Resolving a distribution of charge into intrinsic multipole moments: A rankwise distributed multipole analysis

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We present a method for the rankwise distributed multipole analysis of an arbitrary distribution of charge and its surrounding field. Using the superposition principle, the electrostatic field created by a distribution of charge can be resolved recursively into the contributions of a set of intrinsic multipole moments "tied to" their rank-specific multipole centers. The positions of the multipole centers, which are fixed with respect to the distribution of charge, are determined from a term-by-term optimization of the Taylor's expansion of the electrostatic potential with respect to the charge coordinates. We describe the recursive construction of the intrinsic multipole moments and derive the algebraic expression of the multipole centers. The resulting distributed multipole expansion provides a conceptual framework for the analysis and modeling of the electrostatic field and of its associated distribution of charge.

I. INTRODUCTION

Multipole expansions are a central conceptual and computational technique in the analysis of the electrostatic and, more generally, of any potential field in terms of the spatial distribution of its source. The importance of the method is due in part to the relationship that it establishes between the field "outside" the source and the macroscopic description of the source of field provided by its set of multipole moments. However, the method poses a number of limitations, from both a conceptual and a practical point of view. Here, we address some of these limitations.

The coefficients of the multipole expansion form the components of the multipole moments of the spatial distribution of charge. Except for the lowest-rank nonvanishing multipole, all other moments depend on the center of expansion. Therefore, the expansion is not uniquely defined, depending instead on the expansion center. There is no general guiding principle for choosing a "best" expansion center even though, in practice, it is common to use the center of charge, or the center of mass when the total charge is zero and the center of charge is not defined. In this paper we propose a multipole expansion that removes this ambiguity.

In principle, the center of expansion is not important in the sense that, when the whole multipole series is retained, the potential converges to the exact value, independent of the location of the center of expansion. Moreover, in many practical applications of the multipole expansions, the field is needed at large distances from the source of charge. In those cases, a good approximation can be obtained by truncating the multipole series to a relatively low number of terms, and the location of the center of expansion is not of much importance. In other applications, however, the assumption of a large distance from the observation point to the source is not warranted. In these latter cases, the truncation errors may be very sensitive to the location of the center of expansion, and an optimization of the center of expansion is desirable so that

the rate of convergence is maximized within the retained terms. Then, the reasonable question arises: how does the error in this approximation of the potential depend on the origin of expansion and, related to this, how can one minimize this error? In part, addressing this question led to the development of more specific methods for the use of the multipolar expansions in various physical [for example, the fast multipole method (FMM) [1]] and physical chemistry applications [for example, the distributed multipole analysis (DMA) [2,3]]. We also address this question with the analysis presented here. However, unlike previous methods that are specifically tailored for certain types of applications, the solution we propose is general, being based on intrinsic properties of the multipole moments alone.

This second aspect is especially important for the application of the multipole expansions to the development of coarse grain analytical models for the nonisotropic interaction between molecules [4,5]. This problem is of central importance for the modeling of complex systems, such as those in the biological sciences. While multipole-based models are already in common use for small molecules such as water [6,7], their use for larger molecules has been hindered mainly by the limited accuracy of truncated multipole expansions in reproducing essential features of the field in the immediate vicinity of a molecule [8,9]. The classical DMA method [2,3] can address some of these limitations. However, since it requires adjusting parameters, such as the centers of expansion, to the chemistry of each molecule, it is not easily generalizable. The alternative introduced here requires only the knowledge of multipole moments. Therefore, unlike DMA, which is designed for chemical systems, our method can be applied to any physical system for which a set of multipole moments is known.

Finally, while in most physical problems the relevance of the multipole moments relates to their role in the approximate calculation of the field, in other problems the multipole moments are also important as convenient descriptors of the spatial distribution of the source of the field itself. This is the case, for example, when multipole moments are used as shape descriptors in nuclear physics, or as discriminants in

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the analysis of the spatial anisotropy of the cosmic micro-wave background [10–12], or for the purpose of comparison of chemical structures with respect to various physicochemical properties [13,14]. In some of these applications, the ambiguity of their meaning due to the lack of an objective choice for the center of expansion may represent a significant limitation. The analysis we propose here may also serve in addressing this limitation.

The organization of the paper is as follows. In the next section, we define in more quantitative terms the problem that we seek to solve, and then propose a criterion of optimization of the center of multipole expansion. In Sec. III A we describe the recursive definition of the rankwise distributed multipole analysis (RWDMA) and in Sec. III B we derive the expression for the multipole centers of arbitrary orders. In Sec. IV we illustrate and discuss the performance of our RWDMA method on a physical system of practical importance. Section V concludes the paper.

II. OPTIMAL MULTIPOLE EXPANSION CENTERS

Consider, for simplicity, a discrete distribution of charges $\{e_i\}_{i=\overline{1,N}}$ located at positions $\{\vec{x}_i\}_{i=\overline{1,N}}$. In a standard derivation, the multipole expansion of the scalar potential outside a sphere enclosing the charges and centered at a given point $\vec{X}$ can be obtained by expanding the Coulomb potential of each charge in terms of its position with respect to the center $\vec{X}$, and then adding the resulting series term by term. In a final step, the traces of the terms of each order can be removed, without affecting the result, due to the Coulomb potential satisfying the Laplace equation. The result is an asymptotic series with respect to the relative position of the observation point, and, at the same time, a Taylor series expansion with respect to the set of N relative positions of the charge coordinates. In a compact form, the series can be written as

$$\Phi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \frac{r_{\alpha_1} r_{\alpha_2} \cdots r_{\alpha_l}}{r^{2l+1}} M^{(l)}_{\alpha_1\alpha_2\cdots\alpha_l}, \tag{1}$$

where $\vec{r}=\vec{x}-\vec{X}$ is the relative position of the observation point and r is the length of vector $\vec{r}$. The indices α_i denote the three Cartesian components of a vector. In this form, the power series character of the expansion is given by the coefficients $M^{(l)}_{\alpha_1\alpha_2\cdots\alpha_l}$ which are homogeneous polynomials of degree l in the charge coordinates relative to the center of expansion. They represent the components of the Cartesian multipole moments, which are totally symmetric and traceless tensors of rank l over the three-dimensional space, and are defined by [15]

$$M^{(l)} = \mathcal{T}_l \mu^{(l)}. \tag{2}$$

The tensor $\mu^{(l)}$ is the totally symmetric tensor of the "unabridged" [15] charge moments

$$\mu^{(l)}_{\alpha_1\alpha_2\cdots\alpha_l} = \frac{1}{l!} \sum_{i=1}^{N} e_i r_{i\alpha_1} r_{i\alpha_2} \cdots r_{i\alpha_l}, \tag{3}$$

and $\mathcal{T}_n$ is the detracer operator [15]

$$\mathcal{T}_n\mu^{(n)}_{\alpha_1\cdots\alpha_n} = \sum_{m=0}^{[n/2]} (-1)^m (2n-2m-1)!!$$
$$\times \sum_{\mathcal{P}(\alpha)} \delta_{\alpha_1\alpha_2} \cdots \delta_{\alpha_{2m-1}\alpha_{2m}} \mu^{(n)}_{\nu_1\nu_1\nu_2\nu_2\cdots\nu_m\nu_m\alpha_{2m+1}\cdots\alpha_n}. \tag{4}$$

The $[n/2]$ in the upper limit in Eq. (4) stands for the largest integer smaller than $n/2$, $(2k-1)!!=1\times3\times\cdots\times(2k-1)$, and $\mathcal{P}(\alpha)$ indicates the sum over all permutations of the symbols $\alpha_1\cdots\alpha_n$ [15]. Here, and throughout the rest of the paper, Einstein's summation convention over repeated indices is used to denote contractions with respect to Cartesian coordinates.

Typically, in a multipole expansion we are concerned with the dependence on the observation point relative to the expansion center. Since there is no objective *a priori* rule for choosing the expansion center, let us focus our attention instead on the dependence of the potential on the charge coordinates in Eq. (1) for a fixed, large relative position vector $\vec{r}$ of the observation point. As stated earlier, Eq. (1) converges as a power series in the three-dimensional position vectors of all charges in the system. As with all power series, the accuracy of a partial sum of the series depends on how far from the expansion point the charges are located: the "smaller" the separation, the better the accuracy. As a trivial case, for a single charge, one can choose the expansion point at the position of the charge and then the zero order term provides an exact value of the function. When the system has more than one charge, this cannot be achieved simultaneously for all coordinates, however, and improving the accuracy in this way becomes an optimization problem with respect to the position of the center of expansion. Moreover, in the single charge case, minimization of the linear term of expansion automatically insures the minimization of all higher orders. This is not necessarily true for an arbitrary number of charges.

In the case of a first-order expansion, the natural optimization criterion is the minimization of the magnitude of the charge-weighted average of relative positions of the particles, i.e., the magnitude of the dipole moment. We recognize here the condition that defines the center of charge, a common choice for the center of the potential expansion of a charged system.

The above linear case suggests a criterion for an arbitrary term of the expansion: the minimization of the "magnitude" of the corresponding multipole moment. The magnitude of a given Cartesian multipole moment is the total contraction of the moment with itself, as this is the only positive scalar that can be defined from its components. For the rank l in the expansion, we will therefore seek a center of expansion, $\vec{X}$, that satisfies the extreme condition

$$\nabla_{\vec{X}} \sum_{\alpha_1\cdots\alpha_l} |M^{(l)}_{\alpha_1\alpha_2\cdots\alpha_l}|^2 = 0. \tag{5}$$

We use the traceless rather than the unabridged moments because they are the natural coefficients in the potential expansion (1), and because they can be reduced to a minimum

number of independent parameters. The gradient in Eq. (5) is easily calculated by noticing first that the left side is equivalent with $\sum_{\alpha_2 \cdots \alpha_l} M^{(l)}_{\alpha_1 \alpha_2 \cdots \alpha_l} \nabla_{\vec{X}} \mu^{(l)}_{\alpha_1 \cdots \alpha_l}$ since the partial trace terms in (4) do not make any contribution under the summation sign (the first multipole factor is traceless). Then, the partial derivatives of the unabridged moments are proportional to moments of immediately lower rank. Finally, partial trace terms can be added back liberally to reconstruct a traceless multipole tensor in the second factor. Equation (5) becomes then

$$\sum_{\alpha_2 \cdots \alpha_l} M^{(l)}_{\alpha_1 \alpha_2 \cdots \alpha_l} M^{(l-1)}_{\alpha_2 \cdots \alpha_l} = 0, \quad \alpha_1 = 1, 2, 3. \quad (6)$$

Since a multipole moment of rank l is a polynomial of rank l in the expansion center, Eq. (6) is a polynomial system of three equations of degree $2l-1$. The real solution of minimum value for $\sum_{\alpha_1 \cdots \alpha_l} |M^{(l)}_{\alpha_1 \alpha_2 \cdots \alpha_l}|^2$ provides the best expansion point for the term of rank l.

Operating with the Cartesian form of high-rank multipoles is complex. In practice, it is often more convenient to use their spherical harmonics representation, which has the additional advantage of being nonredundant. The expansion of the electrostatic potential in this basis set is [16]

$$\Phi(\vec{r}) = \frac{1}{\epsilon_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{q_l^m}{r^{l+1}} Y_l^m(\hat{r}), \quad (7)$$

where the unit vector $\hat{r}$ is used as a short notation for the two spherical angles θ, ϕ that form the argument of the spherical harmonic functions Y_{lm}. The coefficients of the expansion are the multipole moments and are defined by

$$q_{lm} = \sum_{i=1}^{N} e_i r_i^l Y_l^{m*}(\hat{r}_i). \quad (8)$$

There is a one-to-one correspondence between a multipole set $\{q_l^m\}_{m=-l \cdots l}$ and its traceless Cartesian counterpart $M^{(l)}$. The $2l+1$ components $\{q_l^m\}_{m=-l \cdots l}$ of a multipole moment of rank l form an irreducible tensorial set [17,18]. The operation of contraction of the Cartesian multipoles is represented in this formalism by tensorial products. We will use the notation $[\mathbf{a}_l \times \mathbf{b}_m]_n$ to denote a product of two irreducible tensors $\mathbf{a}_l$ and $\mathbf{b}_m$ of ranks l and m resulting in a tensor of rank n [18]. The components of this latest tensor are given by

$$[\mathbf{a}_l \times \mathbf{b}_m]_n^k = \sum_{ij} C_{ijk}^{lmn} a_l^i b_m^j, \quad (9)$$

where $k = -n, \ldots, n$, and C_{ijk}^{lmn} are Clebsch-Gordan coefficients [18].

If we denote by $\mathbf{q}_l$ the whole set of components of a multipole of rank l, then its magnitude is $\|\mathbf{q}_l\| = ([\mathbf{q}_l \times \mathbf{q}_l]_0)^{1/2}$. The condition of minimum in Eq. (5) is then equivalent to the minimum of $\|\mathbf{q}_l\|^2$, and Eq. (6) becomes

$$[\mathbf{q}_l \times \mathbf{q}_{l-1}]_1 = 0. \quad (10)$$

Since a rank-1 tensor has three components, the above result provides three equations for the coordinates of the optimal expansion center.

III. DISTRIBUTED MULTIPOLE EXPANSION

A. Recursive derivation of the expansion and intrinsic multipole moments

Returning to the problem of optimizing the series expansion of the electrostatic potential, we note two challenges that arise. First, solving the minimization problem, in either form (6) or (10), may be difficult in practice due to the high order of the polynomial equation. Second, there is an ambiguity with respect to which rank to minimize, since, in typical usage, all terms up to the truncation order are retained for computational purposes. We show now that both inconveniences can be eliminated by a recursive use of the superposition principle.

The change of a multipole moment of a given rank under translation is given by a polynomial function in the translation vector, the coefficients of which are multipole moments of lower rank only. This is a textbook result [16] and can be immediately established from the Cartesian definition of the moments. In the particular case in which only the next lower-rank multipole is nonzero (in which case the multipole is also translation invariant), the polynomial becomes linear and Eqs. (6) and (10) reduce to linear systems of equations.

Let us assume now that, for our system, all multipoles of rank lower than a given order n vanish. Then, the multipole of rank n is translation invariant, and the multipole of rank $n+1$ varies linearly with the position of the expansion point. In other words, Eq. (10) becomes, as stated earlier, linear in the coordinates of the center of expansion. Optimizing the potential expansion by solving Eq. (10) with $l=n+1$ leads to a unique center of expansion where the correction to the term of rank n is minimal. Let us call this optimal expansion center $\vec{X}_n$ and denote by $\mathbf{Q}_n$ and $\{\mathbf{q}_l\}_{l=\overline{n+1,\infty}}$ the multipole moments at the (arbitrary) initial origin of the reference frame. As the origin is moved to the optimal expansion center, the multipole $\mathbf{Q}_n$ remains the same but multipoles starting at rank $n+1$ change into $\{\mathbf{q}_l'\}_{l=\overline{n+1,\infty}}$. The series expansion of the potential field with respect to the center $\vec{X}_n$ is

$$\Phi(\vec{r}) = \frac{1}{\epsilon_0} \frac{1}{2n+1} \sum_{m=-n}^{n} \frac{Q_n^m}{r_n^{n+1}} Y_n^m(\hat{r}_n) + R_{n+1}(\vec{r}), \quad (11)$$

where $\vec{r}_n = \vec{r} - \vec{X}_n$, and $R_{n+1}(\vec{r})$ is the series defined by translated multipole moments of order higher than n. Just as the center of charge in a charged system, the centers $\vec{X}_n$ are fixed with respect to the charge distribution, a property that can be seen as a result of space homogeneity.

Intuitively, Eq. (11) can be interpreted as follows. Let us imagine that we place a pair of elementary multipole moments at point $\vec{X}_n$, one identical to $\mathbf{Q}_n$, and the other of opposite strength. In principle, an elementary moment of rank n can be construed as a spherical shell with surface charge distributed according to an appropriate combination of spherical harmonic functions of order n [16], so that the only nonvanishing moments are those of rank n [10,19]. An opposite moment can be obtained by inverting the sign of the charge, for example. Then, the combination of the original distribution of charge and the two elementary multipole mo-

ments can be partitioned into two systems: (1) a multipole moment identical with $\mathbf{Q}_n$ and (2) the set of original charges plus the second elementary moment of strength opposite to that of $\mathbf{Q}_n$. The set of multipole moments for this latter system is indistinguishable from that of the original system of charges, except for the cancellation of the moment of rank n of the original system by the added elementary multipole.

The transformation described above is an extension of the common process of partitioning of a distribution of charge in a net point charge, located at the center of charge, and a residual neutral system. Similar to that case, according to the superposition principle the potential is the sum of the fields created by the two systems. With respect to point $\vec{X}_n$, the potential of the first elementary multipole (identical to $\mathbf{Q}_n$) is *exactly* represented by the first term in Eq. (11). The second system has a zero multipole of rank n and therefore its translated multipole moment of rank $n+1$, $\mathbf{Q}_{n+1} = \mathbf{q}'_{n+1}$, is translation invariant. It is also minimal as a result of the translation to the optimal expansion point of $\mathbf{Q}_n$. We can now recursively apply the same optimization procedure to this residual system: its series will start with a rank $n+1$ and will be centered as a point $\vec{X}_{n+1}$ which corresponds to the minimum magnitude of its multipole of rank $n+2$. Its multipole moments with respect to the new center will be obtained by the translation of the moments $\mathbf{q}'_l$.

The recursion process can be continued in principle indefinitely, and, at the end of the process, the expansion of the potential acquires a new form

$$\Phi(\vec{r}) = \frac{1}{\epsilon_0} \sum_{l=n}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{Q_l^m}{r_l^{l+1}} Y_l^m(\hat{r}_l). \qquad (12)$$

We name this the rankwise distributed multipole analysis. It can be seen that, in this type of analysis, a distribution of charge is more naturally described by pairs of the form $(\mathbf{Q}_l, \vec{X}_l)$ rather than just multipole moments alone. In other words, the minimal multipole moments $\mathbf{Q}_l$ are "tied" rather than "free" quantities, for the purpose of potential calculation. The associated center of multipole $\mathbf{Q}_l$ is rigidly tied to the distribution of charge and, therefore, is defined in a way independent of the location of a reference frame. This property is similar to the translation invariance of the net charge and, in general, to the translation invariance of the lowest-rank nonvanishing multipole moment. For this reason, we propose to name these moments the intrinsic multipole moments of the distribution of charge.

The vectors $\vec{X}_l$ defining the multipole centers are a generalization to higher-rank multipoles of the notion of center of charge. The concept was introduced before in a different context [13], as a way to define the origin of a body-tied reference frame, for the purpose of comparing two molecules with respect to their electrostatic field. For the comparison to be meaningful, the molecules must be placed in an equivalent position where the descriptors (in this case the multipole moments) are calculated. Naturally, for charged systems, the molecules are placed so that the center of charge represents the origin of the system of coordinates. However, for neutral molecules, the center of charge is not defined. As a substi-

tute, in [13] a dipole center is defined from a condition that is quantitatively equivalent to our criterion, i.e., the minimization of the quadrupole moment. The authors then propose the generalization to higher orders to allow for the comparison of molecules with vanishing multipoles of rank lower than any arbitrary given rank.

We presented above the recursive process of determining the intrinsic multipole moments from initial moments relative to an arbitrary origin. The opposite process is just a reversal of this: the relative position of consecutive centers can be used to translate the multipole moments, step by step, starting with their intrinsic value and transforming them toward their one-center form.

As an important remark, RWDMA only requires the knowledge of the multipole moments with respect to a given center. Of course, the determination of the single-center moments requires the knowledge of the charges and their coordinates, but, once they are determined, the RWDMA can be performed without any further use of that information; the underlying distribution of charge, and therefore the nature of the system, is no longer relevant. From a practical standpoint, if charges are given, the calculation of the multipole moments from charges and their positions is only required once, at the beginning of the analysis. For any subsequent step of the analysis, the moments can be calculated with standard methods for the multipole translation, which are well studied due to their special role in the FMM [1,20,21].

B. Derivation of the expansion centers

While the equation and an expression for the dipole center of a neutral system have been derived in [13], we are not aware of similar results for arbitrary multipole centers. We complete now our analysis by deriving expressions for the center of an arbitrary multipole.

Starting from Eq. (10) and the assumption that all multipoles of rank lower than $l-1$ vanish, we use Eq. (2.41) in Ref. [21] to describe the transformation of the multipole $\mathbf{q}_l$ under a translation of vector (x, y, z). Equation (10) can then be reduced to

$$a \bar{\xi}^{\alpha} + b[\bar{\xi} \times \mathbf{A}_2]_1^{\alpha} = [\mathbf{q}_l \times \mathbf{q}_{l-1}]_1^{\alpha}, \qquad (13)$$

where $\bar{\xi}^{\pm 1} = \mp (x \mp iy)/\sqrt{2}$, and $\bar{\xi}^0 = z$ are the conjugate irreducible components of the translation vector and the quantities a, b, and $\mathbf{A}_2$ are defined by

$$a = \frac{2l+1}{\sqrt{3}} \sqrt{\frac{l}{2l-1}} [\mathbf{q}_{l-1} \times \mathbf{q}_{l-1}]_0^0, \qquad (14)$$

$$b = [(2l-3)(l-1)(2l+1)/6(2l-1)]^{1/2}, \qquad (15)$$

$$\mathbf{A}_2 = [\mathbf{q}_{l-1} \times \mathbf{q}_{l-1}]_2. \qquad (16)$$

Since Eq. (13) form a linear system, the solution can be obtained from Cramer's rule, i.e., $\bar{\xi}^{\alpha} = \Delta_{\alpha}/\Delta$, where the two determinants are

TABLE I. RMSD (arbitrary units) between the potential field calculated by either the one-center multipole expansion about the center of charge (first row) or RWDMA (second row), and the exact field calculated from Coulomb's law. The grid is a $32 \times 36 \times 36$ rectangular mesh with an approximate spacing of 4 Å between points in each of the three spatial dimensions. Only grid points located outside the reunion of spheres centered at the multipole centers, and tightly enclosing all charges, were included in the calculation (20 482 out of a total of 41 472 grid points overall).

Method	Rank						
	1	2	3	4	5	6	7
Center of charge	4.001	1.903	1.234	0.584	0.331	0.230	0.172
RWDMA	4.001	1.415	1.195	0.508	0.324	0.240	0.171

$$\Delta_\alpha = \left(a^2 - \frac{b^2}{2\sqrt{5}} \|\mathbf{A}_2\|^2 \right) [\mathbf{q}_l \times \mathbf{q}_{l-1}]_1^\alpha - ab[\mathbf{A}_2 \times [\mathbf{q}_l \times \mathbf{q}_{l-1}]_1]_1^\alpha$$

$$+ \frac{b^2\sqrt{7}}{2\sqrt{5}} [[\mathbf{A}_2 \times \mathbf{A}_2]_2 \times [\mathbf{q}_l \times \mathbf{q}_{l-1}]_1]_1^\alpha, \tag{17}$$

$$\Delta = a^3 - \frac{3ab^2}{2\sqrt{5}} \|\mathbf{A}_2\|^2 + \frac{b^3\sqrt{7}}{10} [[\mathbf{A}_2 \times \mathbf{A}_2]_2 \times \mathbf{A}_2]_0^0. \tag{18}$$

Note that the vectors $\bar{\xi}^\alpha$ denote relative positions of consecutive centers. To apply this solution to RWDMA, we need to substitute for $\mathbf{q}_{l-1}$ the translation invariant moment of the recursion step (intrinsic multipole), and for $\mathbf{q}_l$ the value of the next-rank tensor. Then, the solution gives the relative position of the center of the multipole of rank $l-1$ with respect to the position at which $\mathbf{q}_l$ (nonintrinsic value) is given. Finally, the multipole centers $\vec{X}_l$ are obtained by recursively summing these relative positions.

Since the above solution for the multipole centers results from a linear system of equations, the multipole centers are, in general, uniquely defined. Exceptions occur when the determinant of the system (13), given by Eq. (18), vanishes. One obvious case is when the multipole moment $\mathbf{q}_{l-1}$ is zero. This is the case, for example, of the charge for a neutral system and of higher-order multipole moments of symmetrical molecules [22]. These cases admit a simple solution: the vanishing multipole moment is skipped and the recursion is resumed with the next rank multipole moment. There is also, at least in principle, the possibility that the determinant accidentally vanishes, even for a nonzero multipole moment, due to peculiarities of the tensor products involved in Eq. (18). Since the general analysis of this case is more complex due to the presence of these high-rank tensor products, we defer it for future work.

IV. ILLUSTRATION OF THE METHOD

The multipole expansion of RWDMA, Eq. (12), converges to the exact potential by virtue of its derivation, and therefore no further proof is needed. Regarding its accuracy, further studies are needed to establish general, rigorous estimations. With this in mind, here we only illustrate its convergence, relative to the regular expansion, on a simple example: the multipole expansion of the electrostatic field around a big biological molecule, a nucleosome protein core, Protein Data Bank ID 1kx3 [23].

The choice of the above molecule was motivated by our interest in the system and availability of the data but otherwise no particular test criteria were used. Table I shows the accuracy of RWDMA in comparison to the regular expansion about the center of charge. As a measure of the accuracy we use the *root mean square deviation* (RMSD) from the exact potential field given by Coulomb's law. The calculation was done on a rectangular grid with the characteristics as reported in the table. We only compared the fields at the grid points in the immediate vicinity of the molecule, but in the region of convergence (see caption), which represent the most challenging region for multipole expansions. As can be seen, there is no difference for truncation at the dipole order since both expansions start at the center of charge and the minimum dipole moment is null. However, the RWDMA converges faster at low truncation orders. For example the RMSD in the quadrupole order is about 26% smaller by comparison with the conventional expansion. The two methods produce indistinguishable results as they both approach the same, exact values, with further addition of higher order terms.

To further illustrate the convergence properties of our multipole expansion, in Fig. 1 we show a comparative view of an electrostatic potential isosurface as generated by the exact Coulomb calculation (a) as well as the RWDMA (b) and regular multipole expansion (c). Note that, unlike the data in Table I, the isosurface is not strictly speaking entirely "outside" the distribution of charge. Therefore, in regions of the isosurface located "inside" the molecule, the multipole expansion is not necessarily an accurate representation of the potential for two reasons: first, the solid spherical harmonic functions do not form a complete set for all points on the
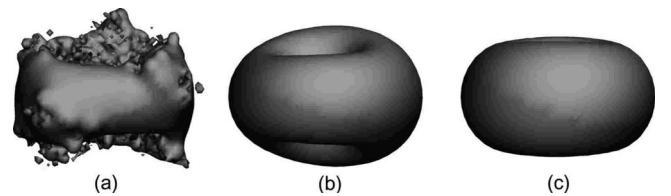

FIG. 1. The same isosurface of the electric potential calculated from the Coulomb law (a), RWDMA expansion (b), and regular multipole expansion with respect to the center of charge (c). The series are truncated in the quadrupole order in both (b) and (c).

surface and, second, the multipole coefficients themselves are not accurate, which makes the multipole expansion an asymptotic rather than a convergent series. We chose, however, such a surface so that we could capture nontrivial features that allow us to more easily discriminate between the practical capabilities of the classical and RWDMA methods. In both Figs. 1(b) and 1(c) the truncation of the series is in the quadrupole order. It is clear that RWDMA captures the "thinning" of the isosurface in the front region as displayed by the exact Coulomb calculation, while the regular expansion produces only a circularly symmetric shape. In order to capture the same feature, a classical multipole expansion would clearly need to go beyond the quadrupole level. The better convergence at lower truncation orders provide an advantage for both analytical modeling and numerical computation due to the simplicity of the energy terms and, also, to the better numerical stability in the computation of the spherical harmonics functions of lower orders.

The intrinsic multipole moments are also useful from a conceptual point of view, since they provide an *objective* description of the charge distribution, due to their independence from the choice of the system of coordinates. The minimization conditions Eqs. (6) and (10) impose an additional constraint which effectively reduces the number of parameters required to describe an *intrinsic* multipole to the minimum possible. For a quadrupole moment, for example, only one parameter is needed [13,24]. In an implicit way, these properties motivated the use of the *intrinsic* quadrupole moment as an essential methodological tool in a recent comparative analysis of the importance of quadrupole moment for correctly describing the water phase diagram in various analytical models [25].

V. CONCLUSION

In this paper we introduce a multipole description, the RWDMA, for the analysis of a distribution of charge and its surrounding field. In a concise description, the derivation of this form of multipole expansion can be seen as the result of combining two distinct steps, repeated recursively *ad infinitum* on the remainder of a regular Taylor's expansion:

(1) Selection of the optimal expansion center from the minimization of the magnitude of the second significant multipole moment.

(2) Partition of the remaining distribution of charge into a distribution modeled exactly by the first significant multipole moment, centered at the optimal center obtained in step 1, and a charge distribution described exclusively by multipole moments of higher order.

From a conceptual point of view, the RWDMA provides a consistent definition of intrinsic multipole moments of arbitrary orders, a concept that until now was only possible for the lowest nonvanishing multipoles of a distribution of charge.

From a computational standpoint, this method may provide an improved convergence of the potential field expansion, of importance for both analytical and numerical modeling. As an important remark in this context, unlike other improved schemes for multipole representation of the electrostatic field [2,3], RWDMA does not require any prior knowledge about the nature of the physical system. In fact, the only imput required is the set of multipole moments with respect to an arbitrary origin.

Note that the analysis we describe is also generalizable from a mathematical standpoint, since it relies on properties of multivariate Taylor's expansions and on the linearity of the Poisson equation satisfied by the electrostatic potential, which is the basis of the superposition principle. As such, the analysis can be expanded to a wider range of problems described by a similar mathematical framework. In particular, the results can be extended to other potential fields, for example, the gravitational field.

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