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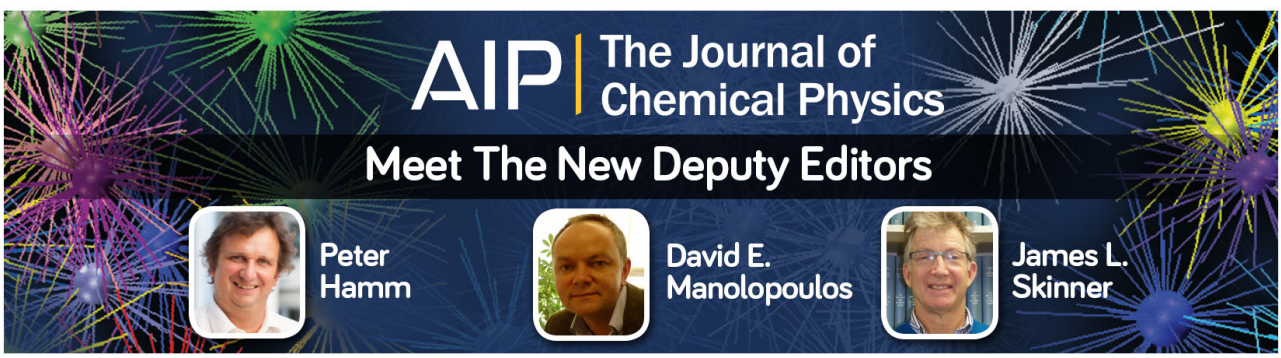


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# Arbitrary order permanent Cartesian multipolar electrostatic interactions

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Recently, there has been a concerted effort to implement advanced classical potential energy surfaces by adding higher order multipoles to fixed point charge electrostatics in a bid to increase the accuracy of simulations of condensed phase systems. One major hurdle is the unwieldy nature of the expressions which in part has limited developers mostly to including only dipoles and quadrupoles. In this paper, we present a generalization of the Cartesian formulation of electrostatic multipolar interactions that enables the specification of an arbitrary order of multipoles. Specifically, we derive formulas for arbitrary order implementation of the particle mesh Ewald method and give a closed form formula for the stress tensor in the reciprocal space. In addition, we provide recurrence relations for common electrostatic potentials employed in molecular simulations, which allows for the generalization to arbitrary order and guarantees a computational cost that scales as $O(p^3)$ for Cartesian multipole interactions of order $p$. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4905952]

## I. INTRODUCTION

The rapid increase in available computing power today has spurred the adaptation of advanced classical electrostatic potential energy surfaces. These provide better accuracy[1–3] than the standard fixed point charge but hitherto had been computationally prohibitive.

The development of distributed multipole analysis by Stone[4] was followed by the introduction of point multipoles in Ewald summation by Smith.[5] Most of the extensions to the work by Smith has been limited to dipoles[6] or up to quadrupoles[7–10] because of the cumbersome form of the Cartesian representation. Sagui, Pedersen, and Darden (SPD)[11] built on initial work by Toukmaji *et al.*[6] and extended the Cartesian representation of the multipolar form of the particle mesh Ewald (PME)[12] method from first order to fourth order. Simmonett *et al.*[13] have recast the real space part of the multipolar Ewald sum in spherical harmonics while employing PME for the reciprocal space part. The work by SPD on multipolar PME has been implemented in the TINKER[14] and Amber[15] simulation softwares as part of the AMOEBA[2] polarizable force field. The authors of this article are currently implementing the AMOEBA force field in the DL_POLY[16] simulation package using the approach developed in this paper.

As computing power increases, the use of multipoles of higher order to gain higher accuracy in simulation has become more and more feasible. This paper generalizes previous work by several groups[7–11] in the spirit of Hättig's[17,18] work with spherical tensor formalism to provide a simple framework for implementing arbitrary order multipolar electrostatic interactions. We apply our framework to PME and other common electrostatic potentials employed in most simulations. Although obtaining higher order multipoles is challenging, the GDMA program[19] by Stone has made this task manageable and offers the opportunity to obtain multipoles up to tenth order.[20]

We note that the AMOEBA force field includes induced-dipoles in addition to permanent multipoles, but this article focuses on the generalization of the permanent multipoles. However, the implementation in DL_POLY includes induced-multipoles as presented in the work of Ren and Ponder[21] and Burnham *et al.*[22]

The rest of the paper is organized as follows: Sec. II introduces the formalism used in our derivations. In Sec. III, we apply the formalism to derive formulas for arbitrary order permanent Cartesian multipolar interaction for general pair potentials and provide recurrence relations for the multi-dimensional derivatives of some kernels in DL_POLY. Section IV applies the method to PME, and in Sec. V, we outline the derivation of a closed form formula for the stress tensor due to an arbitrary order reciprocal space Ewald sum. This is followed by concluding remarks and an appendix with more detailed derivations.

## II. FORMALISM

Following the notation in SPD,[11] we consider a set of $N$ interacting point multipoles and define the multipolar operator, $\hat{L}_i$, by

$$\hat{L}_i = (q_i + \mathbf{p}_i \cdot \nabla_i + \mathbf{Q}_i : \nabla_i\nabla_i + \mathbf{O}_i : \nabla_i\nabla_i\nabla_i + \mathbf{H}_i :: \nabla_i\nabla_i\nabla_i\nabla_i + \cdots), \tag{1}$$

where $\mathbf{p}_i$, $\mathbf{Q}_i$, $\mathbf{O}_i$, and $\mathbf{H}_i$ are the dipole, quadrupole, octupole, and hexadecapole, respectively, of atom $i$. The "dot" products stand for tensor contraction, thus,

$$\begin{aligned}\mathbf{H}_i :: \nabla_i\nabla_i\nabla_i\nabla_i &= \sum_{\alpha,\beta,\gamma,\nu} H_{\alpha\beta\gamma\nu}(\partial/\partial x_\alpha)(\partial/\partial x_\beta)(\partial/\partial x_\gamma)(\partial/\partial x_\nu) \\ &= \sum_{\alpha,\beta,\gamma,\nu} H_{\alpha\beta\gamma\nu} D_{x_\alpha} D_{x_\beta} D_{x_\gamma} D_{x_\nu}.\end{aligned} \tag{2}$$

For any function, $\psi(|\mathbf{r_i} - \mathbf{r_j}|) = \psi(r_{ij})$, $\nabla_j\psi(r_{ij}) = -\nabla_i\psi(r_{ij})$, thus for any pair potential, given the definition of $\hat{L}_i$ in Eq. (1),

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the corresponding multipolar operator for atom $j$ is

$$\hat{L}_{j_i} = (q_j - \mathbf{p}_j \cdot \nabla_i + \mathbf{Q}_j : \nabla_i\nabla_i - \mathbf{O}_j \vdots \nabla_i\nabla_i\nabla_i + \mathbf{H}_j :: \nabla_i\nabla_i\nabla_i\nabla_i + \cdots). \quad (3)$$

Again following SPD, we define a unidimensional vector of independent multipole moments,

$$\mathcal{M} = (q, p_x, p_y, p_z, Q_{xx}, Q_{xy}, Q_{xz}, Q_{yy}, Q_{yz}, Q_{zz}, O_{xxx}, \ldots, H_{xxxx}, H_{xxxy}, \ldots), \quad (4)$$

based on the original multipole vector which has degenerate components for multipoles of order two and higher. We use a triplet $\{a,b,c\}$ to refer to the components of $\mathcal{M}$. Thus, $\mathcal{M}^{abc}$ refers to the component which in Eqs. (1) and (3) multiplies the operator with $a$, $b$, and $c$ derivatives in the $x$, $y$, and $z$ coordinates, respectively. As an example, $\mathcal{M}^{000}$ refers to the zero-order multipole (monopole), i.e., $\mathcal{M}^{000} = q$, which multiplies unity, $\mathcal{M}^{100}$ refers to the x-coordinate of the dipole, i.e., $p_x$ which forms a product with the operator $\partial/\partial x$ and $\mathcal{M}^{211}$ refers to the hexadecapole component $\mathbf{H}_{xxyz}$ which multiplies $\partial^4/\partial x^2 \partial y \partial z$. In addition, individual components of $\mathcal{M}$ contain the sum of all degenerate original multipole components. As an example, the octupole $\mathcal{M}^{111}$, which forms a product with $\partial^3/\partial x \partial y \partial z$, is a sum of all six degenerate original octupole components formed from the permutation of the triplet $\{x, y, z\}$. If we label the original octupole vector as $O'$, then $\mathcal{M}^{111} = O'_{xyz} + O'_{xzy} + O'_{yxz} + O'_{yzx} + O'_{zxy} + O'_{zyx} = 6O'_{xyz}$.

With these definitions, we can rewrite the multipolar operators up to order $p$ on atoms $i$ and $j$, respectively, in a more compact form as

$$\hat{L}_i = \sum_{\mathbf{s}=\mathbf{0}}^{p} \mathcal{M}_i^{\mathbf{s}} \mathbf{D}_i^{\mathbf{s}} \quad (5)$$

and

$$\hat{L}_{j_i} = \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \mathbf{D}_i^{\mathbf{s}}, \quad (6)$$

where $\mathbf{s} = (s_1, s_2, s_3)$ and $\|\mathbf{s}\| = s = s_1 + s_2 + s_3$. As an example, Eq. (6) can be expanded into

$$\hat{L}_{j_i} = \sum_{s_3=0}^{p} \sum_{s_2=0}^{p-s_3} \sum_{s_1=0}^{p-s_3-s_2} (-1)^{s_1+s_2+s_3} \mathcal{M}_j^{s_1 s_2 s_3} D_{z_i}^{s_3} D_{y_i}^{s_2} D_{x_i}^{s_1}, \quad (7)$$

which shows that the sum over $\mathbf{s}$ is actually a triple sum over $s_1$, $s_2$, and $s_3$.

## III. APPLICATION TO SIMPLE PAIR POTENTIALS

For $N$ particles interacting via a pair potential function $\psi$, the multipolar electrostatic potential at position $\mathbf{r_i}$ is given by

$$\begin{aligned}\phi(\mathbf{r_i}) &= \sum_{j\neq i}^{N} \hat{L}_{j_i} \psi(\mathbf{r_{ji}}) \\ &= \sum_{j\neq i}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \mathbf{D}_i^{\mathbf{s}} \psi(r_{ji}) \\ &= \sum_{j\neq i}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \mathbf{D}_i^{\mathbf{s}} \psi(r_{ij}), \end{aligned} \quad (8)$$

the electrostatic field at $\mathbf{r_i}$ is

$$\begin{aligned}\mathbf{E}(\mathbf{r_{ij}}) &= -\nabla_i \phi(r_{ij}) \\ &= -\sum_{j\neq i}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \nabla_i \mathbf{D}_i^{\mathbf{s}} \psi(r_{ij}) \\ &= -\sum_{j\neq i}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \begin{bmatrix} \mathbf{D}_i^{\mathbf{s}+\mathbf{e}_1} \\ \mathbf{D}_i^{\mathbf{s}+\mathbf{e}_2} \\ \mathbf{D}_i^{\mathbf{s}+\mathbf{e}_3} \end{bmatrix} \psi(r_{ij}), \end{aligned} \quad (9)$$

where $\mathbf{e}_1 = \langle 1,0,0\rangle$, $\mathbf{e}_2 = \langle 0,1,0\rangle$, and $\mathbf{e}_3 = \langle 0,0,1\rangle$ and the torque on particle $i$ in the $\alpha$-direction, $\tau_{i,\alpha}$, is obtained as

$$\begin{aligned}\tau_{i,\alpha} &= \sum_{\mathbf{s}=\mathbf{0}}^{p} \mathcal{M}_{i,\alpha}^{\mathbf{s}} \mathbf{D}_i^{\mathbf{s}} \phi(\mathbf{r_{ij}}) \\ &= \sum_{\mathbf{s}=\mathbf{0}}^{p} \mathcal{M}_{i,\alpha}^{\mathbf{s}} \sum_{j\neq i}^{N} \sum_{\mathbf{k}=\mathbf{0}}^{p} (-1)^{\|\mathbf{k}\|} \mathcal{M}_j^{\mathbf{k}} \mathbf{D}_i^{\mathbf{s}+\mathbf{k}} \psi(r_{ij}), \end{aligned} \quad (10)$$

where $\mathcal{M}_{i,\alpha}$ is the infinitesimal counter-clockwise rotation of multipole vector $\mathcal{M}_i$ about the $\alpha$-axis.[11] The torques can be converted to forces using procedures developed by several workers.[6,11,23]

The total electrostatic potential energy is given by

$$\begin{aligned}U &= \sum_{i<j}^{N} \hat{L}_i \hat{L}_{j_i} \psi(r_{ij}) \\ &= \sum_{i<j}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \mathbf{D}_i^{\mathbf{s}} \sum_{\mathbf{k}=\mathbf{0}}^{p} \mathcal{M}_i^{\mathbf{k}} \mathbf{D}_i^{\mathbf{k}} \psi(r_{ij}) \\ &= \sum_{i<j}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \sum_{\mathbf{k}=\mathbf{0}}^{p} \mathcal{M}_i^{\mathbf{k}} \mathbf{D}_i^{\mathbf{s}+\mathbf{k}} \psi(r_{ij}), \end{aligned} \quad (11)$$

where $\mathbf{s}+\mathbf{k} = (s_1+k_1, s_2+k_2, s_3+k_3)$ and the force on atom $i$ is

$$\begin{aligned}\mathbf{f}_i &= -\nabla_i \sum_{j\neq i}^{N} \hat{L}_i \hat{L}_{j_i} \psi(r_{ij}) \\ &= -\sum_{j\neq i}^{N} \sum_{\mathbf{s}=\mathbf{0}}^{p} (-1)^{\|\mathbf{s}\|} \mathcal{M}_j^{\mathbf{s}} \sum_{\mathbf{k}=\mathbf{0}}^{p} \mathcal{M}_i^{\mathbf{k}} \begin{bmatrix} \mathbf{D}_i^{\mathbf{s}+\mathbf{k}+\mathbf{e}_1} \\ \mathbf{D}_i^{\mathbf{s}+\mathbf{k}+\mathbf{e}_2} \\ \mathbf{D}_i^{\mathbf{s}+\mathbf{k}+\mathbf{e}_3} \end{bmatrix} \psi(r_{ij}). \end{aligned} \quad (12)$$

### A. Example

As an example, we consider the case where the multipoles on each atom go up to quadrupoles, i.e., $p = 2$. For an original multipole vector

$$[q', p'_x, p'_y, p'_z, Q'_{xx}, Q'_{xy}, Q'_{xz}, Q'_{yx}, Q'_{yy}, Q'_{yz}, Q'_{zx}, Q'_{zy}, Q'_{zz}], \quad (13)$$

the corresponding independent multipole vector is

$$\begin{aligned}\mathcal{M} &= [q', p'_x, p'_y, p'_z, Q'_{xx}, 2Q'_{xy}, 2Q'_{xz}, Q'_{yy}, 2Q'_{yz}, Q'_{zz}] \\ &= [\mathcal{M}^{000}, \mathcal{M}^{100}, \mathcal{M}^{010}, \mathcal{M}^{001}, \mathcal{M}^{200}, \mathcal{M}^{110}, \mathcal{M}^{101}, \mathcal{M}^{020}, \mathcal{M}^{011}, \mathcal{M}^{002}]. \end{aligned} \quad (14)$$

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In a system where the atoms have just charges and dipoles, that is, $p = 1$, the total electrostatic energy is given by

$$\begin{aligned} U &= \sum_{i<j}^{N}\sum_{\mathbf{s}=\mathbf{0}}^{1}(-1)^{\|\mathbf{s}\|}\mathcal{M}_j^{\mathbf{s}}\sum_{\mathbf{k}=\mathbf{0}}^{1}\mathcal{M}_i^{\mathbf{k}}\mathbf{D}_i^{\mathbf{s}+\mathbf{k}}\psi(r_{ij}) \\ &= \sum_{i<j}^{N}\Big\{\mathcal{M}_j^{000}\big[\mathcal{M}_i^{000}\psi(r_{ij}) + \mathcal{M}_i^{100}\mathbf{D}_i^{100}\psi(r_{ij}) \\ &\quad + \mathcal{M}_i^{010}\mathbf{D}_i^{010}\psi(r_{ij}) + \mathcal{M}_i^{001}\mathbf{D}_i^{001}\psi(r_{ij})\big] \\ &\quad - \mathcal{M}_j^{100}\big[\mathcal{M}_i^{000}\mathbf{D}_i^{100}\psi(r_{ij}) + \mathcal{M}_i^{100}\mathbf{D}_i^{200}\psi(r_{ij}) \\ &\quad + \mathcal{M}_i^{010}\mathbf{D}_i^{110}\psi(r_{ij}) + \mathcal{M}_i^{001}\mathbf{D}_i^{101}\psi(r_{ij})\big] \\ &\quad - \mathcal{M}_j^{010}\big[\mathcal{M}_i^{000}\mathbf{D}_i^{010}\psi(r_{ij}) + \mathcal{M}_i^{100}\mathbf{D}_i^{110}\psi(r_{ij}) \\ &\quad + \mathcal{M}_i^{010}\mathbf{D}_i^{020}\psi(r_{ij}) + \mathcal{M}_i^{001}\mathbf{D}_i^{011}\psi(r_{ij})\big] \\ &\quad - \mathcal{M}_j^{001}\big[\mathcal{M}_i^{000}\mathbf{D}_i^{001}\psi(r_{ij}) + \mathcal{M}_i^{100}\mathbf{D}_i^{101}\psi(r_{ij}) \\ &\quad + \mathcal{M}_i^{010}\mathbf{D}_i^{011}\psi(r_{ij}) + \mathcal{M}_i^{001}\mathbf{D}_i^{002}\psi(r_{ij})\big]\Big\} \end{aligned} \tag{15}$$

and the force on an atom $i$ is

$$\begin{aligned} \mathbf{f}_i &= -\sum_{j\neq i}^{N}\sum_{\mathbf{s}=\mathbf{0}}^{1}(-1)^{\|\mathbf{s}\|}\mathcal{M}_j^{\mathbf{s}}\sum_{\mathbf{k}=\mathbf{0}}^{1}\mathcal{M}_i^{\mathbf{k}}\begin{bmatrix}\mathbf{D}_i^{\mathbf{s}+\mathbf{k}+\mathbf{e}_1}\\ \mathbf{D}_i^{\mathbf{s}+\mathbf{k}+\mathbf{e}_2}\\ \mathbf{D}_i^{\mathbf{s}+\mathbf{k}+\mathbf{e}_3}\end{bmatrix}\psi(r_{ij}) \\ &= -\sum_{j\neq i}^{N}\Bigg\{\mathcal{M}_j^{000}\Bigg(\mathcal{M}_i^{000}\begin{bmatrix}\mathbf{D}_i^{100}\\ \mathbf{D}_i^{010}\\ \mathbf{D}_i^{001}\end{bmatrix} + \mathcal{M}_i^{100}\begin{bmatrix}\mathbf{D}_i^{200}\\ \mathbf{D}_i^{110}\\ \mathbf{D}_i^{101}\end{bmatrix} \\ &\quad + \mathcal{M}_i^{010}\begin{bmatrix}\mathbf{D}_i^{110}\\ \mathbf{D}_i^{020}\\ \mathbf{D}_i^{011}\end{bmatrix} + \mathcal{M}_i^{001}\begin{bmatrix}\mathbf{D}_i^{101}\\ \mathbf{D}_i^{011}\\ \mathbf{D}_i^{002}\end{bmatrix}\Bigg)\psi(r_{ij}) \\ &\quad - \mathcal{M}_j^{100}\Bigg(\mathcal{M}_i^{000}\begin{bmatrix}\mathbf{D}_i^{200}\\ \mathbf{D}_i^{110}\\ \mathbf{D}_i^{101}\end{bmatrix} + \mathcal{M}_i^{100}\begin{bmatrix}\mathbf{D}_i^{300}\\ \mathbf{D}_i^{210}\\ \mathbf{D}_i^{201}\end{bmatrix} \\ &\quad + \mathcal{M}_i^{010}\begin{bmatrix}\mathbf{D}_i^{210}\\ \mathbf{D}_i^{120}\\ \mathbf{D}_i^{111}\end{bmatrix} + \mathcal{M}_i^{001}\begin{bmatrix}\mathbf{D}_i^{201}\\ \mathbf{D}_i^{111}\\ \mathbf{D}_i^{102}\end{bmatrix}\Bigg)\psi(r_{ij}) \\ &\quad - \mathcal{M}_j^{010}\Bigg(\mathcal{M}_i^{000}\begin{bmatrix}\mathbf{D}_i^{110}\\ \mathbf{D}_i^{020}\\ \mathbf{D}_i^{011}\end{bmatrix} + \mathcal{M}_i^{100}\begin{bmatrix}\mathbf{D}_i^{210}\\ \mathbf{D}_i^{120}\\ \mathbf{D}_i^{111}\end{bmatrix} \\ &\quad + \mathcal{M}_i^{010}\begin{bmatrix}\mathbf{D}_i^{120}\\ \mathbf{D}_i^{030}\\ \mathbf{D}_i^{021}\end{bmatrix} + \mathcal{M}_i^{001}\begin{bmatrix}\mathbf{D}_i^{111}\\ \mathbf{D}_i^{021}\\ \mathbf{D}_i^{012}\end{bmatrix}\Bigg)\psi(r_{ij}) \\ &\quad - \mathcal{M}_j^{001}\Bigg(\mathcal{M}_i^{000}\begin{bmatrix}\mathbf{D}_i^{101}\\ \mathbf{D}_i^{011}\\ \mathbf{D}_i^{002}\end{bmatrix} + \mathcal{M}_i^{100}\begin{bmatrix}\mathbf{D}_i^{201}\\ \mathbf{D}_i^{111}\\ \mathbf{D}_i^{102}\end{bmatrix} \\ &\quad + \mathcal{M}_i^{010}\begin{bmatrix}\mathbf{D}_i^{111}\\ \mathbf{D}_i^{021}\\ \mathbf{D}_i^{012}\end{bmatrix} + \mathcal{M}_i^{001}\begin{bmatrix}\mathbf{D}_i^{102}\\ \mathbf{D}_i^{012}\\ \mathbf{D}_i^{003}\end{bmatrix}\Bigg)\psi(r_{ij})\Bigg\}. \end{aligned} \tag{16}$$

Computing the energy, forces, or torques comes down to computing the multi-dimensional derivatives of the pair potential kernel $\psi$. We use recurrence relations to obtain the derivatives of the kernels to a specified order. In Sec. III B, we provide the recurrence relations for kernels of electrostatic pair potentials present in DL_POLY. Once the derivatives of $\psi(r_{ij})$ are at hand, computing the energy or force, for example, due to an interaction between particles $i$ and $j$ involves an execution of the loop structure in Algorithm I.

## B. Recurrence relations

### 1. Kernels of the form $\theta(|\mathbf{x}|) = \frac{1}{|\mathbf{x}|^{\nu}}$

Let $\langle x_1, x_2, x_3\rangle = \mathbf{x}$ and $d_{s_1s_2s_3} = d_{\mathbf{s}} = \mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\theta(|\mathbf{x}|)$ be the multidimensional derivative with respect to $\mathbf{x}$ of the pair potential $\theta(|\mathbf{x}|)$ with $s_1$, $s_2$, and $s_3$ derivatives in the $x$, $y$,

ALGORITHM I. Compute interactions.

```
1  Do s3 = 0, p
2     Do s2 = 0, p − s3
3        Do s1 = 0, p − s3 − s2
4           M̃_j^s = (−1)^(s1+s2+s3) · M_j^(s1 s2 s3)
5           Do k3 = 0, p
6              Do k2 = 0, p − k3
7                 Do k1 = 0, p − k3 − k2
8                    U = U + M̃_j^s · M_i^(k1 k2 k3) D_zi^(s3+k3) D_yi^(s2+k2) D_xi^(s1+k1) ψ(r_ij)
9                    f_i = f_i − M̃_j^s · M_i^(k1 k2 k3) [D_zi^(s3+k3) D_yi^(s2+k2) D_xi^(s1+k1+1);
                                                         D_zi^(s3+k3) D_yi^(s2+k2+1) D_xi^(s1+k1);
                                                         D_zi^(s3+k3+1) D_yi^(s2+k2) D_xi^(s1+k1)] ψ(r_ij)
10                   τ_{i,α} = τ_{i,α} + M_{i,α}^(k1 k2 k3) · M̃_j^s D_zi^(s3+k3) D_yi^(s2+k2) D_xi^(s1+k1) ψ(r_ij)
11                End Do
12             End Do
13          End Do
14       End Do
15    End Do
16 End Do
```

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and $z$ coordinates, respectively, i.e.,

$$d_{\mathbf{s}} = d_{s_1 s_2 s_3} = \frac{\partial^{\|\mathbf{s}\|}\theta(|\mathbf{x}|)}{\partial_{x_1}^{s_1}\partial_{x_2}^{s_2}\partial_{x_3}^{s_3}}. \tag{17}$$

In work by Duan and Krasny,[24] a recurrence relation for the multidimensional Taylor coefficients, $T_{\mathbf{s}}$ of kernels of the form

$$\theta(|\mathbf{x}|) = \frac{1}{|\mathbf{x}|^{\nu}}, \tag{18}$$

was derived as

$$T_{\mathbf{s}} = \frac{1}{|\mathbf{x}|^2}\left\{\left(\frac{2-\nu}{\|\mathbf{s}\|}-2\right)\sum_{i=1}^{3} x_i T_{\mathbf{s}-\mathbf{e}_i} + \left(\frac{2-\nu}{\|\mathbf{s}\|}-1\right)\sum_{i=1}^{3} T_{\mathbf{s}-2\mathbf{e}_i}\right\}, \tag{19}$$

where

$$T_{\mathbf{s}} = \frac{1}{\mathbf{s}!}\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\theta(|\mathbf{x}|) = \frac{1}{s_1!s_2!s_3!}\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\theta(|\mathbf{x}|). \tag{20}$$

Using the definition in Eq. (20), the recurrence in Eq. (19) can be expanded into

$$\frac{1}{\mathbf{s}!}\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\theta(|\mathbf{x}|) = \frac{1}{|\mathbf{x}|^2}\left\{\left(\frac{2-\nu}{\|\mathbf{s}\|}-2\right)\sum_{i=1}^{3}\frac{x_i\cdot\mathbf{D}_{\mathbf{x}}^{\mathbf{s}-\mathbf{e}_i}\theta(|\mathbf{x}|)}{(\mathbf{s}-\mathbf{e}_i)!} + \left(\frac{2-\nu}{\|\mathbf{s}\|}-1\right)\sum_{i=1}^{3}\frac{\mathbf{D}_{\mathbf{x}}^{\mathbf{s}-2\mathbf{e}_i}\theta(|\mathbf{x}|)}{(\mathbf{s}-2\mathbf{e}_i)!}\right\}. \tag{21}$$

Then multiplying through Eq. (21) by $\mathbf{s}!$ generates the recurrence relation for the multidimensional derivatives of the kernel as

$$d_{\mathbf{s}}(\nu) = \mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\theta(|\mathbf{x}|) = \frac{1}{|\mathbf{x}|^2}\left\{\left(\frac{2-\nu}{\|\mathbf{s}\|}-2\right)\sum_{i=1}^{3} s_i x_i d_{\mathbf{s}-\mathbf{e}_i} + \left(\frac{2-\nu}{\|\mathbf{s}\|}-1\right)\sum_{i=1}^{3} s_i(s_i-1)d_{\mathbf{s}-2\mathbf{e}_i}\right\}. \tag{22}$$

Here, we set $\mathbf{x} = \mathbf{r_{ij}}$ to get the recurrence for a kernel written as $\theta(r_{ij})$.

### 2. Recurrence for $\frac{\mathrm{erfc}(|\mathbf{x}|)}{|\mathbf{x}|}$ and $\frac{\mathrm{erf}(|\mathbf{x}|)}{|\mathbf{x}|}$

The other relevant kernels we require are

$$\psi(|\mathbf{x}|) = \frac{\sqrt{\pi}}{2}\frac{\mathrm{erfc}(|\mathbf{x}|)}{|\mathbf{x}|} \quad \text{and} \quad \Gamma(|\bar{\mathbf{x}}|) = \frac{\sqrt{\pi}}{2}\frac{\mathrm{erf}(|\mathbf{x}|)}{|\mathbf{x}|}. \tag{23}$$

A recurrence relation for the Taylor coefficients of $\frac{\mathrm{erfc}(|\mathbf{x}|)}{|\mathbf{x}|}$ has been derived previously.[25,26] The recurrence requires Taylor coefficients of the kernel

$$\Omega(|\mathbf{x}|) = \frac{1}{2}\exp(-|\mathbf{x}|^2). \tag{24}$$

If we let $c_{\mathbf{s}} = \mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\Omega(|\mathbf{x}|)$ and $a_{\mathbf{s}} = \mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\psi(|\mathbf{x}|)$, then by using similar arguments to that used in Sec. III B 1 and the recurrence for the Taylor coefficients of $\psi(|\mathbf{x}|)$ and $\Omega(|\mathbf{x}|)$, we can show that

$$c_{\mathbf{s}} = \frac{-2}{\|\mathbf{s}\|}\sum_{i=1}^{3}\left[s_i x_i c_{\mathbf{s}-\mathbf{e}_i} + s_i(s_i-1)c_{\mathbf{s}-2\mathbf{e}_i}\right] \tag{25}$$

and

$$a_{\mathbf{s}} = \frac{1}{|\mathbf{x}|^2}\left\{\left(\frac{1}{\|\mathbf{s}\|}-2\right)\sum_{i=1}^{3} s_i x_i a_{\mathbf{s}-\mathbf{e}_i} + \left(\frac{1}{\|\mathbf{s}\|}-1\right)\sum_{i=1}^{3} s_i(s_i-1)a_{\mathbf{s}-2\mathbf{e}_i} + c_{\mathbf{s}}\right\}. \tag{26}$$

We can derive an analogous recurrence relation for $b_{\mathbf{s}} = \mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\Gamma(|\mathbf{x}|)$, such that

$$b_{\mathbf{s}} = \frac{1}{|\mathbf{x}|^2}\left\{\left(\frac{1}{\|\mathbf{s}\|}-2\right)\sum_{i=1}^{3} s_i x_i b_{\mathbf{s}-\mathbf{e}_i} + \left(\frac{1}{\|\mathbf{s}\|}-1\right)\sum_{i=1}^{3} s_i(s_i-1)b_{\mathbf{s}-2\mathbf{e}_i} - c_{\mathbf{s}}\right\}. \tag{27}$$

If we let $\mathbf{x} = \eta\cdot\mathbf{r_{ij}}$, then

$$\begin{aligned}\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\left[\frac{\mathrm{erfc}(\eta r_{ij})}{r_{ij}}\right] &= \frac{2}{\sqrt{\pi}}\eta\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\left[\frac{\sqrt{\pi}}{2}\frac{\mathrm{erfc}(\eta\cdot r_{ij})}{\eta\cdot r_{ij}}\right]\\ &= \frac{2}{\sqrt{\pi}}\eta^{\|s\|+1}\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\left[\frac{\sqrt{\pi}}{2}\frac{\mathrm{erfc}(|\mathbf{x}|)}{|\mathbf{x}|}\right]\\ &= \frac{2}{\sqrt{\pi}}\eta^{\|s\|+1}a_{\mathbf{s}},\end{aligned} \tag{28}$$

and similarly,

$$\mathbf{D}_{\mathbf{x}}^{\mathbf{s}}\left[\frac{\mathrm{erf}(\eta\cdot r_{ij})}{r_{ij}}\right] = \frac{2}{\sqrt{\pi}}\eta^{\|s\|+1}b_{\mathbf{s}}. \tag{29}$$

For all the recurrence relations given above, the initial term, $(0, 0, 0)$, is the function value and the terms with negative indices are zero.

## C. Recurrences for common long-ranged electrostatic pair potentials

Computing the energy and the forces boils down to computing the multidimensional derivatives of the pair potential. In this section, we obtain the recurrence relations for the derivatives of common long-ranged electrostatic potentials employed in simulations based on the recurrence relations provided earlier. These potentials are the

1. direct Coulomb sum,
2. force-shifted Coulomb sum,
3. Coulomb sum with distance dependent dielectric, and
4. reaction field.

We will discuss the fifth technique PME in Sec. IV. Without loss of generality, we will set $\frac{1}{4\pi\epsilon_0\epsilon} = 1$.

### 1. Direct Coulomb sum

For two interacting ions $i$ and $j$, the potential energy is given as

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon}\hat{L}_i\hat{L}_{j_i}\left[\frac{1}{r_{ij}}\right], \tag{30}$$

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and the relevant kernel is $\psi(r_{ij}) = \frac{1}{r_{ij}}$. The derivatives for this kernel are obtained by using Eq. (22) with $\nu = 1$. Thus,

$$D_i^{\mathbf{s}}\psi(r_{ij}) = d_{\mathbf{s}}(1). \tag{31}$$

### 2. Force-shifted Coulomb sum

Typically, two forms of the force-shifted Coulomb sum potential[27] are used in simulations. In the first form, the potential energy due to two interacting ions $i$ and $j$ is

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon}\hat{L}_i\hat{L}_{j_i}\left[\frac{1}{r_{ij}} + \frac{r_{ij}}{r_{\text{cut}}^2} - \frac{2}{r_{\text{cut}}}\right], \tag{32}$$

where $r_{\text{cut}}$ is the cutoff radius. The kernel is $\psi(r_{ij}) = \frac{1}{r_{ij}} + \frac{r_{ij}}{r_{\text{cut}}^2} - \frac{2}{r_{\text{cut}}}$. The last term, $\frac{2}{r_{\text{cut}}}$, is a constant which has a zero derivative; hence, the derivatives of the kernel are obtained as a sum of the derivatives of the first term and second terms. We employ Eq. (22) with $\nu = 1$ for the first term and $\nu = -1$ for the second term. Thus,

$$D_i^{\mathbf{s}}\psi(r_{ij}) = d_{\mathbf{s}}(1) + \frac{d_{\mathbf{s}}(-1)}{r_{\text{cut}}^2}. \tag{33}$$

Brommer *et al.*[28] employed the second form to describe a polarizable force field for silica with dipoles. The potential energy due to two interacting ions $i$ and $j$ interacting via the second form of the force-shifted Coulomb sum is

$$\begin{aligned} U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon}\hat{L}_i\hat{L}_{j_i}\Bigg[&\left\{\frac{\operatorname{erfc}(\eta\cdot r_{ij})}{r_{ij}} + \left(\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}^2}\right.\right. \\ &\left.\left. + \frac{2\eta}{\sqrt{\pi}}\frac{\exp(-\eta^2 r_{\text{cut}}^2)}{r_{\text{cut}}}\right) r_{ij}\right\} - \left\{\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}}\right. \\ &\left.\left. + \left(\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}^2} + \frac{2\eta}{\sqrt{\pi}}\frac{\exp(-\eta^2 r_{\text{cut}}^2)}{r_{\text{cut}}}\right) r_{\text{cut}}\right\}\right]. \end{aligned} \tag{34}$$

The kernel, $\psi(r_{ij})$, is the terms in the square bracket but the only terms which contribute to the derivatives are the first and second terms which are functions of $r_{ij}$. The derivative of the first term is obtained from Eqs. (26) and (28) and the derivative for $r_{ij}$ in the second term is given by $d_{\mathbf{s}}(-1)$. Thus,

$$\begin{aligned} D_i^{\mathbf{s}}\psi(r_{ij}) = &\frac{2}{\sqrt{\pi}}\eta^{\|s\|+1}a_{\mathbf{s}} \\ &+ \left(\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}^2} + \frac{2\eta}{\sqrt{\pi}}\frac{\exp(-\eta^2 r_{\text{cut}}^2)}{r_{\text{cut}}}\right)\cdot d_{\mathbf{s}}(-1). \end{aligned} \tag{35}$$

### 3. Coulomb sum with distance dependent dielectric

The potential energy between two interacting ions $i$ and $j$ is

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon}\hat{L}_i\hat{L}_{j_i}\left[\frac{1}{r_{ij}^2}\right], \tag{36}$$

and the kernel is $\psi(r_{ij}) = \frac{1}{r_{ij}^2}$. The derivatives for this kernel are obtained by using Eq. (22) with $\nu = 2$. Hence,

$$\mathbf{D}_i^{\mathbf{s}}\psi(r_{ij}) = d_{\mathbf{s}}(2). \tag{37}$$

### 4. Reaction field

Two forms of the reaction field method based on the work of Neumann[29] are typically used in simulations.

Nymand and Linse[8] derived equations for a dipolar system using the first form. In this form, the effective pair potential energy due to two interacting ions $i$ and $j$ is given as

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon}\hat{L}_i\hat{L}_{j_i}\left[\frac{1}{r_{ij}} + \frac{B_0 r_{ij}^2}{2R_c^3} - 1 - \frac{B_0}{2}\right], \tag{38}$$

where

$$B_0 = \frac{2(\epsilon_1 - 1)}{(2\epsilon_1 + 1)}, \tag{39}$$

$R_c$ is the radius of the spherical cavity, and $\epsilon_1$ is the dielectric constant outside the cavity. Again the kernel, $\psi(r_{ij})$, is the terms in the square bracket and only the first and second terms contribute to its derivatives. The derivatives of the first and second terms are given by Eq. (22) with $\nu = 1$ and $\nu = -2$, respectively. Thus,

$$\mathbf{D}_i^{\mathbf{s}}\psi(r_{ij}) = d_{\mathbf{s}}(1) + \frac{B_0}{2R_c^3}d_{\mathbf{s}}(-2). \tag{40}$$

The second form of the reaction field method is similar to that of the force-shifted Coulomb sum. The potential energy due to two interacting ions $i$ and $j$ is

$$\begin{aligned} U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon}\hat{L}_i\hat{L}_{j_i}\Bigg[&\left\{\frac{\operatorname{erfc}(\eta\cdot r_{ij})}{r_{ij}} + \left(\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}^2}\right.\right. \\ &\left.\left. + \frac{2\eta}{\sqrt{\pi}}\frac{\exp(-\eta^2 r_{\text{cut}}^2)}{r_{\text{cut}}}\right) r_{ij}\right\} - \left\{\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}}\right. \\ &\left.\left. + \left(\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}^2} + \frac{2\eta}{\sqrt{\pi}}\frac{\exp(-\eta^2 r_{\text{cut}}^2)}{r_{\text{cut}}}\right) r_{\text{cut}}\right\}\right. \\ &\left. - \frac{B_0 r_{\text{cut}}^2}{2r_{\text{cut}}^3} + \frac{B_0 r_{ij}^2}{2r_{\text{cut}}^3}\right]. \end{aligned} \tag{41}$$

The kernel, $\psi(r_{ij})$, is the terms in the square bracket and the only terms which contribute to the derivatives are the first, second, and last terms which are functions of $r_{ij}$. The derivative of the first term is obtained from Eqs. (26) and (28), the derivative for $r_{ij}$ in the second term is given by $d_{\mathbf{s}}(-1)$, and the derivative for $r_{ij}^2$ in the last term is given by $d_{\mathbf{s}}(-2)$. Thus,

$$\begin{aligned} D_i^{\mathbf{s}}\psi(r_{ij}) = &\frac{2}{\sqrt{\pi}}\eta^{\|s\|+1}a_{\mathbf{s}} \\ &+ \left(\frac{\operatorname{erfc}(\eta\cdot r_{\text{cut}})}{r_{\text{cut}}^2} + \frac{2\eta}{\sqrt{\pi}}\frac{\exp(-\eta^2 r_{\text{cut}}^2)}{r_{\text{cut}}}\right)\cdot d_{\mathbf{s}}(-1) \\ &+ \frac{B_0}{2r_{\text{cut}}^3}\cdot d_{\mathbf{s}}(-2). \end{aligned} \tag{42}$$

## IV. Application to the smooth particle mesh Ewald

In this section, we will develop an implementation of the smooth PME[12] method to an arbitrary multipole order.

We consider a periodic system of $N$ point multipoles with positions $\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ and net zero total charge. The fundamental simulation cell is defined by the vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ which are the columns of a matrix $h$ and the periodic images

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are translations of the fundamental cell. The simulation cell volume is given by

$$V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|, \tag{43}$$

and the reciprocal cell is defined by the vectors

$$\begin{aligned} \mathbf{a}_1^* &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V}, \\ \mathbf{a}_2^* &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V}, \\ \mathbf{a}_3^* &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V}, \end{aligned} \tag{44}$$

which are the rows of the matrix $2\pi h^{-1}$.

Ewald summation provides an efficient method for evaluating the Coulomb energy of the periodic system by recasting the conditionally convergent Coulomb sum

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{2} \sum_{i,j=1}^{N} \hat{L}_i \hat{L}_{j_i} \sum_{\mathbf{n}}{}' \frac{1}{4\pi\epsilon_0\epsilon |\mathbf{r_{ij}} + \mathbf{nL}|} \tag{45}$$

into two absolutely convergent sums, one in real space and the other in reciprocal space. In Eq. (45), $\mathbf{n} = (n_1, n_2, n_3)$ identifies a unique cell, $n_i$ is an integer, $\mathbf{L} = (L_1, L_2, L_3)$, and the prime on the last sum means that the $i = j$ term is omitted when $\mathbf{n} = (0,0,0)$ which is the fundamental cell. The total electrostatic energy due to the Ewald sum is given by the formula

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = U_{\text{dir}} + U_{\text{rec}} - U_{\text{excl}} - U_{\text{self}}, \tag{46}$$

where

$$U_{\text{dir}} = \frac{1}{2} \sum_{i<j}^{N^*} \sum_{\mathbf{n}}{}' \hat{L}_i \hat{L}_{j_i} \frac{\operatorname{erfc}(\eta \cdot |\mathbf{r_{ij}} + \mathbf{n}|)}{4\pi\epsilon_0\epsilon |\mathbf{r_{ij}} + \mathbf{n}|}, \tag{47}$$

$$U_{\text{excl}} = \frac{1}{4\pi\epsilon_0\epsilon} \sum_{(i,j) \in M^*} \hat{L}_i \hat{L}_{j_i} \frac{\operatorname{erf}(\eta \cdot r_{ij})}{r_{ij}}, \tag{48}$$

$$U_{\text{self}} = \frac{1}{8\pi\epsilon_0\epsilon} \lim_{|\mathbf{r_i}| \to 0} \sum_{i=1}^{N} \hat{L}_i \hat{L}_i \frac{\operatorname{erf}(\eta \cdot |\mathbf{r_i}|)}{|\mathbf{r_i}|}, \tag{49}$$

and

$$U_{\text{rec}} = \frac{1}{2V\epsilon_0\epsilon} \sum_{\mathbf{k} \neq 0} \frac{\exp(-k^2/4\eta^2)}{k^2} |S(\mathbf{k})|^2, \tag{50}$$

with

$$S(\mathbf{k}) = \sum_{i=1}^{N} \hat{L}_i \exp(\imath \mathbf{k} \cdot \mathbf{r_i}). \tag{51}$$

In the expressions above, $M^*$ is the set of all excluded interactions due to intramolecular bonds or frozen atoms in the simulation cell, $N^* = N - M^*$, and $\eta$ controls the relative convergence rates of the real space term $U_{\text{dir}}$ and reciprocal space term $U_{\text{rec}}$. The particle mesh Ewald method provides a fast approximation of the Ewald sum by shifting a substantial amount of the computational work to the reciprocal space though the choice of $\eta$ and then employing interpolation via B-splines and fast Fourier transforms (FFTs) to evaluate the reciprocal space quickly. The real space decays quickly and is handled by a simple cutoff method.

With the expressions above, we can develop the arbitrary order implementation of PME. Essentially what we require are the recurrence relations for derivatives of the kernels of each term.

### A. Real space sum

From Eq. (47), we see that the relevant kernel is $\psi(r_{ij}) = \frac{\operatorname{erfc}(\eta |\mathbf{r_{ij}} + \mathbf{n}|)}{|\mathbf{r_{ij}} + \mathbf{n}|}$. Derivatives for this kernel can be obtained by using Eqs. (26) and (28) with $\mathbf{x} = \eta \cdot |\mathbf{r_{ij}} + \mathbf{n}|$. Typically, the choice of $\eta$ limits the sum to the fundamental cell, thus $\mathbf{n} = (0,0,0)$ and $\mathbf{x} = \eta \cdot r_{ij}$. Thus, the derivatives of the kernel are given as

$$\mathbf{D}_i^{\mathbf{s}} \psi(r_{ij}) = \frac{2}{\sqrt{\pi}} \eta^{\|s\|+1} a_{\mathbf{s}}. \tag{52}$$

### B. Excluded sum

The kernel in Eq. (48) is $\psi(r_{ij}) = \frac{\operatorname{erf}(\eta \cdot r_{ij})}{r_{ij}}$. Derivatives of this kernel are given by Eqs. (27) and (29) with $\mathbf{x} = \eta \cdot r_{ij}$, hence

$$\mathbf{D}_i^{\mathbf{s}} \psi(r_{ij}) = \frac{2}{\sqrt{\pi}} \eta^{\|s\|+1} b_{\mathbf{s}}. \tag{53}$$

### C. Self-interaction

To compute $U_{self}$ from Eq. (49), we will need to evaluate the derivatives of the kernel $\psi(|\mathbf{r_i}|) = \frac{\operatorname{erf}(\eta \cdot |\mathbf{r_i}|)}{|\mathbf{r_i}|}$ in the limit as $|\mathbf{r_i}| \to 0$. We obtain a good approximation by using a regularization to handle the singularity at $|\mathbf{r_i}| = 0$.

Let $r_i = |\mathbf{r_i}|$ and $\delta$ be the smoothing parameter. Then the regularized kernel is given as

$$\psi_\delta(r_i) = \frac{\operatorname{erf}(\eta \sqrt{r_i^2 + \delta^2})}{\sqrt{r_i^2 + \delta^2}} \tag{54}$$

and

$$\lim_{r_i \to 0} \mathbf{D}_i^{\mathbf{s}} \psi(r_i) \approx \mathbf{D}_i^{\mathbf{s}} \psi_\delta(r_i), \tag{55}$$

where with $\mathbf{x} = \eta \cdot r_i$, we can follow previous work by Lindsay and Krasny[30] to show that if $b_{\mathbf{s},\delta} = \mathbf{D}_i^{\mathbf{s}} \psi_\delta(r_i)$, then the recurrence for the derivatives of the regularized kernel is given by

$$\begin{aligned} b_{\mathbf{s},\delta} = \frac{2}{\sqrt{\pi}} \eta^{\|\mathbf{s}\|+1} \frac{1}{(|\mathbf{x}|^2 + \delta^2)} \Bigg\{ \left( \frac{1}{\|\mathbf{s}\|} - 2 \right) \sum_{i=1}^{3} s_i x_i b_{\mathbf{s}-\mathbf{e}_i} \\ + \left( \frac{1}{\|\mathbf{s}\|} - 1 \right) \sum_{i=1}^{3} s_i (s_i - 1) b_{\mathbf{s}-2\mathbf{e}_i} - c_{\mathbf{s}} \Bigg\}. \end{aligned} \tag{56}$$

Note that the recurrence for the regularized kernel given above is similar to that for the normal kernel given in Eqs. (27) and (29) with the factor $\frac{1}{|\mathbf{x}|^2}$ replaced by $\frac{1}{(|\mathbf{x}|^2 + \delta^2)}$. Table I compares exact results of $\lim_{r_i \to 0} \mathbf{D}_i^{\mathbf{s}} \psi(r_i)$ to the results obtained by regularization for a few derivatives up to sixth order. The exact results are obtained by taking analytical derivatives of the Taylor series for $\frac{\operatorname{erf}(\eta \cdot r_i)}{r_i}$. For this test case $\eta = 0.5$, $\mathbf{r_i} = \langle 0,0,0 \rangle$ to approximate $r_i \to 0$ and $\delta = 0.01$. The approximation is within 1% of the exact results for the derivatives considered. However, the approximation gets worse with increasing order because of

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TABLE I. Test case for computing the limit of the derivatives of the kernel in Eq. (49), with $\eta = 0.5$, $\mathbf{r_i} = \langle 0, 0, 0\rangle$, $\delta = 0.01$.

| $(s_1, s_2, s_3)$ | $\lim_{r_i\to 0} D_x^{s_1} D_y^{s_2} D_z^{s_3} \psi(r_i)$ | $D_x^{s_1} D_y^{s_2} D_z^{s_3} \psi_\delta(r_i)$ | % relative error |
|---|---|---|---|
| (0, 0, 0) | $\frac{2\eta}{\sqrt{\pi}} = 0.564\,190$ | 0.564 185 | $8.86 \times 10^{-4}$ |
| (1, 0, 0) | 0.0 | 0.0 | ... |
| (2, 0, 0) | $-\frac{4\eta^3}{3\sqrt{\pi}} = -9.403\,160 \times 10^{-2}$ | $-9.403\,029 \times 10^{-2}$ | $1.39 \times 10^{-3}$ |
| (1, 1, 0) | 0.0 | 0.0 | ... |
| (3, 0, 0) | 0.0 | 0.0 | ... |
| (2, 1, 0) | 0.0 | 0.0 | ... |
| (1, 1, 1) | 0.0 | 0.0 | ... |
| (4, 0, 0) | $\frac{24\eta^5}{5\sqrt{\pi}} = 8.462\,844 \times 10^{-2}$ | $8.462\,692 \times 10^{-2}$ | $1.8 \times 10^{-3}$ |
| (2, 2, 0) | $\frac{8\eta^5}{5\sqrt{\pi}} = 2.820\,948 \times 10^{-2}$ | $2.820\,897 \times 10^{-2}$ | $1.8 \times 10^{-3}$ |
| (5, 0, 0) | 0.0 | 0.0 | ... |
| (3, 1, 1) | 0.0 | 0.0 | ... |
| (6, 0, 0) | $-\frac{240\eta^7}{7\sqrt{\pi}} = -0.151\,122$ | $-0.149\,506$ | 1.07 |
| (4, 2, 0) | $-\frac{48\eta^7}{7\sqrt{\pi}} = -3.022\,44 \times 10^{-2}$ | $-2.990\,118 \times 10^{-2}$ | 1.07 |
| (2, 2, 2) | $-\frac{16\eta^7}{7\sqrt{\pi}} = -1.007\,481 \times 10^{-2}$ | $-9.967\,053 \times 10^{-3}$ | 1.07 |

the increasing sensitivity of the higher order derivatives and the accumulation of numerical errors.

The recursive schemes for the derivatives of the various kernels $\psi$ use the kernel value $\psi(\mathbf{r_{ij}})$ as the initial value to compute the $(2p+1)^3$ derivatives required for evaluating the energies and forces. In a simple implementation, this requires three nested loops whose indices sum up to $2p+1$ which shows that the recurrences scale as $O(p^3)$ similar to the scaling in the spherical tensor formalism.[13,17,18] Analogous nested loops are used in Algorithm I where the indices of the inner nested loop over $(k_1,k_2,k_3)$ and the outer nested loop over $(s_1,s_2,s_3)$ both sum up to $p$.

For the Ewald sum, the bulk of the computational cost comes from the real space and reciprocal sums. The cost of the excluded sum and the self-interaction is small in comparison.

Fig. 1 shows a plot of the overall cost of computing the energy, forces, torques, and stress due to the real space Ewald sum, with constant force error of $10^{-5}$, against order $p$ for a system of 32 000 water molecules on a desktop computer. The circles are the computational cost for $p \in \{0,1,2,3,4\}$ and the cubic curve is the best fit. The plot shows that the overall computational cost is $O(p^3)$. We note that the focus of this plot is not on performance of the code but to show that the algorithm is formally $O(p^3)$. As a result, the code used to generate the plot employed explicit loops as in Algorithm I instead of using more efficient coding such as unrolling the loops.

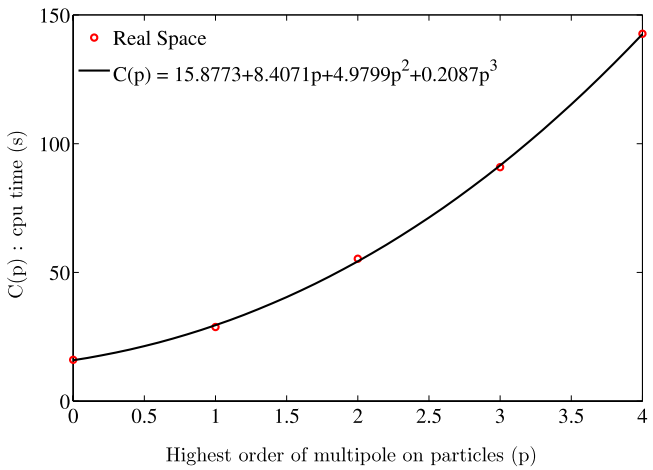


FIG. 1. A plot of cpu time of the real space Ewald sum vs order $p$ for 32 000 water molecules.

Next, we develop an arbitrary order implementation of the reciprocal space PME.

### D. Reciprocal space-particle mesh approximation

The PME algorithm has been presented in several papers[6,11,12,31] as such we will not replicate the development here. The key idea of PME is in approximating the structure factor,

$$S(\mathbf{k}) = \sum_{i=1}^{N} \hat{L}_i \exp(\imath \mathbf{k}\cdot\mathbf{r_i}), \tag{57}$$

in a uniform grid, with $K_1 \times K_2 \times K_3$ dimensions, that fills the simulation cell. If we define the fractional coordinates of an ion $i$ as $\langle s_{i_1}, s_{i_2}, s_{i_3}\rangle = \langle \mathbf{a}_1^*\cdot\mathbf{r_i}, \mathbf{a}_2^*\cdot\mathbf{r_i}, \mathbf{a}_3^*\cdot\mathbf{r_i}\rangle$, $u_{\alpha_i} = K_\alpha \cdot s_i^\alpha$, and $M_n$ is a B-spline of order $n$ then the approximation of the structure factor is given as

$$S(\mathbf{k}) \approx b_1(k_1) b_2(k_2) b_3(k_3) Q^{\mathcal{F}}(k_1,k_2,k_3), \tag{58}$$

where $\mathbf{k} = \langle k_1,k_2,k_3\rangle$ is a reciprocal space vector,

$$b_i(k_i) = \exp(2\pi\imath(n-1)k_i/K_i) \times \left[\sum_{l=0}^{n-2} M_n(l+1)\exp(2\pi\imath k l/K_i)\right]^{-1}, \tag{59}$$

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$Q$ is the multipolar array defined on the uniform grid, and $Q^{\mathcal{F}}$ is its discrete Fourier transform. At position $(l_1,l_2,l_3)$ on the grid, the multipolar array is defined by

$$Q(l_1,l_2,l_3) = \sum_{i=1}^{N} \hat{L}_i \sum_{n_1,n_2,n_3} M_n(u_{1_i} - l_1 - n_1K_1) \times M_n(u_{2_i} - l_2 - n_2K_2) \times M_n(u_{3_i} - l_3 - n_3K_3), \quad (60)$$

where $u_{\alpha_i} - l_\alpha - n_\alpha K_\alpha$ are evaluation points of the B-spline on the grid that spans the fundamental cell and the periodic images. Then from Eq. (5) and considering only the fundamental cell, the multipolar array can be written explicitly as

$$Q(l_1,l_2,l_3) = \sum_{i=1}^{N} \sum_{s_3=0}^{p} \sum_{s_2=0}^{p-s_3} \sum_{s_1=0}^{p-s_3-s_2} \mathcal{M}_i^{s_1s_2s_3} \times D_{x_i}^{s_1} D_{y_i}^{s_2} D_{z_i}^{s_3} \{M_n(u_{1_i} - l_1) M_n(u_{2_i} - l_2) M_n(u_{3_i} - l_3)\}. \quad (61)$$

Let $\mathbf{a}_1^* = \langle a_{11}^*, a_{12}^*, a_{13}^* \rangle$, $\mathbf{a}_2^* = \langle a_{21}^*, a_{22}^*, a_{23}^* \rangle$, and $\mathbf{a}_3^* = \langle a_{31}^*, a_{32}^*, a_{33}^* \rangle$ be the reciprocal space basis vectors and $K_1$, $K_2$, and $K_3$ be the maximum number of grid points in the fundamental cell in the $x$, $y$, and $z$ directions, respectively. Recalling that Leibniz's rule for differentiation of products of functions $f$, $g \in \mathbb{C}^n$ is given by

$$D_x^n[f \cdot g] = \sum_{k=0}^{n} \binom{n}{k} D_x^k[f] D_x^{n-k}[g], \quad (62)$$

and with $u_{\alpha_i} = K_\alpha \mathbf{a}_\alpha^* \cdot \mathbf{r_i}$, we can show that

$$\begin{aligned} &D_{x_i}^{s_1} D_{y_i}^{s_2} D_{z_i}^{s_3} \{M_n(u_{1_i} - l_1) M_n(u_{2_i} - l_2) M_n(u_{3_i} - l_3)\} \\ &= \sum_{k_3=0}^{s_3} \left(K_1 a_{13}^*\right)^{k_3} \binom{s_3}{k_3} \sum_{k_2=0}^{s_2} \left(K_1 a_{12}^*\right)^{k_2} \binom{s_2}{k_2} \\ &\times \sum_{k_1=0}^{s_1} \left(K_1 a_{11}^*\right)^{k_1} \binom{s_1}{k_1} D_{u_{1_i}}^{\|\mathbf{k}\|} M_n(u_{1_i} - l_1) \\ &\times \sum_{j_3=0}^{s_3-k_3} \left(K_2 a_{23}^*\right)^{j_3} \left(K_3 a_{33}^*\right)^{s_3-k_3-j_3} \binom{s_3-k_3}{j_3} \\ &\times \sum_{j_2=0}^{s_2-k_2} \left(K_2 a_{22}^*\right)^{j_2} \left(K_3 a_{32}^*\right)^{s_2-k_2-j_2} \binom{s_2-k_2}{j_2} \\ &\times \sum_{j_1=0}^{s_1-k_1} \left(K_2 a_{21}^*\right)^{j_1} \left(K_3 a_{31}^*\right)^{s_1-k_1-j_1} \\ &\times \binom{s_1-k_1}{j_1} D_{u_{2_i}}^{\|\mathbf{j}\|} M_n(u_{2_i} - l_2) D_{u_{3_i}}^{\|\mathbf{s-k-j}\|} M_n(u_{3_i} - l_3). \end{aligned} \quad (63)$$

Note that Eq. (63) naturally incorporates the transformation vectors used in Eqs. (2.50) and (2.51) of SPD.[11] For simulations in an orthogonal cell,

$$a_{12}^* = a_{13}^* = a_{21}^* = a_{23}^* = a_{31}^* = a_{32}^* = 0, \quad (64)$$

and Eq. (63) simplifies greatly to

$$\begin{aligned} &D_{x_i}^{s_1} D_{y_i}^{s_2} D_{z_i}^{s_3} \{M_n(u_{1_i} - l_1) M_n(u_{2_i} - l_2) M_n(u_{3_i} - l_3)\} \\ &= \left(K_1 a_{11}^*\right)^{s_1} \left(K_2 a_{22}^*\right)^{s_2} \left(K_3 a_{33}^*\right)^{s_3} D_{u_{1_i}}^{s_1} M_n(u_{1_i} - l_1) \\ &\times D_{u_{2_i}}^{s_2} M_n(u_{2_i} - l_2) D_{u_{3_i}}^{s_3} M_n(u_{3_i} - l_3). \end{aligned} \quad (65)$$

We now derive a closed form formula for arbitrary derivatives of the B-splines required in Eqs. (63) and (65).

#### 1. Derivatives of $M_n$

Recall that $M_n(u)$ has compact support on $0 \le u \le n$,

$$M_1(u) = \begin{cases} 1 & \text{if } 0 \le u \le 1, \\ 0 & \text{otherwise,} \end{cases}$$

$M_2(u) = 1 - |u - 1|$ on $0 \le u \le 2$,

$$M_n(u) = \frac{u}{n-1} M_{n-1}(u) + \frac{n-u}{n-1} M_{n-1}(u-1), \quad (66)$$

and

$$\frac{d}{du} M_n(u) = M_{n-1}(u) - M_{n-1}(u-1). \quad (67)$$

From a repeated application of Eq. (67), we see that

$$\frac{d^p}{du^p} M_n(u) = D_u^p M_n(u) = \sum_{t=0}^{p} \binom{p}{t} (-1)^t M_{n-p}(u-t). \quad (68)$$

A proof of Eq. (68) is given in the Appendix, Subsection 1.

$M_n$ has $n$ points of evaluation $\{u_1,u_2,\ldots,u_k,\ldots,u_{n-1},u_n\}$, in the interval $(0,n)$, where $u_j = u_1 + j - 1$. Let $k = n - p$, then

$$\frac{d^p}{du^p} M_n(u) = \sum_{t=0}^{p} \binom{p}{t} (-1)^t M_k(u-t). \quad (69)$$

Let $j \in \{1,2,\ldots,k-1,k,k+1,\ldots,n-1,n\}$, then

$$\frac{d^p}{du^p} M_n(u_j) = \sum_{t=0}^{p} \binom{p}{t} (-1)^t M_k(u_j - t). \quad (70)$$

In Eq. (70), there are non-zero contributions only when

$$\begin{aligned} u_1 \le u_j - t \le u_k, \\ u_1 \le u_1 + j - 1 - t \le u_1 + k - 1, \\ 1 - j \le -t \le k - j, \\ j - k \le t \le j - 1, \\ \max\{0, j-k\} \le t \le \min\{j-1, p\}, \end{aligned} \quad (71)$$

thus

$$\frac{d^p}{du^p} M_n(u_j) = \sum_{t=\max\{0,j-k\}}^{\min\{j-1,p\}} \binom{p}{t} (-1)^t M_k(u_j - t). \quad (72)$$

The combinations $\binom{p}{t}$ can be computed once for all $t$, stored, and used throughout a simulation. The derivatives of the B-splines can also be precomputed and stored for each new configuration of a simulation before the PME algorithm is invoked.

### E. Potential energy and forces from PME

From Eqs. (63) and (72), we can compute Eq. (61), the components of the multipolar array. Then following the same argument given in previous work,[6,11,12,31,32] the reciprocal space potential energy can be approximated as

$$U_{\text{rec}} \approx \frac{1}{2V\epsilon_0\epsilon} \sum_{k_1,k_2,k_3} G^{\mathcal{F}}(k_1,k_2,k_3) Q(k_1,k_2,k_3), \quad (73)$$

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where $G^{\mathcal{F}}$ is the discrete Fourier transform of the function

$$G(k_1,k_2,k_3) = \frac{\exp(-k^2/4\eta^2)}{k^2} B(k_1,k_2,k_3)\left(Q^{\mathcal{F}}(k_1,k_2,k_3)\right)^* \quad (74)$$

and

$$B(k_1,k_2,k_3) = |b_1(k_1)|^2|b_2(k_2)|^2|b_3(k_3)|^2. \quad (75)$$

The translational force on atom $i$ for multipole order $p$ is given by

$$\begin{aligned}\mathbf{f}_i &= -\frac{1}{V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0} G^{\mathcal{F}}(k_1,k_2,k_3)\nabla_i Q(k_1,k_2,k_3)\\ &= -\frac{1}{V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0} G^{\mathcal{F}}(k_1,k_2,k_3)\sum_{\mathbf{s}=\mathbf{0}}^{p}\mathcal{M}_i^{\mathbf{s}}\begin{bmatrix} D_i^{\mathbf{s}+\mathbf{e}_1}\\ D_i^{\mathbf{s}+\mathbf{e}_2}\\ D_i^{\mathbf{s}+\mathbf{e}_3}\end{bmatrix}\\ &\quad\times\left\{M_n(u_{1_i}-l_1)M_n(u_{2_i}-l_2)M_n(u_{3_i}-l_3)\right\}, \quad (76)\end{aligned}$$

which is computed by employing Eqs. (63) and (72).

## V. COMPUTING THE STRESS TENSOR $\sigma$

For the direct space and excluded part of the Ewald sum, the $(\alpha,\beta)$ elements of the stress tensor are given as

$$V\sigma_{\alpha\beta} = \sum_{i<j}^{N^*}(\mathbf{r_{ij}})_\alpha(\mathbf{f}_i^{\mathrm{dir}})_\beta - \sum_{(i,j)\in M^*}(\mathbf{r_{ij}})_\alpha(\mathbf{f}_i^{\mathrm{excl}})_\beta, \quad (77)$$

where the sum for the direct space is limited to the fundamental cell, $\mathbf{n}=\mathbf{0}$.

Nosé and Klein[33] derived the formula for the elements of the stress tensor in the case of point-charges for the reciprocal space Ewald sum. Following this work, stress tensor formulas have been derived for the case where in addition to point charges the particles have dipoles,[6] dipoles and quadrupoles,[7] and dipoles, quadrupoles, octupoles, and hexadecapoles.[11] Here, we provide the formula for the stress tensor from the reciprocal space Ewald sum for an arbitrary order of multipoles and outline the derivation. The full derivation is shown in the Appendix, Subsection 2.

The components of the virial tensor[33] are given by

$$V\sigma_{\alpha\beta} = -\sum_\gamma \frac{\partial U_{\mathrm{rec}}}{\partial h_{\beta\gamma}} h_{\beta\gamma}, \quad (78)$$

and in matrix form as

$$V\sigma = -\frac{\partial U}{\partial h}h^\dagger, \quad (79)$$

where $h$ is the matrix whose columns are the vectors which define the simulation cell. Hence, the $i$th column of $h$ is

$$h_i = h\mathbf{e}_i = \mathbf{a}_i. \quad (80)$$

The rows of the inverse of $h$ are the vectors which define the reciprocal cell divided by $2\pi$, thus the $i$th column of the transpose of $h^{-1}$ is

$$(h^{-1})_i^\dagger = (h^{-1})^\dagger\mathbf{e}_i = \frac{1}{2\pi}\mathbf{a}_i^*. \quad (81)$$

The bulk of the work in computing the components of the virial tensor comes from computing the derivative of $U_{\mathrm{rec}}$ with respect to the components of matrix $h$ which is given as

$$\begin{aligned}\frac{\partial U_{\mathrm{rec}}}{\partial h_{\alpha\beta}} &= \frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{1}{V}\right)\cdot\frac{1}{2\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}|S(\mathbf{k})|^2\\ &\quad+\frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}|S(\mathbf{k})|^2\frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{\exp(-k^2/4\eta^2)}{k^2}\right)\\ &\quad+\frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}\frac{\partial|S(\mathbf{k})|^2}{\partial h_{\alpha\beta}}. \quad (82)\end{aligned}$$

If we define $\mathcal{J}_i^{\boldsymbol{\ell}}(\mathbf{k}) = \mathcal{M}_i^{\boldsymbol{\ell}}D_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r_i}}$ and

$$S_i^\beta(-\mathbf{k}) = \sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\ell_\beta\sum_{i=1}^{N}\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k}), \quad (83)$$

with $\boldsymbol{\ell}=(\ell_1,\ell_2,\ell_3)$, then for multipolar interactions up to an arbitrary order $p$,

$$S(\mathbf{k}) = \sum_{i=1}^{N}\hat{L}_i e^{\imath\mathbf{k}\cdot\mathbf{r_i}} = \sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}\mathcal{M}_i^{\boldsymbol{\ell}}D_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r_i}} = \sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\mathcal{J}_i^{\boldsymbol{\ell}}(\mathbf{k}). \quad (84)$$

Performing the derivative in Eq. (82) results in

$$\begin{aligned}\frac{\partial U_{\mathrm{rec}}}{\partial h_{\alpha\beta}} &= -\frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}\\ &\quad\times\left\{|S(\mathbf{k})|^2\left[h^{-1}_{\beta\alpha}-2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}k_\gamma\right]\right.\\ &\quad\left.+\,2S(\mathbf{k})\sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}J_i^{\boldsymbol{\ell}}(-\mathbf{k})k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}\right\}, \quad (85)\end{aligned}$$

which inserted in Eq. (78) gives the components of the stress tensor as

$$\begin{aligned}V\sigma^{\mathrm{rec}}_{\alpha\beta} &= \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}\\ &\quad\times\left\{|S(\mathbf{k})|^2\left[\delta_{\alpha\beta}-2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha k_\beta\right]\right.\\ &\quad\left.+\,2S(\mathbf{k})S_i^\beta(-\mathbf{k})\frac{k_\alpha}{k_\beta}\right\}. \quad (86)\end{aligned}$$

Note that when the system has only point charges, $p=0$, meaning that $\ell_\beta=0$ and $S_i^\beta(-\mathbf{k})=0$, thus the last term in Eq. (86) evaluates to zero, and we recover the stress tensor for point-charges derived by Nosé and Klein.[33]

Similar to the approximation of $S(\mathbf{k})$ given in Eq. (58), if we define a modified multipolar array at grid points $(r_1,r_2,r_3)$ as

$$\begin{aligned}Q_\beta(r_1,r_2,r_3) &= \sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\ell_\beta\sum_{j=1}^{N}\mathcal{M}_i^{\boldsymbol{\ell}}\mathbf{D}_i^{\boldsymbol{\ell}}\\ &\quad\times\left\{M_n(u_{1_i}-r_1)M_n(u_{2_i}-r_2)M_n(u_{3_i}-r_3)\right\}, \quad (87)\end{aligned}$$

then $S_i^\beta(-\mathbf{k})$ can be approximated on the grid as

$$S_i^\beta(-\mathbf{k}) \approx b_1(-k_1)b_2(-k_2)b_3(-k_3)\left(Q_\beta^{\mathcal{F}}(k_1,k_2,k_3)\right)^*, \quad (88)$$

where $Q_\beta^{\mathcal{F}}$ is the Fourier transform of $Q_\beta$. Since $\beta\in\{1,2,3\}$, computing the stress tensor requires computing all three different $S_i^\beta(-\mathbf{k})$ for $\ell_\beta\in\{\ell_1,\ell_2,\ell_3\}$ which requires three FFTs in addition to the two to compute $S(\mathbf{k})$ and $G^{\mathcal{F}}$ in Eq. (74).

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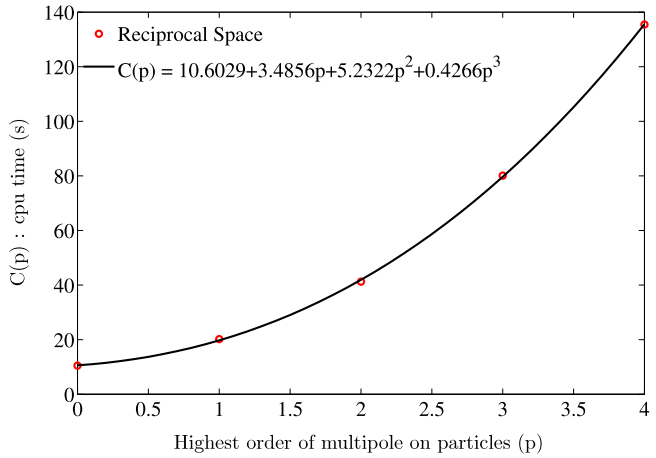


FIG. 2. A plot of cpu time of the reciprocal space PME vs order $p$ for 32 000 water molecules.

Fig. 2 is a plot of the overall cost of computing the energy, forces, torques, and stress due to the reciprocal space PME, with constant force error $10^{-5}$ for different multipole orders $p$ for a system of 32 000 water molecules on a desktop computer. The Ewald convergence parameter $\eta$ is the same as was used for the real space sum and $(K_1,K_2,K_3) = (72,72,72)$. The circles are the computational cost for $p \in \{0,1,2,3,4\}$ and the cubic curve is the best fit. The cost of the reciprocal sum is dominated by the construction of the multipolar arrays in Eq. (61) and the forces from Eq. (76), which are both $O(p^3)$ operations for a fixed number of particles. We note again that in order to capture the formal $O(p^3)$ cost of the reciprocal space, the plot was generated with a simple code with a nested loop structure and not optimized for performance.

## VI. CONCLUSION

We have formulated permanent Cartesian multipolar electrostatics which simplifies the unwieldy expressions and enables an arbitrary order implementation. This formulation has been applied to several common pair potentials present including the particle mesh Ewald method. Our Cartesian formulation grows as $O(p^3)$ for multipolar order $p$ which makes it formally as competitive as the spherical harmonic based approach recently introduced by Simmonett *et al.*[13] Finally for constant pressure simulations, we derived a closed form formula for the stress tensor due to an arbitrary order implementation of the reciprocal space Ewald.

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## APPENDIX: PROOFS AND DERIVATIONS

### 1. Proof of Eq. (68)-formula for higher order derivatives of B-splines

We claim that the $p$th derivative of the B-spline of order $n$ is given by

$$\frac{d^p}{du^p}M_n(u) = \sum_{t=0}^{p}\binom{p}{t}(-1)^t M_{n-p}(u-t). \tag{A1}$$

We prove by induction. First note that the formula holds for $p = 1$,

$$\begin{aligned}\frac{d}{du}M_n(u) &= \binom{1}{0}(-1)^0 M_{n-1}(u) + \binom{1}{1}(-1)^1 M_{n-1}(u-1)\\ &= M_{n-1}(u) - M_{n-1}(u-1).\end{aligned} \tag{A2}$$

We assume the formula holds for $p = k$, hence

$$\frac{d^k}{du^k}M_n(u) = \sum_{t=0}^{k}\binom{k}{t}(-1)^t M_{n-k}(u-t). \tag{A3}$$

Then to complete the proof, we have to show that the formula holds for $p = k+1$, that is,

$$\frac{d^{k+1}}{du^{k+1}}M_n(u) = \sum_{t=0}^{k+1}\binom{k+1}{t}(-1)^t M_{n-(k+1)}(u-t). \tag{A4}$$

We proceed by using our assumption that the formula holds for $p = k$, thus

$$\begin{aligned}\frac{d^{k+1}}{du^{k+1}}M_n(u) &= \frac{d}{du}\left(\frac{d^k}{du^k}M_n(u)\right)\\ &= \sum_{t=0}^{k}\binom{k}{t}(-1)^t \frac{d}{du}M_{n-k}(u-t)\\ &= \sum_{t=0}^{k}\binom{k}{t}(-1)^t \{M_{n-(k+1)}(u-t)\\ &\quad - M_{n-(k+1)}[u-(t+1)]\}\\ &= \sum_{t=0}^{k}\binom{k}{t}(-1)^t M_{n-(k+1)}(u-t)\\ &\quad + \sum_{t=0}^{k}\binom{k}{t}(-1)^{t+1} M_{n-(k+1)}[u-(t+1)]\\ &= \sum_{t=0}^{k}\binom{k}{t}(-1)^t M_{n-(k+1)}(u-t)\\ &\quad + \sum_{t=1}^{k+1}\binom{k}{t-1}(-1)^t M_{n-(k+1)}(u-t)\\ &= \binom{k}{0}M_{n-(k+1)}(u)\\ &\quad + \sum_{t=1}^{k}\left[\binom{k}{t}+\binom{k}{t-1}\right](-1)^t M_{n-(k+1)}(u-t)\\ &\quad + \binom{k}{k}M_{n-(k+1)}[u-(k+1)].\end{aligned} \tag{A5}$$

Now note that

$$\binom{k}{0} = \binom{k+1}{0}, \qquad \left[\binom{k}{t}+\binom{k}{t-1}\right] = \binom{k+1}{t}, \quad \text{and} \quad \binom{k}{k} = \binom{k+1}{k+1},$$

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thus

$$\frac{d^{k+1}}{du^{k+1}}M_n(u) = \binom{k+1}{0}M_{n-(k+1)}(u) + \sum_{t=1}^{k}\binom{k+1}{t}(-1)^t M_{n-(k+1)}(u-t) + \binom{k+1}{k+1}M_{n-(k+1)}[u-(k+1)] = \sum_{t=0}^{k+1}\binom{k+1}{t}(-1)^t M_{n-(k+1)}(u-t). \quad \text{(A6)}$$

## 2. Derivation of the stress tensor

The components of the virial tensor are given as[33]

$$V\sigma_{\alpha\beta} = -\sum_{\gamma}\frac{\partial U_{\text{rec}}}{\partial h_{\beta\gamma}}h_{\beta\gamma} \quad \text{(A7)}$$

and the derivative of $U_{\text{rec}}$ is given by

$$\frac{\partial U_{\text{rec}}}{\partial h_{\alpha\beta}} = \frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{1}{V}\right)\cdot\frac{1}{2\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}|S(\mathbf{k})|^2 + \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}|S(\mathbf{k})|^2\frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{\exp(-k^2/4\eta^2)}{k^2}\right) + \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}\frac{\partial|S(\mathbf{k})|^2}{\partial h_{\alpha\beta}}. \quad \text{(A8)}$$

First, we show that

$$\frac{\partial}{\partial h_{\alpha\beta}}V = V\left(h^{-1}_{\alpha\beta}\right)^{\dagger} = Vh^{-1}_{\beta\alpha}. \quad \text{(A9)}$$

The volume

$$V = |\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)| = |\mathbf{a}_2\cdot(\mathbf{a}_3\times\mathbf{a}_1)| = |\mathbf{a}_3\cdot(\mathbf{a}_1\times\mathbf{a}_2)| = h_\alpha\cdot h_\gamma\times h_\mu, \quad \text{(A10)}$$

where $\alpha,\gamma,\mu\in\{1,2,3\}$, they are all distinct and $\gamma$ and $\mu$ can be flipped to ensure a positive output. The proof of Eq. (A9) is shown as

$$\frac{\partial V}{\partial h_{\alpha\beta}} = \frac{\partial}{\partial h_{\alpha\beta}}(h_\alpha\cdot h_\gamma\times h_\mu) = \frac{\partial h_\alpha}{\partial h_{\alpha\beta}}\cdot(h_\gamma\times h_\mu) = \mathbf{e}_\beta\cdot(h_\gamma\times h_\mu) = \mathbf{e}_\beta\cdot\mathbf{a}^*_\alpha\frac{V}{2\pi} = \mathbf{e}_\beta\cdot(h^{-1})^{\dagger}_{\alpha}V = V(h^{-1})^{\dagger}_{\alpha,\beta} = Vh^{-1}_{\beta\alpha}. \quad \text{(A11)}$$

Then we find that

$$\frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{1}{V}\right) = -\frac{1}{V^2}Vh^{-1}_{\beta\alpha} = -\frac{h^{-1}_{\beta\alpha}}{V}. \quad \text{(A12)}$$

In addition,

$$\frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{\exp(-k^2/4\eta^2)}{k^2}\right) = \frac{k^2\frac{\partial}{\partial h_{\alpha\beta}}e^{-k^2/4\eta^2} - e^{-k^2/4\eta^2}\frac{\partial}{\partial h_{\alpha\beta}}k^2}{k^4} \quad \text{(A13)}$$

$$= \frac{k^2e^{-k^2/4\eta^2}\left(-\frac{1}{4\eta^2}\right)\frac{\partial k^2}{\partial h_{\alpha\beta}} - e^{-k^2/4\eta^2}\frac{\partial k^2}{\partial h_{\alpha\beta}}}{k^4} \quad \text{(A14)}$$

$$= -\frac{e^{-k^2/4\eta^2}}{k^2}\left(\frac{\frac{k^2}{4\eta^2}+1}{k^2}\right)\frac{\partial k^2}{\partial h_{\alpha\beta}}. \quad \text{(A15)}$$

Now, we find the derivative of $k^2 = \mathbf{k}\cdot\mathbf{k}$. First note that the reciprocal cell vector

$$\mathbf{k} = 2\pi(h^{-1})^{\dagger}\mathbf{n}, \quad \text{(A16)}$$

where $\mathbf{n} = \langle n_1,n_2,n_3\rangle$, and $n_i$ is an integer. Then we differentiate

$$k^2 = 4\pi^2\mathbf{n}^{\dagger}h^{-1}(h^{-1})^{\dagger}\mathbf{n}, \quad \text{(A17)}$$

with respect to $h_{\alpha\beta}$ to get

$$\begin{aligned}\frac{\partial k^2}{\partial h_{\alpha\beta}} &= 4\pi^2\frac{\partial}{\partial h_{\alpha\beta}}\mathbf{n}^{\dagger}h^{-1}(h^{-1})^{\dagger}\mathbf{n}\\ &= 4\pi^2\mathbf{n}^{\dagger}\frac{\partial}{\partial h_{\alpha\beta}}[h^{-1}(h^{-1})^{\dagger}]\mathbf{n}\\ &= 4\pi^2\mathbf{n}^{\dagger}\left[\frac{\partial}{\partial h_{\alpha\beta}}[h^{-1}](h^{-1})^{\dagger} + h^{-1}\frac{\partial}{\partial h_{\alpha\beta}}(h^{-1})^{\dagger}\right]\mathbf{n}\\ &= 4\pi^2\mathbf{n}^{\dagger}\left[\left(\frac{\partial}{\partial h_{\alpha\beta}}h^{-1}\right)(h^{-1})^{\dagger} + h^{-1}\left(\frac{\partial}{\partial h_{\alpha\beta}}h^{-1}\right)^{\dagger}\right]\mathbf{n}\\ &= -4\pi^2\mathbf{n}^{\dagger}\left[h^{-1}\frac{\partial h}{\partial h_{\alpha\beta}}h^{-1}(h^{-1})^{\dagger} + h^{-1}(h^{-1})^{\dagger}\frac{\partial h^{\dagger}}{\partial h_{\alpha\beta}}(h^{-1})^{\dagger}\right]\mathbf{n}\\ &= -2\pi[\mathbf{n}^{\dagger}h^{-1}]\frac{\partial h}{\partial h_{\alpha\beta}}h^{-1}2\pi[(h^{-1})^{\dagger}\mathbf{n}] - 2\pi[\mathbf{n}^{\dagger}h^{-1}](h^{-1})^{\dagger}\frac{\partial h^{\dagger}}{\partial h_{\alpha\beta}}2\pi[(h^{-1})^{\dagger}\mathbf{n}]\\ &= -\mathbf{k}^{\dagger}\frac{\partial h}{\partial h_{\alpha\beta}}h^{-1}\mathbf{k} - \mathbf{k}^{\dagger}(h^{-1})^{\dagger}\frac{\partial h^{\dagger}}{\partial h_{\alpha\beta}}\mathbf{k}. \end{aligned} \quad \text{(A18)}$$

Noting that $\frac{\partial h}{\partial h_{\alpha\beta}}$ is a matrix of zeroes except for the $(\alpha,\beta)$ element which is one gives $\left(\frac{\partial h}{\partial h_{\alpha\beta}}\right)_{\mu\nu} = \delta_{\mu\alpha}\delta_{\nu\beta}$ and similarly, $\left(\frac{\partial h^{\dagger}}{\partial h_{\alpha\beta}}\right)_{\mu\nu} = \delta_{\mu\beta}\delta_{\nu\alpha}$. Then we see that

$$\mathbf{k}^{\dagger}\frac{\partial h}{\partial h_{\alpha\beta}} = \frac{\partial h^{\dagger}}{\partial h_{\alpha\beta}}\mathbf{k} = (\mathbf{k})_\alpha\hat{\mathbf{e}}^{\dagger}_\beta, \quad \text{(A19)}$$

where $\hat{\mathbf{e}}_\beta$ is the standard basis vectors in the $\beta$ direction and since

$$h^{-1}\mathbf{k} = \mathbf{k}^{\dagger}(h^{-1})^{\dagger}, \quad \text{(A20)}$$

Equation (A18) becomes

$$\frac{\partial k^2}{\partial h_{\alpha\beta}} = -2\mathbf{k}^{\dagger}\frac{\partial h}{\partial h_{\alpha\beta}}h^{-1}\mathbf{k} = -2k_\alpha\hat{\mathbf{e}}^{\dagger}_\beta\cdot h^{-1}\mathbf{k} = -2k_\alpha\sum_{\gamma}h^{-1}_{\beta\gamma}k_\gamma. \quad \text{(A21)}$$

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Inserting Eq. (A21) into Eq. (A15) yields

$$\frac{\partial}{\partial h_{\alpha\beta}}\left(\frac{\exp(-k^2/4\eta^2)}{k^2}\right) = -2\frac{e^{-k^2/4\eta^2}}{k^2}\left(\frac{\frac{k^2}{4\eta^2}+1}{k^2}\right)k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}k_\gamma, \quad \text{(A22)}$$

and with Eq. (A12), we arrive at

$$\frac{\partial U_{\rm rec}}{\partial h_{\alpha\beta}} = -\frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}|S(\mathbf{k})|^2 \times\left[h^{-1}_{\beta\alpha}-2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}k_\gamma\right] + \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}\frac{\partial|S(\mathbf{k})|^2}{\partial h_{\alpha\beta}}. \quad \text{(A23)}$$

Next, we find $\frac{\partial|S(\mathbf{k})|^2}{\partial h_{\alpha\beta}}$ by first noting that

$$\frac{\partial|S(\mathbf{k})|^2}{\partial h_{\alpha\beta}} = S(\mathbf{k})\left[\frac{\partial S(-\mathbf{k})}{\partial h_{\alpha\beta}}\right]+\left[\frac{\partial S(\mathbf{k})}{\partial h_{\alpha\beta}}\right]S(-\mathbf{k}). \quad \text{(A24)}$$

If we define $\mathcal{J}_i^{\boldsymbol{\ell}}(\mathbf{k}) = \mathcal{M}_i^{\boldsymbol{\ell}}D_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i}$, where $\boldsymbol{\ell}=(\ell_1,\ell_2,\ell_3)$, then for multipolar interactions up to an arbitrary order $p$,

$$S(\mathbf{k}) = \sum_{i=1}^N\hat{L}_i e^{\imath\mathbf{k}\cdot\mathbf{r}_i} = \sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p\mathcal{M}_i^{\boldsymbol{\ell}}D_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i} = \sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p\mathcal{J}_i^{\boldsymbol{\ell}}(\mathbf{k}). \quad \text{(A25)}$$

In addition,

$$D_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i} = D_{z_i}^{\ell_3}D_{y_i}^{\ell_2}D_{x_i}^{\ell_1}e^{\imath\mathbf{k}\cdot\mathbf{r}_i} = (\imath)^{\boldsymbol{\ell}}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}e^{\imath\mathbf{k}\cdot\mathbf{r}_i}, \quad \text{(A26)}$$

hence,

$$S(\mathbf{k}) = \sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p(\imath)^{\boldsymbol{\ell}}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}\mathcal{M}_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i} = \sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p\mathcal{J}_i^{\boldsymbol{\ell}}(\mathbf{k}), \quad \text{(A27)}$$

which means that

$$\mathcal{J}_i^{\boldsymbol{\ell}}(\mathbf{k}) = (\imath)^{\boldsymbol{\ell}}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}\mathcal{M}_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i} \quad \text{(A28)}$$

and similarly

$$\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k}) = (-\imath)^{\boldsymbol{\ell}}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}\mathcal{M}_i^{\boldsymbol{\ell}}e^{-\imath\mathbf{k}\cdot\mathbf{r}_i}. \quad \text{(A29)}$$

We see then that

$$\frac{\partial S(\mathbf{k})}{\partial h_{\alpha\beta}} = \sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p(\imath)^{\boldsymbol{\ell}}\mathcal{M}_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i}\frac{\partial}{\partial h_{\alpha\beta}}\left\{(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}\right\} \quad \text{(A30)}$$

and

$$\frac{\partial}{\partial h_{\alpha\beta}}\left\{(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}\right\} = (k_2)^{\ell_2}(k_3)^{\ell_3}\frac{\partial}{\partial h_{\alpha\beta}}(k_1)^{\ell_1}+(k_1)^{\ell_1}(k_3)^{\ell_3}\frac{\partial}{\partial h_{\alpha\beta}}(k_2)^{\ell_2} + (k_1)^{\ell_1}(k_2)^{\ell_2}\frac{\partial}{\partial h_{\alpha\beta}}(k_3)^{\ell_3}. \quad \text{(A31)}$$

Recalling the definition of the reciprocal space vector

$$\mathbf{k} = 2\pi\left[h^{-1}\right]^\dagger\mathbf{n} = 2\pi\sum_{\mu=1}^3\langle h^{-1}_{\mu 1}n_\mu, h^{-1}_{\mu 2}n_\mu, h^{-1}_{\mu 3}n_\mu,\rangle = \langle k_1,k_2,k_3\rangle, \quad \text{(A32)}$$

we find that

$$\frac{\partial(k_j)^{\ell_j}}{\partial h_{\alpha\beta}} = \ell_j(k_j)^{\ell_j-1}\cdot\frac{\partial}{\partial h_{\alpha\beta}}k_j = 2\pi\ell_j(k_j)^{\ell_j-1}\sum_{\mu=1}^3\left[\frac{\partial h^{-1}_{\mu j}}{\partial h_{\alpha\beta}}\right]n_\mu. \quad \text{(A33)}$$

By differentiating through the equation $hh^{-1}=I$ with respect to $h_{\alpha,\beta}$, we find that

$$\frac{\partial h^{-1}_{\mu j}}{\partial h_{\alpha\beta}} = -h^{-1}_{\mu\alpha}h^{-1}_{\beta j}, \quad \text{(A34)}$$

and we arrive at

$$\frac{\partial(k_j)^{\ell_j}}{\partial h_{\alpha\beta}} = -2\pi\ell_j(k_j)^{\ell_j-1}\sum_{\mu=1}^3h^{-1}_{\mu\alpha}h^{-1}_{\beta j}n_\mu = -\ell_j(k_j)^{\ell_j-1}\left(2\pi\sum_{\mu=1}^3h^{-1}_{\mu\alpha}n_\mu\right)h^{-1}_{\beta j} = -\ell_j(k_j)^{\ell_j-1}k_\alpha h^{-1}_{\beta j}. \quad \text{(A35)}$$

Therefore, we can write Eq. (A31) in a more compact form as

$$\begin{aligned}\frac{\partial}{\partial h_{\alpha\beta}}&\left\{(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}\right\}\\ &= -l_1(k_1)^{\ell_1-1}(k_2)^{\ell_2}(k_3)^{\ell_3}k_\alpha h^{-1}_{\beta 1}\\ &\quad-\ell_2(k_1)^{\ell_1}(k_2)^{\ell_2-1}(k_3)^{\ell_3}k_\alpha h^{-1}_{\beta 2}\\ &\quad-\ell_3(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3-1}k_\alpha h^{-1}_{\beta 3}\\ &= -(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}k_\alpha\left[\frac{\ell_1}{k_1}h^{-1}_{\beta 1}+\frac{\ell_2}{k_2}h^{-1}_{\beta 2}+\frac{\ell_3}{k_3}h^{-1}_{\beta 3}\right]\\ &= -(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}, \end{aligned} \quad \text{(A36)}$$

and Eq. (A30) becomes

$$\frac{\partial S(\mathbf{k})}{\partial h_{\alpha\beta}} = -\sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p(\imath)^{\boldsymbol{\ell}}\mathcal{M}_i^{\boldsymbol{\ell}}e^{\imath\mathbf{k}\cdot\mathbf{r}_i}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}k_\alpha\times\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}. \quad \text{(A37)}$$

Similarly,

$$\frac{\partial S(-\mathbf{k})}{\partial h_{\alpha\beta}} = -\sum_{i=1}^N\sum_{\boldsymbol{\ell}=\mathbf{0}}^p(-\imath)^{\boldsymbol{\ell}}\mathcal{M}_i^{\boldsymbol{\ell}}e^{-\imath\mathbf{k}\cdot\mathbf{r}_i}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}k_\alpha\times\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}. \quad \text{(A38)}$$

It follows from the above equations that

$$S(\mathbf{k})\left[\frac{\partial S(-\mathbf{k})}{\partial h_{\alpha\beta}}\right] = \left[\frac{\partial S(\mathbf{k})}{\partial h_{\alpha\beta}}\right]S(-\mathbf{k}), \quad \text{(A39)}$$

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and hence Eq. (A24) becomes

$$\frac{\partial|S(\mathbf{k})|^2}{\partial h_{\alpha\beta}} = 2S(\mathbf{k})\left[\frac{\partial S(-\mathbf{k})}{\partial h_{\alpha\beta}}\right]$$
$$= -2S(\mathbf{k})\sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}(-\imath)^{\boldsymbol{\ell}}\mathcal{M}_i^{\boldsymbol{\ell}}$$
$$\times \mathrm{e}^{-\imath\mathbf{k}\cdot\mathbf{r}_i}(k_1)^{\ell_1}(k_2)^{\ell_2}(k_3)^{\ell_3}k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}$$
$$= -2S(\mathbf{k})\sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k})k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}. \quad \text{(A40)}$$

Inserting Eq. (A40) into Eq. (A23) gives

$$\frac{\partial U_{\mathrm{rec}}}{\partial h_{\alpha\beta}} = -\frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}$$
$$\times\left\{|S(\mathbf{k})|^2\left[h^{-1}_{\beta\alpha} - 2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}k_\gamma\right]\right.$$
$$\left. + 2S(\mathbf{k})\sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k})k_\alpha\sum_\gamma h^{-1}_{\beta\gamma}\frac{\ell_\gamma}{k_\gamma}\right\}, \quad \text{(A41)}$$

which is used in Eq. (A7) to get

$$V\sigma^{\mathrm{rec}}_{\alpha\beta} = \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}$$
$$\times\left\{|S(\mathbf{k})|^2\left[\sum_\gamma h^{-1}_{\gamma\alpha}h_{\beta\gamma} - 2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha\right.\right.$$
$$\left.\times\sum_\gamma\sum_\mu h^{-1}_{\gamma\mu}k_\mu h_{\beta\gamma}\right] + 2S(\mathbf{k})\sum_{i=1}^{N}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k})k_\alpha$$
$$\left.\times\sum_\gamma h_{\beta\gamma}\sum_\mu h^{-1}_{\gamma\mu}\frac{\ell_\mu}{k_\mu}\right\}. \quad \text{(A42)}$$

Now, we note that

$$\sum_\gamma h^{-1}_{\gamma\alpha}h_{\beta\gamma} = \delta_{\alpha\beta}, \quad \text{(A43)}$$

since the operation is just a scalar product of the row-$\beta$ of matrix $h$ and column-$\alpha$ of matrix $h^{-1}$ and these two vectors are orthonormal. Then,

$$\sum_\gamma\sum_\mu h^{-1}_{\gamma\mu}h_{\beta\gamma}k_\mu = \sum_\mu k_\mu\sum_\gamma h^{-1}_{\gamma\mu}h_{\beta\gamma} = \sum_\mu k_\mu\delta_{\mu\beta} = k_\beta \quad \text{(A44)}$$

and similarly

$$\sum_\gamma\sum_\mu h^{-1}_{\gamma\mu}h_{\beta\gamma}\frac{\ell_\mu}{k_\mu} = \frac{\ell_\beta}{k_\beta}. \quad \text{(A45)}$$

Using Eqs. (A43)–(A45) to simplify Eq. (A42), we find the reciprocal space virial tensor as

$$V\sigma^{\mathrm{rec}}_{\alpha\beta} = \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}$$
$$\times\left\{|S(\mathbf{k})|^2\left[\delta_{\alpha\beta} - 2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha k_\beta\right]\right.$$
$$\left. + 2S(\mathbf{k})\frac{k_\alpha}{k_\beta}\sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\ell_\beta\sum_{i=1}^{N}\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k})\right\}. \quad \text{(A46)}$$

If we define

$$S_i^\beta(-\mathbf{k}) = \sum_{\boldsymbol{\ell}=\mathbf{0}}^{p}\ell_\beta\sum_{i=1}^{N}\mathcal{J}_i^{\boldsymbol{\ell}}(-\mathbf{k}), \quad \text{(A47)}$$

then Eq. (A46) can be written in a more compact form as

$$V\sigma^{\mathrm{rec}}_{\alpha\beta} = \frac{1}{2V\epsilon_0\epsilon}\sum_{\mathbf{k}\neq 0}\frac{\exp(-k^2/4\eta^2)}{k^2}$$
$$\times\left\{|S(\mathbf{k})|^2\left[\delta_{\alpha\beta} - 2\left(\frac{k^2/4\eta^2+1}{k^2}\right)k_\alpha k_\beta\right]\right.$$
$$\left. + 2S(\mathbf{k})S_i^\beta(-\mathbf{k})\frac{k_\alpha}{k_\beta}\right\}. \quad \text{(A48)}$$


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