Recurrence Relations for Calculation of the Cartesian Multipole Tensor

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We demonstrate that the Cartesian multipole interaction tensor may be evaluated with recurrence relations analogous to the McMurchie-Davidson algorithm for calculation of electron repulsion integrals. With these recursion relations all elements of the Cartesian multipole tensor through order $\mathcal{L}$ may be calculated in $\mathcal{O}(\mathcal{L}^4)$ cpu time, in contrast to current methods that scale as $\mathcal{O}(\mathcal{L}^6)$.

I. INTRODUCTION

In large molecular systems, the dominant component of the two-electron energy is due to (classical) electrostatic interaction. When penetration between the two electron densities ρ_A and ρ_B is negligible, the electrostatic energy of their interaction

$$E_{\text{el.}}^{AB} = \int d\mathbf{r} \int d\mathbf{r}' \rho_A(\mathbf{r}) \left|\mathbf{r}-\mathbf{r}'\right|^{-1} \rho_B(\mathbf{r}') \tag{1}$$

may be approximated accurately by developing $|\mathbf{r}-\mathbf{r}'|^{-1}$ in a multipole (series) expansion. In many areas of computational chemistry, such as molecular mechanics, only the first order (monopole-monopole) term in a multipole expansion is retained. However, in a variety of other fields, such as quantum chemistry and potential theory, high order multipole approximations are often required to obtain sufficient accuracy. In quantum chemistry, the effectiveness of multipole approximations for accelerating assembly of the Coulomb matrix has been demonstrated [1–6]. In potential theory, a variety of fast hierarchical methods have recently been developed [4,5,7–17]. These fast methods are capable of computing the electrostatic interaction between N point charges of arbitrary distribution in at best $\mathcal{O}(N \log^2 N)$ cpu time [11].

The basic mathematical apparatus for evaluating multipole expansions has been well established for some time, involving the development of $|\mathbf{r}-\mathbf{r}'|^{-1}$ in either spherical harmonics [18,19] or a Taylor series in Cartesian coordinates [20]. Each representation offers different advantages, and the choice of representation is often application dependent. For example, while the calculation of molecular electrostatics using the spherical tensor formalism has a long tradition in chemical physics [18,19], the use of Cartesian Gaussian-type basis functions by modern quantum chemical programs makes the use of Cartesian multipoles preferable in many cases. Fast methods based on Cartesian multipole expansions [10–17], and others based on spherical tensor theory [4,5,7–9] have been found especially effective in the solution of chemical and astrophysical N-body problems. Although the field is not yet mature, it appears that fast methods employing Cartesian multipoles achieve breakeven much sooner than those based on the spherical tensor formalism [10,14].

For a given rank ℓ, Cartesian multipoles involve $\binom{\ell+2}{2}$ independent elements, while spherical multipoles involve only $2\ell+1$ elements. On the other hand, Cartesian multipoles and the Cartesian multipole tensor are typically more convenient to compute. The computation of arbitrary order multipole interaction tensors in a spherical representation requires looping over ranks, which limits the maximum vector length achievable to $\mathcal{O}(\mathcal{L})$, where $\mathcal{L}$ is the order (maximum rank) of the multipole expansion. While current methods for computing elements of the Cartesian multipole tensor [21,22] of arbitrarily high order do allow significant vector lengths for large $\mathcal{L}$ [22], their computational cost scales rapidly as $\mathcal{O}(\mathcal{L}^6)$.

In this letter, we present a new method for evaluating all elements of the Cartesian multipole tensor through order $\mathcal{L}$ in $\mathcal{O}(\mathcal{L}^4)$ cpu time using recurrence relations that derive from the McMurchie-Davidson (MD) 3-term recurrence relations [23–25]. A particularly attractive feature of our approach is that a large fraction of the Cartesian multipole tensor elements may be evaluated in vector loops of length $\mathcal{O}(\mathcal{L}^3)$.

II. THE CARTESIAN MULTIPOLE EXPANSION

If the separation between the densities ρ_A and ρ_B is large and/or their decay is rapid, then $|\mathbf{r}-\mathbf{r}'|^{-1}$ in Eq. (1) may be expanded in a Taylor series about both point $\mathbf{A}$ and point $\mathbf{B}$, leading to

$$E_{\text{el.}}^{AB} = \sum_{LMN} \sum_{L'M'N'} (-1)^{L'+M'+N'} Q_{LMN}^{A} T_{L+L',M+M',N+N'}(\mathbf{AB})\, Q_{L'M'N'}^{B} \ , \tag{2}$$

where $\mathbf{AB} \equiv \mathbf{A} - \mathbf{B}$ and

$$Q_{LMN}^{A} = \frac{1}{L!M!N!} \int d\mathbf{r}\, x^L y^M z^N \rho_A\left(\mathbf{r}\right) \tag{3}$$

is an unmodified Cartesian multipole moment of rank $\ell_a = L + M + N$. In Eq. (2), and in the following, we assume that the multipole expansion is truncated at order $\mathcal{L} = \mathcal{L}_a + \mathcal{L}_b$, where $\mathcal{L}_a$ is the order of the series expansion about center $\mathbf{A}$, and $\mathcal{L}_b$ is the order of the series expansion about center $\mathbf{B}$.

Alternatively, Eq. (2) can be re-summed and expressed in terms of Buckingham's traceless multipole moments [20]

$$M_{LMN}^{A} = (-1)^{\ell_a} \frac{1}{\ell_a!} \int d\mathbf{r}\, \rho_A\left(\mathbf{r}\right)\ |\mathbf{r}|^{2\ell_a+1} \frac{\partial^{\ell_a}}{\partial x^L \partial y^M \partial z^N} \frac{1}{|\mathbf{r}|} \qquad \left(\ell_a = L + M + N\right) \ , \tag{4}$$

which may be used in Eq. (2) by replacing Q_{LMN}^{A} with $2^{\ell_a}\ell_a! M_{LMN}^{A} / \left(2\ell_a\right)!$. In either case, elements of the Cartesian multipole tensor are

$$T_{lmn}\left(\mathbf{AB}\right) = \frac{\partial^{\ell}}{\partial AB_x^l\ \partial AB_y^m\ \partial AB_z^n} \frac{1}{|\mathbf{AB}|} \qquad \left(\ell = l + m + n\right), \tag{5}$$

where AB_x, AB_y and AB_z are the Cartesian components of $\mathbf{AB}$.

In 1982, Cipriani and Silvi [21] deduced the expression

$$\begin{aligned} T_{lmn}\left(\mathbf{AB}\right) = \frac{(-1)^{\ell} l!m!n!}{2^{\ell} |\mathbf{AB}|^{\ell+1}} \sum_{s=0}^{[l/2]} \sum_{t=0}^{[m/2]} \sum_{u=0}^{[n/2]} \Bigg[& \\ & \frac{(-1)^{s+t+u}\left(2\ell - 2s - 2t - 2u\right)!}{s!t!u!(l-2s)!(m-2t)!(n-2u)!(\ell-s-t-u)!} \\ & \times \left(\frac{AB_x}{|\mathbf{AB}|}\right)^{l-2s} \left(\frac{AB_y}{|\mathbf{AB}|}\right)^{m-2t} \left(\frac{AB_z}{|\mathbf{AB}|}\right)^{n-2u} \Bigg] , \end{aligned} \tag{6}$$

which is currently the basis for computing Cartesian multipole interactions through arbitrary order [22].

III. RECURSION RELATIONS FOR THE CARTESIAN MULTIPOLE TENSOR

Electrostatic interaction energies between electron densities, as in Eq. (1), are typically evaluated from electron repulsion integrals (ERIs) between products of basis functions (distributions). Quantum chemical methods for the calculation of ERIs between Cartesian Gaussian-type distributions have been well developed in the last two decades. One of the first efficient methods was developed by McMurchie and Davidson (MD) [23–25]. The MD algorithm employs Hermite Gaussian-type functions (HGTFs) as intermediates in the calculation of Cartesian Gaussian-based ERIs. The HGTFs are

$$\begin{aligned} \Lambda_{LMN}^{a}(\mathbf{r}) &= \frac{\partial^L}{\partial A_x^L} \frac{\partial^M}{\partial A_y^M} \frac{\partial^N}{\partial A_z^N} \exp\left[-\zeta_a (\mathbf{r}-\mathbf{A})^2\right] \\ &= \zeta_a^{(L+M+N)/2} H_L\left[\zeta_a^{1/2}(x - A_x)\right] H_M\left[\zeta_a^{1/2}(y - A_y)\right] \\ &\qquad \times H_N\left[\zeta_a^{1/2}(z - A_z)\right] \exp\left[-\zeta_a (\mathbf{r}-\mathbf{A})^2\right] \ , \end{aligned} \tag{7}$$

where H_L is the L^{th} order Hermite polynomial

$$H_L(x) = \sum_{s=0}^{[L/2]} \frac{(-1)^s L!}{s!(L-2s)!}(2x)^{L-2s} \ . \tag{8}$$

The Hermite polynomials satisfy the recursion relation

$$H_L(x) = 2xH_{L-1}(x) - 2(L-1)H_{L-2}(x) \ , \tag{9}$$

which forms the basis of the MD algorithm.

The HGTF-based ERIs,

$$\begin{aligned}\left(\Lambda^a_{LMN}\middle|\Lambda^b_{L'M'N'}\right) &= \int d\mathbf{r} \int d\mathbf{r}' \Lambda^p_{LMN}(\mathbf{r}) \left|\mathbf{r}-\mathbf{r}'\right|^{-1} \Lambda^q_{L'M'N'}(\mathbf{r}') \\ &= (-1)^{L'+M'+N'} \left(\frac{2\pi^{5/2}}{\zeta_a\zeta_b\sqrt{\zeta_a+\zeta_b}}\right) R_{L+L',M+M',N+N',0}(t) \ ,\end{aligned} \tag{10}$$

may be obtained from a smaller set of auxiliary integrals R_{lmn0}, where

$$R_{lmn0}(t) = \frac{\partial^l}{\partial AB_x^l} \frac{\partial^m}{\partial AB_y^m} \frac{\partial^n}{\partial AB_z^n} F_0(t) \ , \tag{11}$$

and $F_0(t)$ is the 0^{th} order reduced incomplete gamma function [26]

$$F_0(t) = \sqrt{\frac{\pi}{4t}} \operatorname{erf}\left(\sqrt{t}\right) = \int_0^1 e^{-tu^2} du \ , \tag{12}$$

with argument

$$t = \omega \left|\mathbf{AB}\right|^2 \ , \tag{13}$$

and

$$\omega = \frac{\zeta_a\zeta_b}{\zeta_a+\zeta_b} \ . \tag{14}$$

Differentiation of $F_0(t)$ leads to higher order reduced incomplete gamma functions $F_{j+1}(t) = -F_j'(t)$, which we refer to hereafter simply as "gamma" functions. For a class of HGTF-based ERIs the MD algorithm efficiently calculates all $\binom{\mathcal{L}+3}{3}$ auxiliary functions R_{lmn0} with $l+m+n \le \mathcal{L}$ from an initial set,

$$R_{000j}(t) = (-2\omega)^j F_j(t) \qquad (j = 0, 1, \ldots, \mathcal{L}), \tag{15}$$

using three-term recursion relations that derive from Eq. (9) [23–25].

In the multipole limit, HGTFs are related to derivatives of the Dirac delta function by

$$\delta^a_{LMN}(\mathbf{r}) = \frac{\partial^L}{\partial A_x^L} \frac{\partial^M}{\partial A_y^M} \frac{\partial^N}{\partial A_z^N} \delta(\mathbf{r}-\mathbf{A}) = \lim_{\zeta_a \to \infty} \left(\frac{\zeta_a}{\pi}\right)^{3/2} \Lambda^a_{LMN}(\mathbf{r}) \ . \tag{16}$$

The Dirac delta function obeys the identity [27]

$$\int d\mathbf{r} f(\mathbf{r}) \, \delta^a_{LMN}(\mathbf{r}) = (-1)^{L+M+N} \frac{\partial^L}{\partial A_x^L} \frac{\partial^M}{\partial A_y^M} \frac{\partial^N}{\partial A_z^N} f(\mathbf{A}) \ . \tag{17}$$

The following equation relating HGTF-based ERIs in the multipole limit to elements of the Cartesian multipole tensor can readily be obtained from Eq. (10) with Eqs. (16) and (17):

$$\left(\Lambda^a_{LMN}\middle|\Lambda^b_{L'M'N'}\right) = (-1)^{L'+M'+N'} \left(\frac{\pi}{\zeta_a}\right)^{3/2} T_{L+L',M+M',N+N'}(\mathbf{AB}) \left(\frac{\pi}{\zeta_b}\right)^{3/2} \ . \tag{18}$$

This expression identifies elements of the Cartesian multipole tensor within the MD 3-term recursion relations; in particular, by inspection of Eqs. (10), (15) and (18) the correspondence

$$T_{000j} \Longleftrightarrow \frac{(\zeta_a\zeta_b)^{3/2}}{\pi^3}\left(\frac{2\pi^{5/2}}{\zeta_a\zeta_b\sqrt{\zeta_a+\zeta_b}}\right) R_{000j} \tag{19}$$

is established. Substituting the multipole limit of the gamma functions,

$$F_j\left(t\right) = \int_0^\infty u^{2m} e^{-tu^2} du = \frac{\pi^{1/2}(2j-1)!!}{2^{(j+1)}t^{(j+1/2)}} \qquad (t \to \infty) \ , \tag{20}$$

into Eq. (19), we find that, from an initial set of auxiliary tensor elements

$$T_{000j}\left(\mathbf{AB}\right) = (-1)^j (2j-1)!! \left|\mathbf{AB}\right|^{-(2j+1)} \qquad (j = 0, 1, \ldots, \mathcal{L}) \ , \tag{21}$$

all $\binom{\mathcal{L}+3}{3}$ elements of the Cartesian multipole tensor T_{lmn0} with $l+m+n \leq \mathcal{L}$ may be calculated with the 3-term recursion relations

$$T_{l,0,0,j} = AB_x T_{l-1,0,0,j+1} + (l-1) T_{l-2,0,0,j+1} \ , \tag{22}$$

$$T_{l,m,0,j} = AB_y T_{l,m-1,0,j+1} + (m-1) T_{l,m-2,0,j+1} \ , \tag{23}$$

$$T_{l,m,n,j} = AB_z T_{l,m,n-1,j+1} + (n-1) T_{l,m,n-2,j+1} \ . \tag{24}$$

The appropriate control structures for implementation of Eqs. (22-24) are outlined in Ref. [23].

Hermite functions are also intermediates in the Van der Velde algorithm [25] for the calculation of Cartesian Gaussian-based ERIs. The Van der Velde algorithm is based on the explicit formula for Hermite polynomials, given in Eq. (8), rather than the recursion relation given in Eq. (9). It is interesting to note a correspondence, in the multipole limit, between the Van der Velde algorithm and the Cipriani and Silvi formulae, Eq. (6).

IV. CONCLUSION

Three term recursion relations may be used to compute elements of the Cartesian multipole tensor. This new approach has the following advantages:

- Evaluation of all Cartesian multipole tensor elements through order $\mathcal{L}$ scales as $\mathcal{O}(\mathcal{L}^4)$, as compared to $\mathcal{O}(\mathcal{L}^6)$ with the Cipriani and Silvi equation.
- Storage of intermediate values is not required.
- The dominant portion of the work, involving Eq. (24), may be performed in vector loops of *average* length $\frac{1}{4}\binom{\mathcal{L}+3}{3}$, resulting in enhanced performance on vector computers and RISC-based platforms alike [28].
- The multipole expansion, Eq. (2), may be evaluated with either vector loops of length $\binom{\mathcal{L}_a+3}{3}$ or $\binom{\mathcal{L}_b+3}{3}$, requiring only a small fraction of the time spent evaluating Eqs. (22-24) [28].

Recently, hybrid methods involving compression matrices [29] or coupling tensors [30] have been developed that link Cartesian multipoles and the Cartesian multipole tensor in a reduced representation of the multipole expansion. Cartesian multipoles of rank ℓ involve $\binom{\ell+2}{2}$ independent elements, in contrast to a reduced (*e.g.* spherical) representation that involves only $2\ell+1$ elements. The relative merits of the Cartesian, reduced-Cartesian, and spherical multipole expansions are clearly application dependent; applications that require the repeated use of the same multipole interaction tensors will favor a reduced representation. If however, the storage of interaction tensors is memory intensive, or if the interaction tensors are needed only once, then a conventional Cartesian multipole expansion based on the recursion relations put forward here may be advantageous. As calculation of the Cartesian multipole tensor is central to the reduced-Cartesian methods [29,30], we expect that our approach will also favor the use of Cartesian multipoles when a reduced representation is appropriate.

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