}}$ summation switches back to the ordinary $1/r$ summation. Equation (11) is then written as:

$$E^{\mathrm{ele}'} = \frac{1}{2}\sum_{i=1}^{N}\left(\sum_{\substack{j\neq i \\ r_{ij}\le R_c}}\frac{q_i q_j}{r_{\mathrm{eff}}} + \sum_{\substack{j\neq i \\ r_{ij}>R_c}}\frac{q_i q_j}{r}\right) \tag{16}$$

To utilize the original Wolf sum, equation (16) is transformed to the following:

$$E^{\mathrm{ele}'} = \frac{1}{2}\sum_{i=1}^{N}\left(\sum_{\substack{j\neq i \\ r_{ij}\le R_c}}\frac{q_i q_j}{r_{\mathrm{eff}}} + \sum_{\substack{j\neq i \\ r_{ij}>R_c}}\frac{q_i q_j}{r} + \sum_{\substack{j\neq i \\ r_{ij}\le R_c}}\frac{q_i q_j}{r} - \sum_{\substack{j\neq i \\ r_{ij}\le R_c}}\frac{q_i q_j}{r}\right) \tag{17}$$

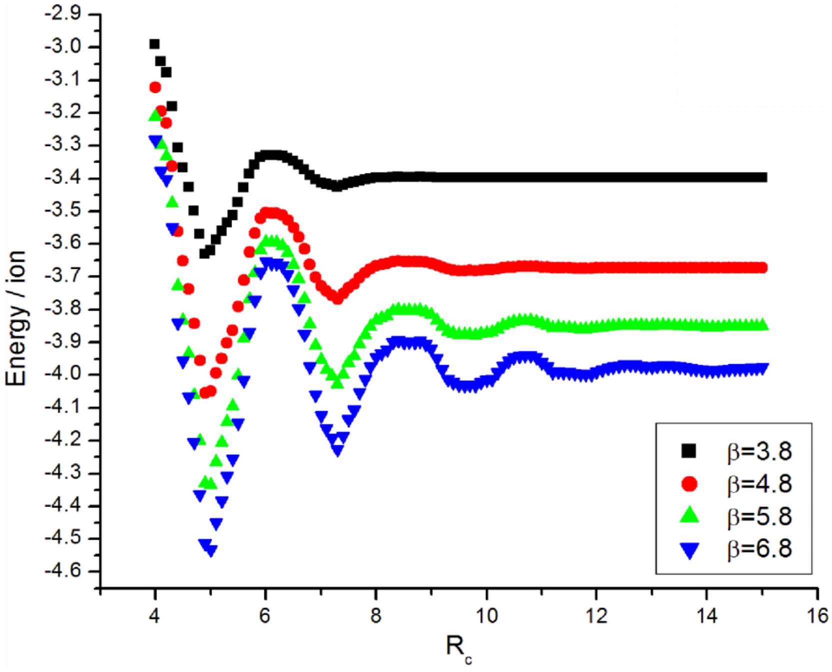

Figure 3. Inappropriate inclusion of charge overlap effect (see text for analysis). The systematic error thus introduced is huge. Both α-quartz and β-SiC exhibit the same kind of behavior.

Rearranging equation (17), yields:

$$E^{\mathrm{ele}'} = \frac{1}{2}\sum_{i=1}^{N}\left(\sum_{\substack{j\neq i\\ r_{ij}\le R_c}}\frac{q_iq_j}{r_{\mathrm{eff}}} - \sum_{\substack{j\neq i\\ r_{ij}\le R_c}}\frac{q_iq_j}{r}\right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_iq_j}{r} \tag{18}$$

The last term in equation (18) is exactly the same as in equation (1) and thus can be decomposed similarly according to equation (3), gives:

$$E^{\mathrm{ele}'} = \frac{1}{2}\sum_{i=1}^{N}\left(\sum_{\substack{j\neq i\\ r_{ij}\le R_c}}\frac{q_iq_j}{r_{\mathrm{eff}}} - \sum_{\substack{j\neq i\\ r_{ij}\le R_c}}\frac{q_iq_j}{r}\right) + E_{(1)}^{\mathrm{ele}} + E_{(2)}^{\mathrm{ele}} \tag{19}$$

where $E_{(1)}^{\mathrm{ele}}$ and $E_{(2)}^{\mathrm{ele}}$ are given in equation (4) and (5), respectively.

The first two summations in equation (19) only involve finite summation within the cutoff distance and can be calculated exactly. Thus all the systematic error comes from damping, which is represented by $E_{(2)}^{\mathrm{ele}}$. Also, the systematic error takes exactly the same form as in the original Wolf sum. Since it has already been proved that $E_{(2)}^{\mathrm{ele}}$ only represents small correction to $E_{(1)}^{\mathrm{ele}}$ for a range of damping parameters, omitting $E_{(2)}^{\mathrm{ele}}$ in the total electrostatic energy given in equation (19) is justified.

Provided that the systematic error is negligible, following the same route as in the original Wolf sum, the charge-neutralized total electrostatic energy then can be written as:

$$\begin{aligned} E^{\mathrm{ele}'} \approx{}& \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j\neq i\\ r_{ij}< R_c}}\left(\frac{q_iq_j}{r_{\mathrm{eff}}} - \frac{q_iq_j}{r_{ij}} - \lim_{r_{ij}\to R_c}\left\{\frac{q_iq_j}{r_{\mathrm{eff}}} - \frac{q_iq_j}{r_{ij}}\right\}\right) \\ &+ \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j\neq i\\ r_{ij}< R_c}}\left(\frac{q_iq_j\,erfc(r_{ij}/\beta)}{r_{ij}} - \lim_{r_{ij}\to R_c}\left\{\frac{q_iq_j\,erfc(r_{ij}/\beta)}{r_{ij}}\right\}\right) \\ &- \left(\frac{erfc(R_c/\beta)}{2R_c} + \frac{1}{2R_{\mathrm{eff}c}} - \frac{1}{2R_c} + \frac{1}{\beta\pi^{1/2}}\right)\sum_{i=1}^{N}q_i^2 \end{aligned} \tag{20}$$

where $R_{\mathrm{eff}c}$ represents the limit of r_{eff} when $r_{ij}\to R_c$. Equation (20) thus represents the modified, spherical truncated and charge-neutralized $1/r_{\mathrm{eff}}$ Wolf summation.

The pair potential then takes the following form:

$$\begin{aligned} V(r_{ij}) ={}& \frac{q_iq_j}{r_{\mathrm{eff}}} - \frac{q_iq_j}{r_{ij}} - \lim_{r_{ij}\to R_c}\left\{\frac{q_iq_j}{r_{\mathrm{eff}}} - \frac{q_iq_j}{r_{ij}}\right\} \\ &+ \frac{q_iq_j\,erfc(r_{ij}/\beta)}{r_{ij}} \\ &- \lim_{r_{ij}\to R_c}\left\{\frac{q_iq_j\,erfc(r_{ij}/\beta)}{r_{ij}}\right\} \end{aligned} \tag{21}$$

While the self energy is:

$$E_{\mathrm{self}} = \left(\frac{erfc(R_c/\beta)}{2R_c} + \frac{1}{2R_{\mathrm{eff}c}} - \frac{1}{2R_c} + \frac{1}{\beta\pi^{1/2}}\right)\sum_{i=1}^{N}q_i^2 \tag{22}$$

The forces between pairs of atoms can be obtained by taking appropriate derivative of equation (21). In analogy to the original Wolf sum, the operations of taking the limit and differential are assumed to commute:

$$\begin{aligned} f_{ij} ={}& \sum_{\substack{j\neq i\\ r_{ij}< R_c}} q_iq_j\left\{\left(\frac{r_{ij}^2}{r_{\mathrm{eff}}^4} - \frac{1}{r_{ij}^2} + \frac{erfc(r_{ij}/\beta)}{r_{ij}^2} + \frac{2}{\beta\pi^{1/2}}\frac{\exp(-r_{ij}^2/\beta^2)}{r_{ij}}\right)\right. \\ &\left. - \left(\frac{R_c^2}{R_{\mathrm{eff}c}^4} - \frac{1}{R_c^2} + \frac{erfc(R_c/\beta)}{R_c^2} + \frac{2}{\beta\pi^{1/2}}\frac{\exp(-R_c^2/\beta^2)}{R_c}\right)\right\} \end{aligned} \tag{23}$$

The energies and forces defined in equation (21) and (23) are not quite consistent with each other, as discussed in the case of original Wolf sum. The reason that energies and forces are defined in such a way is that all energies, forces and higher derivatives smoothly approach zero at cutoff distance thus avoiding any truncation artifacts.

At this point, we have achieved our goals. The modified Wolf sum takes similar form as the original one, and charge overlap effect has been taken into account empirically. The energy and force expression are somewhat more complicated than those in the original Wolf sum, but the actually implementation is exactly the same: they are all evaluated in the charge-neutralized, spherical truncated real space. The contribution from reciprocal space is the same for both cases. Any conclusion resulting from detailed analysis of error term in the original Wolf sum is equally applicable here. Thus the lengthy and complicated error analysis is skipped. For details, see the original paper by Wolf *et al.* [3].

3. Model calculations

3.1 Zero-temperature perfect crystal

Applying the modified Wolf sum, the total electrostatic energies for α-quartz and β-SiC perfect crystal are calculated and shown in figure 4 and 5, respectively. The dramatic improvement over figure 3 can be easily seen. More importantly, the effect of charge overlap is obvious. The electrostatic energy for either system has decreased significantly which is more realistic for the two covalent systems. Although no detailed error analysis is given, the fact that the total electrostatic energy converges to the same value for different β

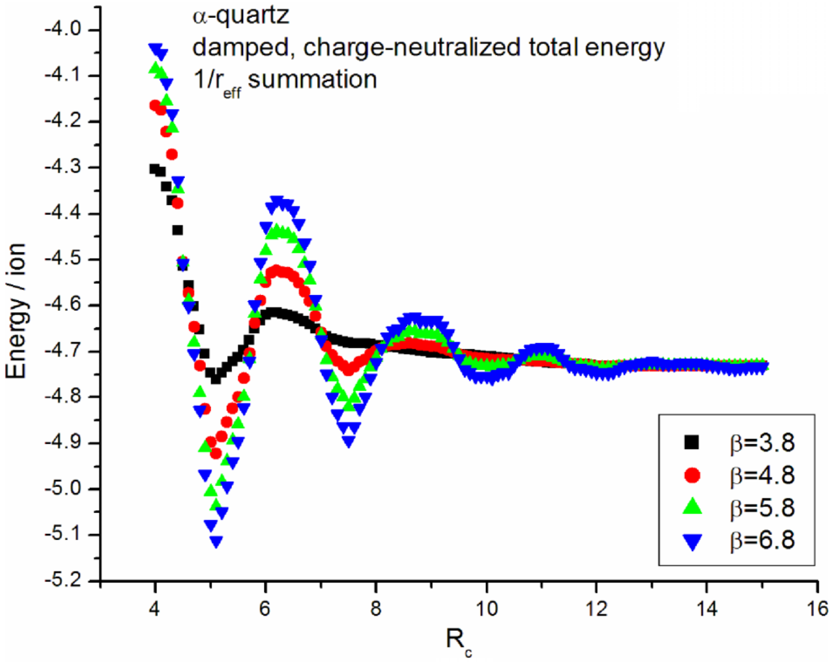

Figure 4. The total electrostatic energy calculated by modified Wolf sum for α-quartz. The improvement over figure 3 is obvious. Compared with figure 1, the charge overlap effect is clear. See text for details.

strongly suggests that the systematic error is negligible, at least for all the β values used.

3.2 High temperature crystal/melt

Since the modified Wolf sum has essentially the same systematic error as the original one, one would expect that at high temperature, the systematic error will increase significantly and is no longer negligible. Also, a smaller β value will correspond to a larger error. The calculated results for α-quartz at high temperature are shown in figure 6, which verified our expectation. The equilibrium high-T structure was obtained by molecular dynamics calculation. The total electrostatic energy was then calculated as a function of R_c based on the equilibrium structure, using different β values. The total energy given by $\beta = 3.8$ deviates clearly from the other three, which indicates the existence of a large systematic error.

As discussed by Wolf *et al.* [3], the systematic error introduced by thermal disorder can be reduced by adding correction term to the total electrostatic energy:

$$E^{(k\neq 0)} \approx \frac{Nk_BT}{2\rho\pi^{3/2}}\beta^{-3} \tag{24}$$

where ρ is the atom density *N*/*V*, and has also been proved in our calculations. The correction term in equation (24), which represents the contribution from non-zero reciprocal space vector, was then incorporated and the results are shown in figure 7. The discrepancy in total energies calculated by different β values is clearly reduced.

3.3 Energy conservation

As pointed out previously, any system described by the modified Wolf sum does not necessarily conserve energy. This is of course a problem in the context of molecular dynamics simulations under NVE ensemble, especially when the resulting energy drift is large. To test the exact energy conservation behavior of the modified Wolf sum, we thus carried out molecular dynamics simulations under micro canonical ensemble. Clearly, only electrostatic interaction would not be enough for the description of covalent systems such as SiO_2 or SiC. A simple, short-ranged Morse-stretch energy is then added to describe the covalent interactions between atoms:

$$E^{M-S} = \sum_i\sum_{j<i} D_0\{\exp[\gamma_0(1 - r_{ij}/R_0)] \\ -2\exp[\gamma_0/2(1 - r_{ij}/R_0)]\} \tag{25}$$

The equations of motion were integrated by a time-reversible, symplectic velocity-Verlet type algorithm [11], which is believed to have essentially no energy drift. To minimize any possible energy drift from the numerical integrator, a small time step of 0.5 fs was used. The resulting total energy for α-quartz in 30 ps is shown in figure 8. A small upward drift about only 0.00001 eV/molecule/ps is observed. Such a small drift is quite acceptable in molecular dynamics simulations.

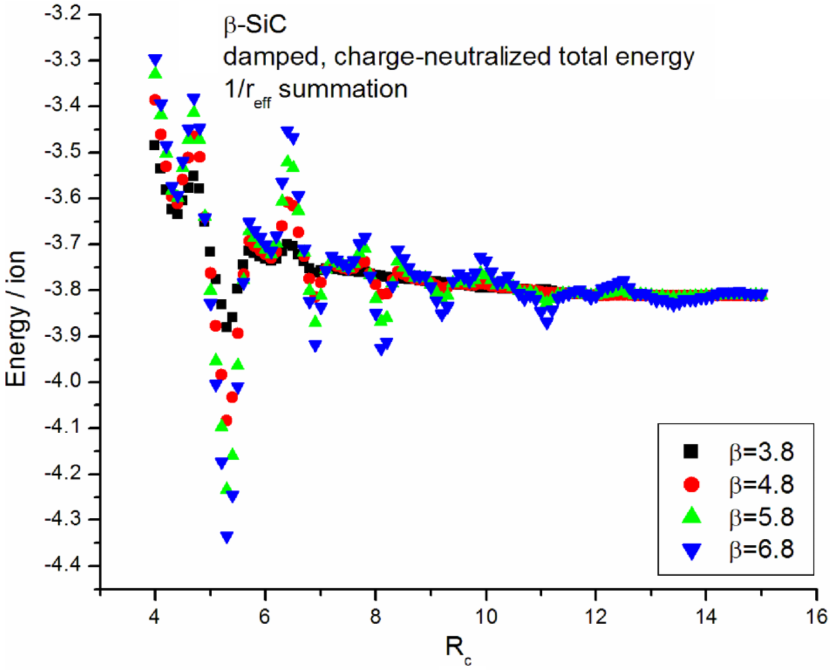

Figure 5. The total electrostatic energy calculated by modified Wolf sum for β-SiC. The results are similar to those obtained in the case of α-quartz.

Even a larger time step of 1 fs was used, the energy drift is on the order of 0.0001 eV/molecule/ps. The energy drift observed in β-SiC is comparable. The conclusion is that the energy is conserved for practical purposes.

4. Conclusion

By recognizing the invalidity of using direct 1/r coulomb interaction in covalent systems, the original Wolf sum was modified to account for the charge overlap effect in an

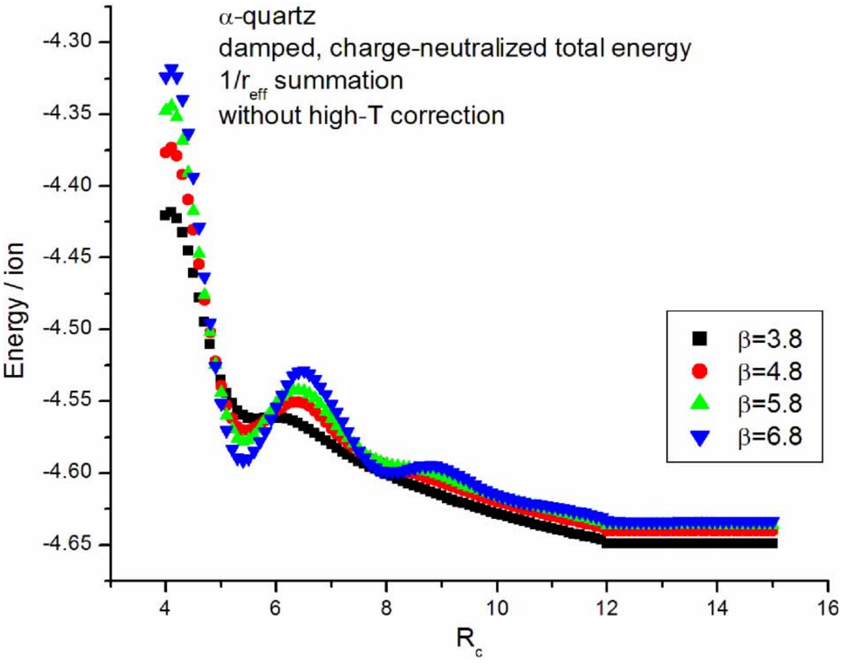

Figure 6. Calculated total electrostatic energy for α-quartz at high temperature, using different β values. The difference in the resulting total energy suggests the existence of non-negligible systematic error.

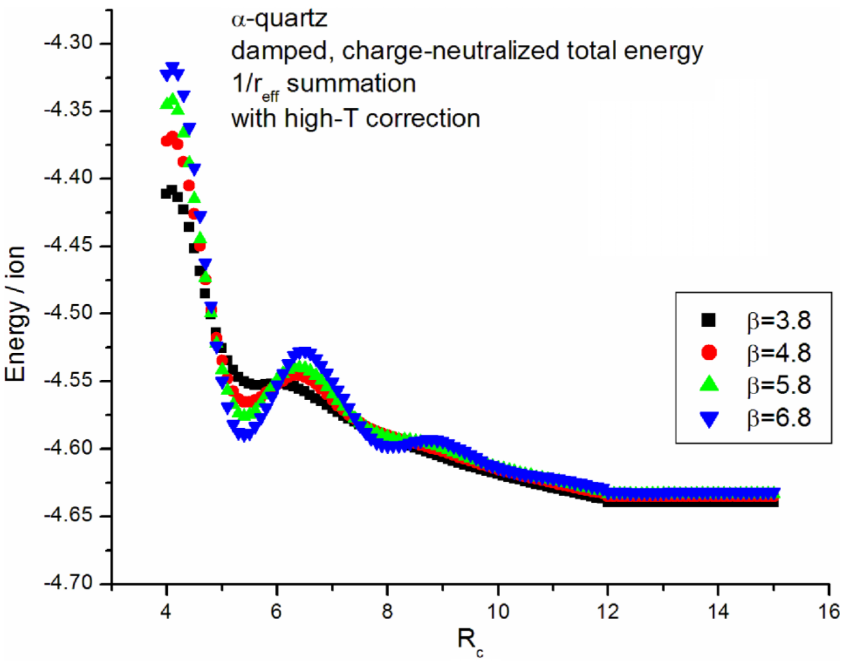

Figure 7. The total energy calculated after introducing the energy correction term. The systematic error is clearly reduced. Similar results are obtained for β-SiC (not shown).

empirical manner. Detailed analysis showed that the modified Wolf sum takes similar form as the original one. More importantly, the inclusion of charge overlap effect would not introduce any additional systematic error. Thus the error analysis can be evaluated either analytically for 3D periodic systems or estimated numerically for general cases, which is the same as in the original Wolf sum.

Application of this modified Wolf sum to covalent systems such as SiO_2 and SiC shows that it gives more realistic description of the electrostatic interaction in those systems. Although such a method does not conserve energy in principle, in practice the energy is conserved very well. Thus this method is particular suitable in molecular dynamics simulations.

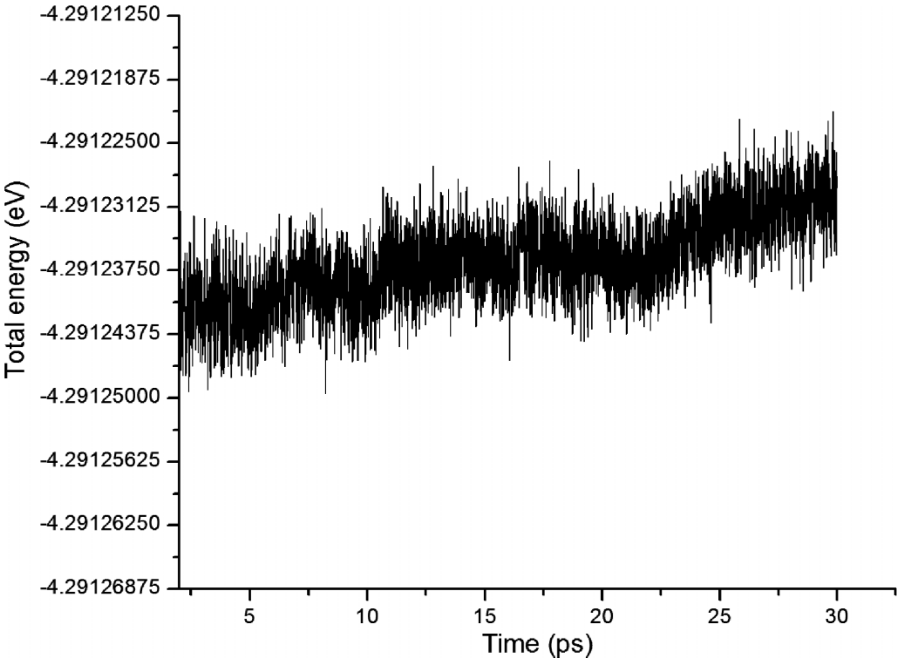

Figure 8. Total energy calculated by the modified Wolf sum plus short-ranged Morse-stretch interaction for α-quartz. A small upward energy drift is observed.

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