CALCULATING PER-ATOM AND GROUP/GROUP QUANTITIES USING THE LATTICE SUM METHOD

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A. Introduction

Because Coulombic interactions decay very slowly, these interactions are frequently handled using the Ewald (lattice) sum method.[1,2] In an Ewald sum, the total Coulombic potential U_{C} is divided into a real space portion $U_{\mathrm{C}}^{\mathrm{real}}$ and reciprocal k-space portion $U_{\mathrm{C}}^{\mathrm{recip}}$ as

$$U_{\mathrm{C}} = U_{\mathrm{C}}^{\mathrm{real}} + U_{\mathrm{C}}^{\mathrm{recip}} - U_{\mathrm{C}}^{\mathrm{self}}, \tag{1}$$

where $U_{\mathrm{C}}^{\mathrm{self}}$ is a self-correction term which must also be included (see below).

The real-space portion of the energy is calculated for $r \leq r_{\mathrm{cut}}$ as

$$U_{\mathrm{C}}^{\mathrm{real}} = \frac{1}{4\pi\,\varepsilon_0} \sum_{i,j<i} \frac{q_i\,q_j \mathrm{erfc}\left(\alpha\,r_{ij}\right)}{r_{ij}}\,, \tag{2}$$

where α is the constant that controls how the potential is divided between real and reciprocal space.

The k-space portion of the energy is efficiently handled using a Fourier series as

$$U_{\mathrm{C}}^{\mathrm{recip}} = \frac{1}{2\,V\,\varepsilon_0} \sum_{\mathbf{k}\neq 0} \Gamma(k)\,\chi(\mathbf{k})\,, \tag{3}$$

where $\mathbf{k}$ are the reciprocal lattice vectors, $k = |\mathbf{k}|$, and $\Gamma(k)$ are Fourier coefficients given as

$$\Gamma(k) = k^{-2}\,e^{-k^2/4\alpha^2}\,. \tag{4}$$

The quantity $\chi(\mathbf{k})$ can be defined as a double sum over particle positions as

$$\chi(\mathbf{k}) = \sum_{i=1}^{N} \sum_{j=1}^{N} q_i\,q_j\,e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}} \tag{5}$$

where N is the total number of atoms, $\mathtt{i}$ is the imaginary number, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. However, the double sum in Eq. 5 is very expensive, so normally one reduces the double sum in Eq. 5 to a single sum as

$$\begin{aligned}\chi(\mathbf{k}) &= \sum_{i=1}^{N}\sum_{j=1}^{N} q_i\, q_j\, e^{\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}} \\ &= \sum_{i=1}^{N} q_i\, e^{\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_i} \sum_{j=1}^{N} q_j\; e^{-\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_j} \\ &= S(\mathbf{k})\, S(-\mathbf{k})\,, \end{aligned} \tag{6}$$

where $S(\mathbf{k})$ is the structure factor:

$$S(\mathbf{k}) = \sum_{i=1}^{N} q_i\, e^{\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_i}\,. \tag{7}$$

In the traditional lattice sum, a particle interacts with itself, all periodic images of itself, all of its neighbors, and all periodic images of its neighbors. Because a particle interacts with itself, an energy self-correction term must be subtracted from the total energy:

$$U_{\mathrm{C}}^{\mathrm{self}} = \frac{\alpha}{4\pi^{3/2}\,\varepsilon_0} \sum_i q_i^2\,. \tag{8}$$

B. Group-Group Ewald Sum

Eq. 5 includes a double sum over particles. In order to get interactions of group A atoms on group B atoms, one can restrict the double sum in Eq. 5 to include only groups A and B as:

$$\begin{aligned}\chi(\mathbf{k}) &= \sum_{i=1}^{N_{\mathrm{A}}}\sum_{j=1}^{N_{\mathrm{B}}} q_i\, q_j\, e^{\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}} \\ &= \sum_{i=1}^{N_{\mathrm{A}}} q_i\, e^{\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_i} \sum_{j=1}^{N_{\mathrm{B}}} q_j\, e^{-\mathtt{i}\,\mathbf{k}\cdot\mathbf{r}_j} \\ &= S_{\mathrm{A}}(\mathbf{k})\, S_{\mathrm{B}}(-\mathbf{k})\,, \end{aligned} \tag{9}$$

where N_{A} is the number of atoms in group A, N_{B} is the number of atoms in group B, $S_{\mathrm{A}}(\mathbf{k})$ is the group A structure factor:

$$S_{\mathrm{A}}(\mathbf{k}) = \sum_{i=\mathrm{type\,A}} q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \,. \tag{10}$$

and $S_{\mathrm{B}}(\mathbf{k})$ is the group B structure factor:

$$S_{\mathrm{B}}(\mathbf{k}) = \sum_{j=\mathrm{type\,B}} q_j \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_j} \,. \tag{11}$$

One can think of this as all group A atoms and periodic images interacting with all group B atoms and periodic images. If an atom is in both groups A and B, one must also include the energy self-correction for that atom (see Eq. 8). One can obtain group-group forces in a similar manner by using the same group structure factors.

C. Per-atom Ewald Sum

In a similar manner, one can think of per-atom energy as one atom interacting with a group of all other atoms. Per-atom values can therefore be obtained by replacing $\chi(\mathbf{k})$ in Eqs. 9 with a per-atom version[3–5]

$$\begin{aligned} \chi_i(\mathbf{k}) &= \sum_i q_i \, q_j e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}} \\ &= S(-\mathbf{k})\, S_i(\mathbf{k}) \,, \end{aligned} \tag{12}$$

where $S_i(\mathbf{k})$ is a per-atom structure factor defined as

$$S_i(\mathbf{k}) = q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \,. \tag{13}$$

One must also include a per-atom version of the self-correction term (Eq. 8).

D. PPPM

In the PPPM method, group-group energy and force can be obtained in a similar manner. One interpolates charges for groups A and B to a mesh and then uses two forward FFTs (one for each group) to obtain group A and B structure factors. Total energy and force are then obtained using these group structure factors in a manner very similar to the Ewald sum.

Because only the total force is needed, no reverse FFTs are necessary and all calculations are performed in reciprocal space.

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