A Simpler and More Efficient Formulation of The Cell Multipole Method

Ramzi Kutteh
High Performance Computing Group
Molecular Science Research Center
Pacific Northwest Laboratory
Richland, WA 99352

I examine the particular forms of the potential multipole expansion and multipole moments used in the cell multipole method (CMM) of Ding *et al.* [1]. I show that alternative definitions of the moments corresponding to a common alternative form of the multipole expansion, may be more advantageous to use in CMM than the moment definitions adopted by Ding *et al.* [1]. Specifically, the shifting expressions for the new quadrupole and higher order moments are easier to derive, more simple and symmetric (i.e., easier to code), and more computationally efficient than the shifting expressions for the previously adopted moments.

I demonstrate here that an alternative form of the potential multipole expansion, with corresponding multipole moment definitions, may be more advantageous for use in the cell multipole method (CMM) of Ding *et al.* [1] than the particular form adopted by the authors.

CMM consists of an upward pass followed by a downward pass. In the upward pass, the multipole moments of the cells are first computed at the finest level of refinement. I refer to this computation as step (I). The definitions used to compute the moments correspond to the following form of multipole expansion of the potential of a collection of charges inside a cell A (this expansion is obtainable from a Taylor or equivalently a binomial expansion of the Coulomb potential):

$$V(\mathbf{r}) = \frac{Z}{R} + \frac{\sum_\alpha \mu_\alpha R_\alpha}{R^3} + \frac{\sum_{\alpha,\beta} Q_{\alpha\beta} R_\alpha R_\beta}{R^5} + \frac{\sum_{\alpha,\beta,\gamma} O_{\alpha\beta\gamma} R_\alpha R_\beta R_\gamma}{R^7} + \cdots , \tag{1}$$

where $Z = \sum_i q_i$ is the monopole moment, $\mu_\alpha = \sum_i q_i \bar{r}_{i\alpha}$ is the dipole moment, and

$$\begin{aligned} Q_{\alpha\beta} &= \frac{1}{2}\sum_i q_i[3\bar{r}_{i\alpha}\bar{r}_{i\beta} - \delta_{\alpha\beta}\bar{r}_i^2] \\ O_{\alpha\beta\gamma} &= \frac{1}{2}\sum_i q_i[5\bar{r}_{i\alpha}\bar{r}_{i\beta}\bar{r}_{i\gamma} - (\bar{r}_{i\alpha}\delta_{\beta\gamma} + \bar{r}_{i\beta}\delta_{\alpha\gamma} + \bar{r}_{i\gamma}\delta_{\alpha\beta})\bar{r}_i^2] \end{aligned} \tag{2}$$

are the quadrupole and octopole moments, respectively. In the above equations $\mathbf{R} = \mathbf{r} - \mathbf{r}_A$, where $\mathbf{r}_A$ is the position of the center of cell A; q_i is the charge of particle i, and $\bar{r}_{i\alpha}$ is the α component of the position vector of particle i with respect to the center of cell A. I refer to the definition of the quadrupole and all higher moments as in Eq (2), as definition (A). At coarser levels, the multipole moments of every parent cell at level $(l-1)$ are computed by shifting and adding the multipole moments of its eight children cells at level l. I refer to this computation as step (II). For example, the shifting expression for the quadrupole moment with definition (A) is

$$\begin{aligned} Q_{\alpha\beta}^{(l-1)} &= \sum_{k=1}^{8}[Q_{\alpha\beta}^{(l)}]_k + \frac{3}{2}\sum_{k=1}^{8}\{[\mu_\alpha^{(l)}]_k[C_\beta]_k + [\mu_\beta^{(l)}]_k[C_\alpha]_k\} - \sum_{k=1}^{8}[\mu^{(l)}]_k \cdot [C]_k\delta_{\alpha\beta} \\ &+ \frac{1}{2}\sum_{k=1}^{8}[Z^{(l)}]_k\{3[C_\alpha]_k[C_\beta]_k - [C^2]_k\delta_{\alpha\beta}\} , \end{aligned} \tag{3}$$

and for the octopole moment with definition (A)

$$\begin{aligned} O_{\alpha\beta\gamma}^{(l-1)} &= \sum_{k=1}^{8}[O_{\alpha\beta\gamma}^{(l)}]_k + \sum_{k=1}^{8}\{[Q_{\alpha\beta}^{(l)}]_k[C_\gamma]_k + [Q_{\alpha\gamma}^{(l)}]_k[C_\beta]_k + [Q_{\beta\gamma}^{(l)}]_k[C_\alpha]_k\} \\ &+ \sum_{k=1}^{8}\{[Q_{\alpha\beta}'^{(l)}]_k[C_\gamma]_k + [Q_{\alpha\gamma}'^{(l)}]_k[C_\beta]_k + [Q_{\beta\gamma}'^{(l)}]_k[C_\alpha]_k\} \\ &- \sum_{k=1}^{8}\{[Q_\alpha'^{(l)}]_k \cdot [C]_k\delta_{\beta\gamma} + [Q_\beta'^{(l)}]_k \cdot [C]_k\delta_{\alpha\gamma} + [Q_\gamma'^{(l)}]_k \cdot [C]_k\delta_{\alpha\beta}\} \\ &+ \frac{1}{2}\sum_{k=1}^{8}\{5([\mu_\alpha^{(l)}]_k[C_\beta]_k[C_\gamma]_k + [\mu_\beta^{(l)}]_k[C_\alpha]_k[C_\gamma]_k + [\mu_\gamma^{(l)}]_k[C_\alpha]_k[C_\beta]_k) \\ &- ([\mu_\alpha^{(l)}]_k\delta_{\beta\gamma} + [\mu_\beta^{(l)}]_k\delta_{\alpha\gamma} + [\mu_\gamma^{(l)}]_k\delta_{\alpha\beta})[C^2]_k\} \\ &- \sum_{k=1}^{8}[\mu^{(l)}]_k \cdot [C]_k\{[C_\alpha]_k\delta_{\beta\gamma} + [C_\beta]_k\delta_{\alpha\gamma} + [C_\gamma]_k\delta_{\alpha\beta}\} \\ &+ \frac{1}{2}\sum_{k=1}^{8}[Z^{(l)}]_k\{5[C_\alpha]_k[C_\beta]_k[C_\gamma]_k - ([C_\alpha]_k\delta_{\beta\gamma} + [C_\beta]_k\delta_{\alpha\gamma} + [C_\gamma]_k\delta_{\alpha\beta})[C^2]_k\} , \end{aligned} \tag{4}$$

where $[C]_k$ is the vector from the center of a parent cell to the center of its kth child cell, and $Q'_{\alpha\beta}$ is defined in Eq (6). In the downward pass, the Taylor coefficients of the cells are first computed at the coarsest level (level 2 for vacuum boundary conditions) by Taylor expanding Eq (1). I refer to this computation as step (III). At finer levels, the Taylor coefficients of every child cell are the sum of two contributions. The first contribution is the sum of the Taylor coefficients from the cell's interaction list. I refer to this computation as step (IV). The second contribution comes from shifting the Taylor coefficients of the parent cell. I refer to this computation as step (V).

An alternative common form of the potential multipole expansion [2, 3] is obtained by rewriting

Eq (1) in the form

$$V(\mathbf{r}) = \frac{Z}{R} + \frac{\sum_\alpha \mu_\alpha R_\alpha}{R^3} + \frac{1}{2}\frac{\sum_{\alpha,\beta} Q'_{\alpha\beta}[3R_\alpha R_\beta - \delta_{\alpha\beta}R^2]}{R^5} + \frac{1}{2}\frac{\sum_{\alpha,\beta,\gamma} O'_{\alpha\beta\gamma}[5R_\alpha R_\beta R_\gamma - (R_\alpha\delta_{\beta\gamma} + R_\beta\delta_{\alpha\gamma} + R_\gamma\delta_{\alpha\beta})R^2]}{R^7} + \cdots , \tag{5}$$

where the quadrupole and octopole moments are now given by

$$Q'_{\alpha\beta} = \sum_i q_i \bar{r}_{i\alpha}\bar{r}_{i\beta} \quad , \quad O'_{\alpha\beta\gamma} = \sum_i q_i \bar{r}_{i\alpha}\bar{r}_{i\beta}\bar{r}_{i\gamma} \quad , \tag{6}$$

respectively. I refer to the definition of the quadrupole and all higher moments as in Eq (6), as definition (B). In the following, I show that the multipole expansion in Eq (5), with definition (B) of the moments, may be more advantageous for use in CMM than the expansion in Eq (1), with definition (A) of the moments.

The quadrupole and all higher order moments in definition (B) have simpler forms than the quadrupole and all higher order moments in definition (A) (compare Eq (2) with Eq (6)). More explicitly, the moments in Eq (6) do not require the computation of atomic distances. The optimum number κ of particles per cell at the finest level depends on the nature of the system, its size, the order of approximation, and the number of levels. For example, for five levels of refinement, the finest level has 32768 cells. Typically, I have found κ for this case will range in value from 10 to 100. Adopting definition (B) for the moments, instead of definition (A), results for this case in a savings of $\kappa \times 32768$ or on average ≈ 2 million atomic distance computations, leading to a more computationally efficient step (I). The expansion in Eq (5) has a more complex functional form (i.e., dependence on $\mathbf{R}$) than the expansion in Eq (1). Hence the Taylor coefficients obtained by Taylor expanding Eq (5) also have more complex forms than the coefficients obtained by Taylor expanding Eq (1). However, in contrast to the difference between Eq (2) and Eq (6) noted above, the Taylor coefficients obtained from Eq (1) and Eq (5) *both* require cell-cell distance computations (i.e., from R). This means that no additional quantities (such as cell-cell distances) are required to compute the extra terms in the Taylor coefficients introduced by adopting definition (B) of the moments. Therefore using definition (B) for the moments, instead of definition (A), leads to a negligible computational overhead in step (III). Step (IV) involves the computation of the Taylor coefficients of 189 cells for every cell, starting at level 3 and down to the finest level. For example, for five levels of refinement and taking the interaction list of any cell to be 189 cells (this number is actually smaller for non-interior cells), levels 3, 4, and 5 require the computation of ≈ 7 million cell-cell distances, *regardless* of which definition of the moments is adopted. As for step (III), the additional cost of incorporating the extra terms in the Taylor expansions is small, since cell-cell distances are already available.

In step (V), the shifting expressions for the Taylor coefficients are independent of the forms of the coefficients. Hence, even though the Taylor coefficients obtained by Taylor expanding Eq (5) (i.e., using definition (B) for the moments) are more complex than the coefficients obtained by expanding Eq (1) (i.e., using definition (A) for the moments), the Taylor shifting expressions are identical in both cases. This is the key difference between the Taylor shifting expressions and the moment shifting expressions which is exploited below. With regard to steps (I), (III), (IV), and (V), using definition (B) of the moments instead of definition (A) will most likely result in a speed-up, although in some cases there may be no advantage in selecting one definition over the other.

However, in step (II) there are two clear advantages to favoring definition (B) for the quadrupole and higher moments, over definition (A). First, the shifting expressions for the moments with definition (B) are easier to derive than the shifting expressions for the moments with definition (A). They are also simpler, and more symmetric (i.e., easier to code) than the shifting expressions with definition (A). They parallel in simplicity and symmetry the Taylor shifting expressions in step (V). For example, the shifting expression for the quadrupole moment with definition (B) is

$$Q'^{(l-1)}_{\alpha\beta} = \sum_{k=1}^{8}[Q'^{(l)}_{\alpha\beta}]_k + \sum_{k=1}^{8}\{[\mu^{(l)}_{\alpha}]_k[C_\beta]_k + [\mu^{(l)}_{\beta}]_k[C_\alpha]_k\} + \sum_{k=1}^{8}[Z^{(l)}]_k[C_\alpha]_k[C_\beta]_k \ , \tag{7}$$

and for the octopole moment with definition (B)

$$\begin{aligned} O'^{(l-1)}_{\alpha\beta\gamma} &= \sum_{k=1}^{8}[O'^{(l)}_{\alpha\beta\gamma}]_k + \sum_{k=1}^{8}\{[Q'^{(l)}_{\alpha\beta}]_k[C_\gamma]_k + [Q'^{(l)}_{\alpha\gamma}]_k[C_\beta]_k + [Q'^{(l)}_{\beta\gamma}]_k[C_\alpha]_k\} \\ &+ \sum_{k=1}^{8}\{[\mu^{(l)}_{\alpha}]_k[C_\beta]_k[C_\gamma]_k + [\mu^{(l)}_{\beta}]_k[C_\alpha]_k[C_\gamma]_k + [\mu^{(l)}_{\gamma}]_k[C_\alpha]_k[C_\beta]_k\} \\ &+ \sum_{k=1}^{8}[Z^{(l)}]_k[C_\alpha]_k[C_\beta]_k[C_\gamma]_k \ . \end{aligned} \tag{8}$$

Eqs (7) and (8) are clearly more compact expressions than Eqs (3) and (4), respectively. The relative ease in deriving and coding the shifting expressions for moments with definition (B) becomes more significant when higher order moments are needed. Shifting expressions for octopole (see Eq (4)) and higher moments (e.g., hexadecapoles,...) with definition (A), are increasingly tedious to derive and code. Second, the shifting expressions for the moments with definition (B) contain fewer terms (i.e., operations) than the shifting expressions for the moments with definition (A) (compare Eqs (7) and (8) with Eqs (3) and (4), respectively). Again, Eqs (7) and (8) do not require child-parent distance computations. They are much cheaper to compute than the shifting expressions with definition (A). Again, the relative gain in efficiency increases with increasing order of moments used. The gain in efficiency in step (II), resulting from the use of definition (B) for the moments, will result in substantial speed-up. Overall then, adopting definition (B) for the moments (with expansion in Eq (5)) in CMM is more beneficial than using definition (A) (with expansion in Eq (1)).

ACKNOWLEDGMENTS

The author is supported by a fellowship administered by the Associated Western Universities-Northwest Division under grant DE-FG06-89ER-75522 with the U.S. Department of Energy (CAS). This work was done in part to support the Environmental and Molecular Sciences Laboratory (EMSL) project at Pacific Northwest Laboratory, a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Funding for this aspect of the work was provided by the EMSL Construction Project, Office of Health and Environmental Research, Office of Energy Research.

References

[1] Hong-Qiang Ding, Naoki Karasawa, and William A. Goddard III. *J.Chem.Phys.*, 97:4309, 1992.

[2] C.J.F. Böttcher. *Theory of Electric Polarization.* Elsevier, Amsterdam, second edition, 1973. Vol. 1, Chapter 1.

[3] W. K. H. Panofsky and M. Phillips. *Classical Electricity and Magnetism.* Addison-Wesley, Reading, Mass., second edition, 1962. Chapter 1.