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Analytic stress tensor with the periodic fast multipole method

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An efficient algorithm for the direct space analytic evaluation of the Coulomb stress tensor in 1-, 2-, and 3-dimensional periodic systems is presented. These stress tensor components are required for energy optimizations with respect to unit-cell dimensions. The proposed scheme is incorporated into the periodic fast multipole method and has a small computational cost. Convergence problems arising from the nonzero dipole moment of the unit cell are treated with the help of fictitious charges. The accuracy of the proposed method is such that the stress tensor components for benchmark NaCl and CsCl structures agree to machine precision with those obtained by direct differentiation of the Madelung energy.

I. INTRODUCTION

Simulations on periodic systems involve two different sets of coordinates: the particle positions in the unit cell and the lattice dimensions. To find an energy minimum it is necessary to optimize both sets of coordinates. The optimization procedure requires knowledge of energy gradients with respect to particle positions as well as lattice parameters. We will refer to the former as *particle forces*. The latter is known as the stress tensor, which represents the derivatives of the energy of a periodic system with respect to the strain tensor components.

We are particularly interested in simulations of chemical systems with periodic boundary conditions. A physical model in this case includes the Coulomb potential. Since the potential is long ranged, special care must be taken to insure a converged result. The Ewald summation method is adequate to properly converge the arising infinite Coulomb sum.[1] In this approach one part of the Coulomb contribution is computed in direct space and another - in reciprocal space. Alternatively, the infinite summation can be done using the periodic fast multipole method (FMM).[2–7] In this case the procedure is carried out entirely in direct space. With either method, the evaluation of analytic particle forces is quite similar to the calculation of the Coulomb potential itself. Thus, only minor modifications to these techniques are required for obtaining particle forces, even if dealing with quantum (Gaussian) charge distributions as required for electronic structure calculations.[8–10]

Similar to the potential and forces, the stress tensor can be computed either in direct and reciprocal spaces or in direct space only. The former approach was first employed in the simulations of solids with plane-wave basis by Nielsen and Martin[11] and later extended to calculations with Gaussian basis sets by Feibelman.[12] To the best of our knowledge, no method has been described for the computation of the Coulomb stress tensor entirely in direct space. Such method would be preferable in cases where the direct space only approach is applied for the evaluation of energy and forces as well. For example, in Ref. 13 we extended the periodic FMM to energy calculations for systems with Gaussian charge distributions and demonstrated $O(N)$ scaling properties for the algorithm. In this particular situation, the FMM has certain advantages over the Ewald summation such as its universal applicability to systems periodic in one, two, and three dimensions. Therefore, in this paper we introduce a method for the direct space analytic evaluation of the stress tensor for the Coulomb potential with the help of the periodic FMM. Here, we limit our discussion to the case of point charges and point multipoles; the generalization required to deal with Gaussian charge distributions will be reported elsewhere.[14]

II. THE DERIVATIVES OF THE COULOMB POTENTIAL IN PERIODIC SYSTEMS

Let's consider a set of charges q_i located at coordinates $\mathbf{r}_i=(r_{1i},r_{2i},r_{3i})$ in the central cell 0. Every other cell α contains replicas $q_{i\alpha}$ of the charges in the central cell and their positions are $\mathbf{r}_{i\alpha}$. In our notation when $\alpha=0$ (the central cell) we drop the second subindex, i.e., $q_{i0}\equiv q_i$ and $r_{i0}\equiv r_i$. The Coulomb energy per cell for this periodic system can be written as

$$E=\frac{1}{2}\sum_{i,j\alpha}{}' \frac{q_i q_{j\alpha}}{|\mathbf{r}_i-\mathbf{r}_{j\alpha}|}, \tag{2.1}$$

where the modified sum Σ' excludes the terms for which both charges are the same ($j\alpha=i0$). Differentiating Eq. (2.1) one obtains derivatives of the unit-cell energy with respect to particle positions

$$\mathbf{F}_k=\frac{dE}{d\mathbf{r}_k}=\sum_{\alpha}\frac{dE}{d\mathbf{r}_{k\alpha}}=\frac{1}{2}\sum_{j\alpha}{}' \frac{d}{d\mathbf{r}_k}\frac{q_k q_{j\alpha}}{|\mathbf{r}_k-\mathbf{r}_{j\alpha}|} + \frac{1}{2}\sum_{i\alpha}{}' \frac{d}{d\mathbf{r}_{k\alpha}}\frac{q_i q_{k\alpha}}{|\mathbf{r}_i-\mathbf{r}_{k\alpha}|}, \tag{2.2}$$

where we denote the three derivatives $(d/dr_k^1, d/dr_k^2, d/dr_k^3)$ as $d/d\mathbf{r}_k$. We emphasize that derivative $\mathbf{F}_k$ corresponds to

the change in the unit cell energy due to the identical displacement of all the charges $q_{k\alpha}$ in every cell α. For later use, we also introduced above derivatives of the unit-cell energy with respect to the position $\mathbf{r}_{k\alpha}$ of a given charge $q_{k\alpha}$. Due to symmetry, both contributions in Eq. (2.2) are the same and the derivatives become

$$\mathbf{F}_k = \sum_{j\alpha}{}' \frac{d}{d\mathbf{r}_k} \frac{q_k q_{j\alpha}}{|\mathbf{r}_k - \mathbf{r}_{j\alpha}|}. \tag{2.3}$$

In order to derive equations for the stress tensor, we want to find the change in the system energy under a uniform lattice strain defined as

$$R_a \rightarrow \sum_b (\delta_{ab} + \epsilon_{ab}) R_b, \tag{2.4}$$

where a and b are Cartesian indices, and δ_{ab} is the Kronecker delta. For a given strain component ϵ_{ab} the stress can be calculated as

$$\frac{\delta E}{\delta \epsilon_{ab}} = \sum_{j\alpha} r^b_{j\alpha} \frac{dE}{dr^a_{j\alpha}}, \tag{2.5}$$

where the sum runs over every particle j in each cell α, and the derivatives $dE/dr^a_{j\alpha}$ are the same as those in Eq. (2.2). Now let us examine a periodic system in only one dimension with translational vector $\mathbf{t}=(t^1,t^2,t^3)$. The coordinates of replicas of the charges in the central cell are

$$r^a_{i\alpha} = r^a_i + \alpha t^a. \tag{2.6}$$

Applying the differentiation scheme (2.5) to the energy Eq. (2.1), we derive the following expression for the stress tensor components

$$\begin{aligned}\frac{\delta E}{\delta \epsilon_{ab}} &= \frac{1}{2} \sum_{i,j\alpha}{}' r^b_i \frac{d}{dr^a_i} \frac{q_i q_{j\alpha}}{|\mathbf{r}_i - \mathbf{r}_{j\alpha}|} \\ &+ \frac{1}{2} \sum_{i,j\alpha}{}' (r^b_j + \alpha t^b) \frac{d}{dr^a_{j\alpha}} \frac{q_i q_{j\alpha}}{|\mathbf{r}_i - \mathbf{r}_{j\alpha}|} \\ &= \sum_i r^b_i F^a_i - t^b \frac{1}{2} \sum_\alpha \alpha \sum_{ij} \frac{d}{dr^a_i} \frac{q_i q_{j\alpha}}{|\mathbf{r}_i - \mathbf{r}_{j\alpha}|},\end{aligned} \tag{2.7}$$

where we have used Eq. (2.3) for F^a_i. Equation (2.7) describes the change in energy due to an elastic strain as the sum of two terms. In the first term, the particles are elastically shifted with respect to one another within each cell while the translational vector $\mathbf{t}$ is kept fixed. Therefore, the first term is just a sum of the forces acting on each particle multiplied by their coordinates. In the second term, all the cells in the system are elastically displaced with respect to the central cell, keeping distances between particles within each cell fixed. Since in this process the cells remain rigid, we will refer to the second term of the elastic stress in Eq. (2.7) as the *rigid cell stress*. If all forces on particles are zero, then the elastic stress is simply equal to the rigid cell stress, and only the second part of Eq. (2.7) needs to be calculated. This situation appears when only the particle coordinates are relaxed and not the cell dimensions.

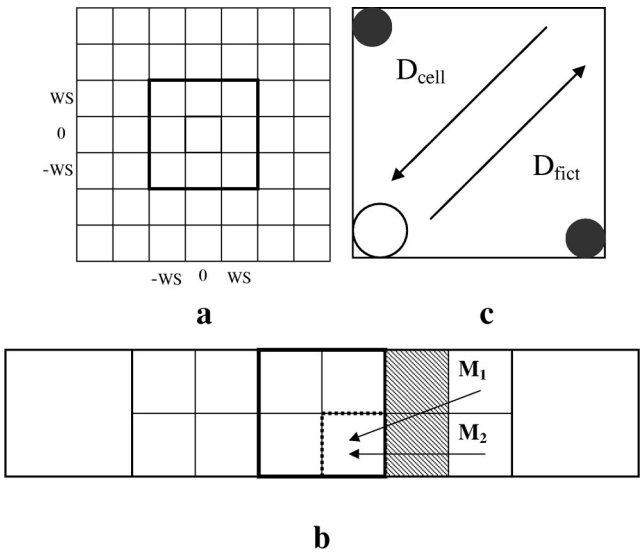

FIG. 1. (a) The FMM and the infinite zones ($WS=1$); (b) contributions for a box in the central cell that come from cell α. Near-field boxes are filled, far-field boxes are indicated by moments M_1 and M_2; (c) cancellation of the dipole moment of the cell with the help of fictitious charges. The sum of these charges is 0.

A general three-dimensional periodic system has 3 translational vectors $\mathbf{t}_1,\mathbf{t}_2,\mathbf{t}_3$ with coordinates (t^1_1,t^2_1,t^3_1), (t^1_2,t^2_2,t^3_2), (t^1_3,t^2_3,t^3_3). Each cell α is indexed by 3 integer indices $(\alpha_1,\alpha_2,\alpha_3)$. The stress with respect to ϵ_{ab} for such a system is:

$$\begin{aligned}\frac{\delta E}{\delta \epsilon_{ab}} &= \sum_i r^b_i F^a_i - t^b_1 \frac{1}{2} \sum_\alpha \alpha_1 \sum_{ij} \frac{d}{dr^a_i} \frac{q_i q_{j\alpha}}{|\mathbf{r}_i - \mathbf{r}_{j\alpha}|} \\ &- t^b_2 \frac{1}{2} \sum_\alpha \alpha_2 \sum_{ij} \frac{d}{dr^a_i} \frac{q_i q_{j\alpha}}{|\mathbf{r}_i - \mathbf{r}_{j\alpha}|} \\ &- t^b_3 \frac{1}{2} \sum_\alpha \alpha_3 \sum_{ij} \frac{d}{dr^a_i} \frac{q_i q_{j\alpha}}{|\mathbf{r}_i - \mathbf{r}_{j\alpha}|}.\end{aligned} \tag{2.8}$$

We note that combinations of the strain tensor components such as $(\epsilon_{xy} - \epsilon_{yx})$ represent pure rotations and therefore do not affect the energy of the system. In total, 3 rotations can be eliminated yielding only 6 independent values out of 9 derivatives.

All the expressions derived above are general in nature and one can also use them for other potentials, such as Lennard-Jones. In the case of Coulomb interactions the expressions are valid for lattices of multipoles as well, one just needs to change the interaction potential $|\mathbf{r}_i - \mathbf{r}_j|^{-1}$ to the appropriate expression.

III. RIGID CELL STRESS WITH THE FMM

Let us first discuss how to compute contributions to the rigid cell stress from cells that are located in some vicinity of the central cell [$|\alpha| \leq WS$, see Fig. 1(a)]. According to Eq. (2.7) one has to compute derivatives of all pair-wise interactions between charges from the central cell (cell 0) and some other cell α from the vicinity, add them up, and multiply by α. This can be visualized as if all the charges in cell α are

being displaced with respect to charges in the central cell by αdr_a.

The fast multipole method[15,16] can speed up things considerably since it replaces individual charge-charge interactions between well-separated sets of charges by collective multipole-multipole interactions. Each set of charges is represented as a multipole moment M_{lm} with order up to l. The energy (or a derivative) of 2 interacting multipoles can be evaluated directly by using corresponding tensorial expressions.[17] However, within the FMM it is more convenient to compute first the local moments L_{lm}, which are essentially Taylor expansions of the electrostatic potential due to a distant set of charges. Since both multipole and local moments are expanded in orthogonal spherical harmonics, it is extremely easy to compute their interaction energy when their expansion centers s coincide

$$M^s \odot L^s = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{m=l} M^s_{lm} L^s_{lm}. \tag{3.1}$$

In this paper, we will use the compact notation $\odot$ to replace the summation on l and m. Both multipole and local moments can be differentiated very efficiently[18] and the derivative of the electrostatic energy will have the following form

$$\frac{d}{dr_a}(M^s \odot L^s) = \frac{dM}{dr_a} \odot L = -M \odot \frac{dL}{dr_a}. \tag{3.2}$$

An important part of the FMM is the $M2L$ translational operator, which allows local moments L to be computed around point a from multipole moments M computed at point b

$$L^a = T^{(b-a)} \otimes M^b, \tag{3.3}$$

where $T^{(b-a)}$ are translational coefficients related to the local moments of the point $(b-a)$. The $\otimes$ operation is a two index summation of $T^{l'm'}_{lm}$ with $M_{l'm'}$, and its detailed description can be found in Refs. 15 and 16.

A key component to achieve linear scaling in the FMM is the subdivision of the system into cubic boxes, which create a tree structure. If there are WS boxes in between two given boxes under consideration, these boxes are considered well separated and can be treated by multipole expansions (far-field). Otherwise, the interactions are computed via pairwise terms (near-field). Using this concept we can also classify cells around the central cell into two groups. The first group, which includes the central cell and some of its neighbors, we call the ''FMM zone.'' For example, in the three-dimensional (3D) case the FMM zone includes cells whose positions lie within the boundaries $(-WS,WS;-WS,WS;-WS,WS)$ where WS is the FMM well separatedness criterion [Fig. 1(a), $WS=1$]. The second group of cells we call the ''infinite zone.'' These cells satisfy requirements for the convergence of the $M2L$ operator and their multipole moments can be translated directly into the central cell. Consequently, in the FMM zone we do care about individual charges, whereas interactions of the central cell charges with the infinite zone can be replaced by interactions of a multipole with a lattice of equivalent multipoles.

Let us now examine how we incorporate the solid cell stress into the FMM procedure in the FMM zone. In the following, we assume the unit cell to be cubic. For the generalization to non-cubic cells, see Ref. 7. In Fig. 1(b), one can see near-field (NF) and far-field (FF) contributions to a box in the central cell from a neighboring cell α. For the NF we explicitly compute derivatives of pairwise interactions. In the FF, the multipole moments M_1 and M_2 are translated to the box in the central cell, and then the electrostatic derivatives are computed according to Eq. (3.2). Such computations are carried out for each box in the central cell, and contributions are added up. The sum is multiplied by α and added to the solid stress. The operation is repeated for each cell α. We want to emphasize that the derivatives of pairwise interactions computed in the near field are also needed for particle forces, and local moments of the cells from the far field are used for potential and forces, and therefore the added computational effort for the stress is negligible.

All the cells in the infinite zone [Fig. 1(a)] are replicas of the central cell and have the same multipole moment. In order to convert multipoles into local contributions one has to perform the $M2L$ translations for each cell. However, due to the fact that the $M2L$ operator defined in Eq. (3.3) has to be applied to identical multipole moments over and over, one can first add up the translational coefficients and then perform a single translation, as first suggested by Schmidt and Lee.[2] In the case of cell α, the contributions are multiplied by α, and we need to include these α as weights into the sums of translational coefficients. For a system periodic in three dimensions there will be 3 sums, one for each periodicity direction. Combining these with 3 subsequent differentiations, one obtains 9 stress components. The infinite sum of translational coefficients may be computed by either one of the following three methods: the one first proposed in Ref. 2, the renormalization method introduced in Ref. 3, or by cre-

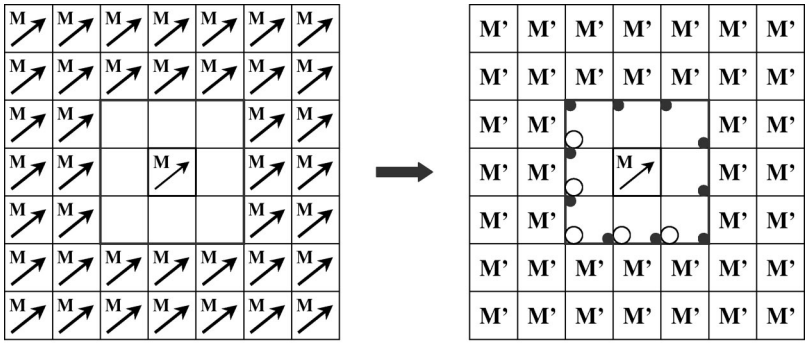

FIG. 2. (a) Original form of the infinite FMM sum, each cell has moment M with the non-zero dipole term; (b) final form of the infinite FMM sum, moments M' have zero dipole moment, compensating charges appear on the border of the FMM zone.

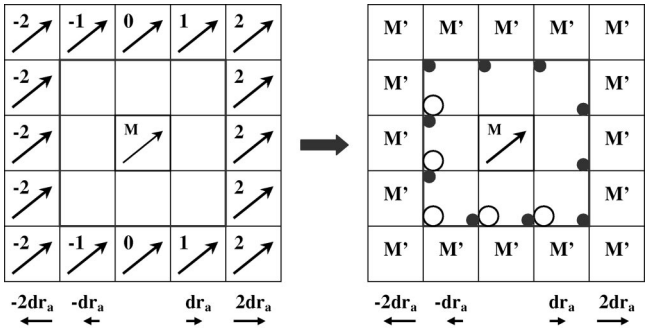

FIG. 3. Contribution from the infinite zone to the solid cell stress, displacements of the cells are shown by arrows below the picture.

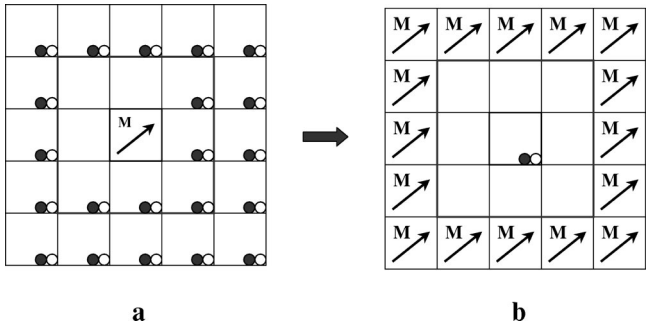

FIG. 4. Removal of the extra term appearing due to the use of the fictitious charges in the computation of the solid cell stress.

ating a hierarchy of supercells.[4] We prefer to use the latter approach as discussed in Ref. 7.

IV. CONVERGENCE OF THE INFINITE SUMMATIONS

In the periodic FMM, the infinite summations take place completely in real space, so it is necessary to make sure that the sums are convergent. Three-dimensional periodicity represents the most difficult case since we need to perform the summation over R^3 space. Charge-charge interactions have a R^{-1} dependence and therefore are divergent. To avoid this problem, the total charge of the cell must be 0. Dipole-dipole terms are on the edge of convergence (R^{-3}) and lead to a shift in the total cell energy. This shift is caused by an extra electric field in the direction of the dipole moment of the cell. The boundaries of the unit cell are arbitrary, and if they are changed, the dipole moment of the cell may change as well, leading to a different electric field and different total energy. To avoid this problem one may introduce an external electric field that would cancel this dipole dependent field. Another possibility is to introduce fictitious charges, and we employ this method in our program. Its application to arbitrary lattices was discussed in Ref. 7, and here we just briefly review this strategy. Fictitious charges are placed at the corners of the lattice such that they cancel the dipole moment of the simulation cell [Fig. 1(c)]. When the cells are brought together, their corners coincide, and the fictitious charges cancel each other everywhere except on the surface. We also prefer to remove these fictitious charges from the FMM zone so a second layer of the uncancelled charges is formed at the border of the FMM zone (Fig. 2). Local moments for this layer of charges can be computed directly. As a result, the infinite translation step uses a modified cell multipole moment that does not contain dipole terms along the periodicity directions. Therefore, we effectively reduced the dipole-dipole R^{-3} interaction of the central cell multipole moment with all the other cell moments to dipole-quadrupole interactions of the same moments. The latter has R^{-4} dependence and is absolutely convergent. We would like to point out that the largest portion of the contribution to the potential comes from the FMM zone and the border charges, whereas the infinite zone yields a contribution which is comparatively small. Such border correction would also be useful in methods that neglect the infinite part altogether and use some type of cutoffs since the arbitrary placement of the cell boundaries and the resulting dipole moment will be accounted for properly.

Similar convergence problems to those described above arise in the evaluation of the stress. Differentiation of the multipole interactions transforms R^{-n} terms into $R^{-(n+1)}$. However, subsequent multiplication by r_a, as in Eq. (2.5), restores the original R^{-n} dependence of a given contribution and therefore the rigid stress calculations have the same convergence properties as the potential. To get convergent results, we employ fictitious charges in this part of the code as well (Fig. 3). The border contribution from fictitious charges now has to be weighted by the α index of the cell. In a 3D periodic system, 3 different border terms are present for each α. There is also another contribution related to the compensating charges. A fictitious charge at the corner of cell α is displaced by αr_a, whereas a charge in the cell $(\alpha+1)$ is displaced by $(\alpha+1)r_a$. The consequence is that an uncompensated dipole appears in all cells and at the border [Fig. 4(a)], and interacts with the multipole moment of the central cell, so we have to subtract this contribution from the stress. It is easiest to compute this term when we view it as an interaction of a dipole in the central cell with a lattice of cell multipole moments [Fig. 4(b)]. In the energy and force calculation, we already computed local moments from the infinite zone using cell multipole moments and properly compensating the dipole moment (see the discussion at the top of this section and Fig. 2). So we just use this local moment and interact it with the extra dipole, and the spurious term is removed.

To summarize, the non-zero dipole moment of the cell does add a few terms to the computation of the elastic stress, but in return, these modifications allow us to treat systems with any periodicity and dipole moment. Also, in spite of the added complexity of the described manipulations, the required CPU time to evaluate the additional contribution due to the dipole moment is negligible and independent of system size.

V. IMPLEMENTATION ISSUES

Madelung energies for ionic systems such as NaCl and CsCl offer an extremely convenient way to check the results of our program. Since there is an explicit inter-ionic parameter (R), we can differentiate the Madelung energy with respect to R. The system is compressed uniformly so the derivative with respect to R represents a sum of energy

TABLE I. Convergence of the energies and elastic forces for NaCl and CsCl as a function of l_{max} used ($WS=2$). The exact values are taken from Ref. 19.

LMax	NaCl energy	NaCl elastic force	CsCl energy	CsCl elastic force
4	−1.7475639	0.58230	−1.7634	0.583
8	−1.7475645927	0.58252164	−1.7626737	0.58750
12	−1.74756459467	0.5825215300	−1.76267491	0.5875555
16	−1.74756459463313	0.5825215315436	−1.762674759	0.58755832
20	−1.747564594633188	0.582521531544375	−1.76267477324	0.5875582568
24	−1.747564594633188	0.582521531544375	−1.7626747730694	0.58755825772
28	−1.747564594633188	0.582521531544375	−1.76267477307101	0.5875582576978
32	−1.747564594633188	0.582521531544375	−1.76267477307101	0.5875582576982
Exact	−1.747564594633182	0.5825215315443940	−1.762674773070988	0.587558257690329

derivatives with respect to the 3 strain tensor components ϵ_{xx}, ϵ_{yy}, and ϵ_{zz}

$$\frac{\delta E}{\delta \epsilon_{xx}}+\frac{\delta E}{\delta \epsilon_{yy}}+\frac{\delta E}{\delta \epsilon_{zz}}=R\frac{d}{dR}\left(\frac{C_M}{R}\right)=-\frac{C_M}{R}, \qquad (5.1)$$

where C_M is the Madelung constant. Due to the system symmetry, these 3 derivatives are equal to each other, so each derivative is 1/3 of the energy derivative with respect to R. In both NaCl and CsCl all particle forces are zero so that only the rigid cell force is important.

NaCl serves as a benchmark without a dipole moment, whereas CsCl offers an opportunity to check the part of the algorithm that uses the dipole moment correction terms. Table I illustrates the convergence of the energy and elastic forces as a function of l_{max}. In order to make the results easier to analyze, we have scaled all the entries in Table I by a constant such that the exact energies are now equal to the Madelung constants of the systems. The results for the dipoleless NaCl system converge much faster than for CsCl, which has a dipole moment. Also, for a given l_{max} the relative accuracy of the elastic stress is worse than the accuracy of the energy. This is not very surprising since the approximations used in FMM are expected to affect energy derivatives more than the energy itself.

The computational overhead caused by the evaluation of elastic forces is very small. The infinite summation procedure takes about 1-4 s on an IBM 3CT workstation depending on the l_{max} employed. The differentiation step added to the $M2L$ step of the FMM algorithm always takes less than 1% of the CPU time required for the $M2L$ step itself. This is a very small computational overhead for these very useful quantities.

VI. CONCLUSIONS

In this paper, we have developed a direct space analytic procedure for the calculation of elastic stress for the Coulomb potential in systems with point charges. Two different contributions are present in the stress; one coming from particle gradients and the other from the rigid cell stress. In our method, the FMM is used to compute both contributions. The rigid cell stress requires calculation of some inexpensive quantities during the near-field portion of the algorithm and the multipole to local translation step. The contribution from the infinite part of the system to the rigid stress is converged using a strategy similar to the one employed in energy calculations.[7] The dipole moment of the unit cell leads to non-convergent contributions and therefore is eliminated from the infinite summation procedure with the help of fictitious charges. When the rigid cell stress is computed together with energy and particle gradients, the computational overhead is very small, thus leading to a very efficient direct space algorithm for the analytic evaluation of Coulomb elastic stress in system with periodic boundary conditions. We are currently implementing the method described in this paper for the analytic evaluation of elastic stress in electronic structure calculations with Gaussian basis sets. The details of this implementation will be described elsewhere.[14]

ACKNOWLEDGMENTS

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