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Note

Efficient Construction of Directional Derivatives of a Function of a Vector Magnitude and Maxwell's Invariant Multipole Form*

1. Introduction

Directional derivatives of functions of a vector magnitude are required, for example, by multipole calculations in the invariant form developed by Maxwell [1]. Recently, an algorithm has been developed to obtain the required n characteristic directions for a general spherical harmonic of order n [2]. One of the advantages of the latter form is that the same algorithm required for the calculation of permanent multipole energies can be coupled with an additional simple step to calculate induced dipole moments and energies [3]. Furthermore, the published work can be extended to higher-order moments in terms of the elements of their polarizability tensors. The purpose of this paper is to present: (a) alternative recursive constructions (Section 2) to previously published procedures [4], and (b) an analysis of the efficiency of various procedures for different types of problems (Section 3).

2. Equations for New Recursions

Let $f(R)$ be any function of

$$R = |\,\mathbf{R}\,|, \qquad \mathbf{R} = \langle x_1, x_2, x_3\rangle. \tag{1}$$

In a paper on lattice sums [4a] it is shown that for any n for which $f(R)$ is differentiable, the nth directional derivative defined by

$$\{\mathbf{S}_k : \mathbf{S}_k = \langle S_k^1, S_k^2, S_k^3\rangle \text{ a unit vector, } 1 \leqslant k \leqslant n\} \tag{2a}$$

is given by

$$\prod_{j=1}^{n} (\mathbf{S}_j \cdot \nabla) f(R) = \sum_{j=q}^{n} a_j^n(\{\mathbf{S}_k\}, \mathbf{R})\, F_j[f(R)]; \tag{2b}$$

$$q = \{\text{if } n \text{ is even, } (n/2); \text{ if n is odd, } [(n+1)/2]\}; \tag{2c}$$

$$F_1[f(R)] \equiv R^{-1}\, df(R)/dR; \quad j \geqslant 2: \qquad F_j[f(R)] = R^{-1}\, dF_{j-1}[f(R)]/dR. \tag{2d}$$

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Each a_j^n is given as a sum of products over a set of partitions, $\{D_j^n\}$:

$$a_j^n(\{\mathbf{S}_k\}, \mathbf{R}) = \sum_{\{D_j^n\}} P(D_j^n, \{\mathbf{S}_k\}, \mathbf{R}); \tag{2e}$$

$$D_j^n\text{: a partition of } \eta(n) \equiv \{1,..., n\} \text{ into } (n - j + 1) \text{ sets, } C_g(D_j^n); \tag{2f}$$

$$\begin{aligned} &j < n,\ 1 \leqslant g \leqslant n - j\text{: } C_g(D_j^n) \text{ contains two elements, } \{\alpha_1(C_g), \alpha_2(C_g)\}, \\ &\text{no account is taken of the order of these first } (n - j) \text{ subsets;} \end{aligned} \tag{2g.1}$$

$$j < n, \qquad g = n - j + 1: \qquad C_g(D_j^n) = \eta(n) - \bigcup_{k=1}^{n-j} C_k(D_j^n). \tag{2g.2}$$

$$j = n: \qquad C_1(D_n^n) = \eta(n); \tag{2g.3}$$

The products for each such partition are:

$$j = n/2: \qquad P(D_{n/2}^n, \{\mathbf{S}_k\}, \mathbf{R}) = \prod_{g=1}^{n/2} (\mathbf{S}_{\alpha_1(C_g)} \cdot \mathbf{S}_{\alpha_2(C_g)}); \tag{2h.1}$$

$$j \neq n, \quad j \neq n/2: \qquad P(D_j^n, \{\mathbf{S}_k\}, \mathbf{R}) = \left\{\prod_{g=1}^{n-j} (\mathbf{S}_{\alpha_1(C_g)} \cdot \mathbf{S}_{\alpha_2(C_g)})\right\} \prod_{k \in C_{n-j+1}} (\mathbf{S}_k \cdot \mathbf{R}); \tag{2h.2}$$

$$j = n: \qquad P(D_n^n, \{\mathbf{S}_k\}, \mathbf{R}) = \prod_{k=1}^{n} (\mathbf{S}_k \cdot \mathbf{R}). \tag{2h.3}$$

The above formulas are illustrated for both cases n even and odd in Appendix A.

It follows from Eqs. (2e–h) that each $a_j^n(\{\mathbf{S}_k\}, \mathbf{R})$ is a homogeneous polynomial in the X_i of degree $(2j - n)$:

$$a_j^n(\{\mathbf{S}_k\}, \mathbf{R}) = \sum_{H(j,n)} b(j, \mathbf{h}, \mathscr{S}_n) \prod_{i=1}^{3} X_i^{h_i}; \tag{3a}$$

$$H(j, n) \equiv \{\mathbf{h}\text{: } h_i \text{ is a nonnegative integer, } h_1 + h_2 + h_3 = (2j - n)\}; \tag{3b}$$

$$\mathscr{S}_n \equiv \{\mathbf{S}_1,..., \mathbf{S}_n\}. \tag{3c}$$

Consider the recursive construction of the a_j^n. For $n > 1$, substitution of Eq. (3) into Eq. (2b) and the use of Eq. (2d) defining the F_j gives:

$$\begin{aligned} (\mathbf{S}_n \cdot \nabla) \left\{\prod_{k=1}^{n-1} (\mathbf{S}_k \cdot \nabla) f(R)\right\} &= \sum_{m=1}^{3} \sum_{H(j,n-1)} S_n{}^m b(j, \mathbf{h}, \mathscr{S}_{n-1}) \\ &\times \left\{\prod_{i=1}^{3} \{[1 + \delta_{im}(h_i - 1)]\, X_i^{h_i - \delta_{im}}\}\, F_j[f(R)] + \prod_{i=1}^{3} X_i^{h_i + \delta_{im}} F_{j+1}[f(R)]\right\}. \end{aligned} \tag{4}$$

$$\begin{aligned} &\text{Let } A = [b(j, \mathbf{h}, \mathscr{S}_n)] \equiv \text{an accumulator for the calculation of} \\ &\qquad b(j, \mathbf{h}, \mathscr{S}_n), \qquad \text{in the recursive construction.} \end{aligned} \tag{5}$$

Equation (4) yields the following recursion. $n = j = 1$: $H(1, 1)$ = a set of the three basis vectors,

$$\mathbf{e}_m = \langle \delta_m{}^1, \delta_m{}^2, \delta_m{}^3 \rangle, \qquad (m = 1, 2, 3). \tag{6a.1}$$

Moreover, the set $\mathscr{S}_1$ has just one element, $\mathbf{S}_1$. Therefore,

$$b(1, \mathbf{e}_m, \mathscr{S}_1) = S_1{}^m, \qquad (m = 1, 2, 3). \tag{6a.2}$$

For $n > 1$, each $b(j, \mathbf{h}, \mathscr{S}_{n-1})$ yields the following six additions to the accumulators for the nth level, $A[b(j, \mathbf{h}, \mathscr{S}_{n-1})]$:

$$A[b(j, \mathbf{h} - \mathbf{e}_m, \mathscr{S}_n)] + h_m S_n{}^m b(j, \mathbf{h}, \mathscr{S}_{n-1}), \qquad (m = 1, 2, 3); \tag{6b.1}$$

$$A[b(j + 1, \mathbf{h} + \mathbf{e}_m, \mathscr{S}_n)] + S_n{}^m b(j, \mathbf{h}, \mathscr{S}_{n-1}), \qquad (m = 1, 2, 3). \tag{6b.2}$$

For the special case $F(R) = R^{-1}$, which occurs, for example, in the multipole expansion for the interaction energy of two charge distributions, an alternative recursion can be derived using the fact that by Eq. (2d)

$$F_{j+1}(R^{-1}) = -(2j + 1)\, R^{-2} F_j(R^{-1}) \tag{7}$$

It follows from Eqs. (2b), (3), and (7) that

$$\prod_{j=1}^{n-1} (\mathbf{S}_j \cdot \nabla)\, R^{-1} = R^{-(2n-1)} \sum_{N(n-1)} d(\boldsymbol{\nu}, \mathscr{S}_{n-1}) \prod_{i=1}^{3} x_i^{\nu_i}; \tag{8a}$$

$$N(n-1) = \{\boldsymbol{\nu}: \nu_i \text{ is a nonnegative integer and } \nu_1 + \nu_2 + \nu_3 = n - 1,\ n \geqslant 2\}. \tag{8b}$$

As in Eq. (5), let A denote an accumulator. Application of $(\mathbf{S}_n \cdot \nabla)$ to Eq. (8.a) yields the following recursion:

$n = 1$: $N(1)$ = a set of the three basis vectors, $\mathbf{e}_m = \langle \delta_m{}^1, \delta_m{}^2, \delta_m{}^3 \rangle$,

$$(m = 1, 2, 3); \tag{9a.1}$$

$$\mathscr{S}_1 = \{\mathbf{S}_1\}; \qquad d(\mathbf{e}_m, \mathscr{S}_1) = S_1{}^m, \qquad (m = 1, 2, 3). \tag{9a.2}$$

For $n > 1$ each $d(\boldsymbol{\nu}, \mathscr{S}_{n-1})$ yields the following 12 additions to the accumulators for the $d(\boldsymbol{\nu}, \mathscr{S}_n)$:

$$1 \leqslant k \leqslant 3: \qquad A[d(\boldsymbol{\nu} + \mathbf{e}_k, \mathscr{S}_n)] - (2n - 1)\, S_n{}^k d(\boldsymbol{\nu}, \mathscr{S}_{n-1}); \tag{9b.1}$$

$$1 \leqslant k \leqslant 3, \quad 1 \leqslant m \leqslant 3: \qquad A[d(\boldsymbol{\nu} + 2\mathbf{e}_k - \mathbf{e}_m, \mathscr{S}_n)] + \nu_m S_n{}^m d(\boldsymbol{\nu}, \mathscr{S}_{n-1}). \tag{9b.2}$$

3. Analysis of the Efficiency of Procedures for Different Problems

Practical problems can require the calculation of higher-order directional derivatives. Consider, e.g., the electrostatic contribution to the intermolecular potential. Theoretically, the potential defined by a charge distribution possesses a multipole expansion about any center, c, which converges outside any sphere centered at c containing all of the charge in the distribution. Pack, Wang, and Rein [6a] have examined the practical question: When does a truncated series give an adequate representation of the potential? For the case of pyridine, they used both multicenter expansions, splitting the total distribution into distributions assigned to the nuclear centers and a single center expansion for the total molecular density. Their results were compared with a direct evaluation of the Coulomb integral

$$V(\mathbf{R}) \sim \int \frac{\psi(\mathbf{r})\,\psi^*(\mathbf{r})}{|\,\mathbf{R}-\mathbf{r}\,|}\,d\mathbf{r},$$

for an approximate wave function ψ. Their results showed that an expansion including terms of order $\leqslant 3$: (a) is, of course, useless for a point 1 Å from the N nucleus (in a region that contains significant charge density); (b) the discrepancy between the exact integral and the multipole expansion has already decreased to ca. 10% for (i) the distance of the van der Waal's radius, $\sim$1.5 Å from N, in the case of the multicenter expansion; (ii) about 3.6 Å from N, in the case of the single center expansion. Clearly, at such distances that are involved in intermolecular interactions, it is more economical to use the a priori charge densities from large basis set calculations to compute moments and then evaluate the multipole series instead of evaluating integrals of the form $\int \{\rho_i\rho_j/\|\,\mathbf{r}_i - \mathbf{r}_j\,\|\}\,d\mathbf{r}_i\,d\mathbf{r}_j$ for the Coulomb interaction between distributions i and j for each of an extended series of orientations and positions. However, Mulliken [5] has emphasized, "it is definitely *not* adequate to compute dipole–dipole or quadrupole–dipole interactions assuming plausibly located point dipoles with moments equal to observed over-all moments." Mulliken's thesis is quantitatively supported by the aformentioned work [6], which showed that the terms of order 3 make a very significant contribution to the potential at distances corresponding to those for intermolecular interaction [6]. This corresponds to terms of order 6 in the energy. In the practically important case of H bonding, the shorter distance $0 \cdots H \sim 1.8$ Å in ice coupled with the comparatively small energies of transition between different ice forms, makes it desirable to include terms of order 10 in calculations on molecular orientations and positions [7a]. Whereas basis sets do not employ functions of high enough harmonic types to give accurate higher-order moments for actual molecules, answers to structural questions can be much more sensitive to inconsistent treatment of a given model (viz. premature truncation of a multipole series), than to "reasonable" variations in the model [7b].

The feasibility of using terms of the order required to obtain the desired consistency depends crucially on the efficiency of the algorithm for their evaluation. For this reason, algebraic formulas have been derived for the operation count for constructing a representative Nth-order derivative as functions of the order N, N even, for what we believe to be efficient algorithms for four different procedures. These counts were verified by computer results for one set of comparisons. Details are available on request, and only the conclusions will be summarized here.

The procedures will be denoted as follows: I, an algorithm based on Eq. (2); II, an algorithm based on Eq. (39) of [3] as modified in Appendix B to remove the assumed application to a particular procedure for crystals; III, an algorithm based on the recursion of Eq. (6); IV, for $f(R) = 1/R$, an algorithm based on the recursion of Eq. (9).

A. Table I shows that from the standpoint of total operation count, Procedure I is the most efficient for $N \leqslant 4$. Whereas the previous paper assumed that I was in general more efficient than II from this standpoint, II is clearly the best of all for $10 \geqslant N \geqslant 6$ and I becomes rapidly impossible. The facts that

TABLE I[a]

N	(II/I)	(III/I)	(IV/I)	(III/II)	(IV/II)
4	2.2(0)	2.5(0)	3.1(0)	1.1(0)	1.4(0)
6	4.8(−1)	6.8(−1)	7.5(−1)	1.4(0)	1.6(0)
8	8.6(−2)	1.3(−1)	1.5(−1)	1.6(0)	1.7(0)
10	1.1(−2)	1.8(−2)	1.6(−1)	1.7(0)	1.4(0)

[a] The entries in the column headed by the Roman numeral ratio (α/β) give the ratio of the total number of operations for procedure α to the total number for procedure β respectively. The figure in parenthesis gives the power of 10. Thus $4.8(-1) = 4.8 \times 10^{-1}$.

asymptotically the number of operations in Method I increases more rapidly than $(N/2)!$, while those of Methods II, III, and IV increase as N^5, N^4, and N^3, respectively, show: (a) even $N = 10$ is far from the asymptotic range for Methods II, III, and IV; (b) the use of the asymptotic estimates without check of the approach to the limit would have led to false conclusions.

B. The choice can be determined from A only if the calculation is to be repeated for approximately the same number of sets of positions ($\mathbf{R}$) as of orientations ($\{\mathbf{S}_k\}$). Whenever these numbers differ greatly, then Procedures II, III, IV have the advantage of decomposing the calculation into a part that depends only on the $\{\mathbf{S}_k\}$, and a part that depends only on $\mathbf{R}$. Table II gives the ratios of the

number of operations involving only either the $\{\mathbf{S}_k\}$ or $\mathbf{R}$ to the total number of operations for each procedure.

The column for Method II shows that its advantage in having the lowest total number of operations for $10 \geqslant N \geqslant 6$ is enhanced as the ratio of the number of orientations to the number of positions increases. Conversely, this advantage can be outweighed by the greater economy of III and especially IV in the $\mathbf{R}$ calculations as the ratio of the number of positions to the number of orientations increases.

TABLE II[a]

N	II(S/T)	III(R/T)	IV(R/T)
4	1.7(−1)	1.4(−1)	8.4(−2)
6	2.0(−1)	9.9(−2)	5.5(−2)
8	2.0(−1)	7.6(−2)	3.6(−2)
10	1.9(−1)	6.1(−2)	3.3(−2)

[a] A column designated by (α/T) gives the ratios for the number of operations involving α to the total number of operations. $\alpha = S$ signifies the $\{\mathbf{S}_k\}$ and $\alpha = R, \mathbf{R}$. The figure in parenthesis gives the power of 10. Thus, $1.7(-1) = 1.7 \times 10^{-1}$.

Appendix A

Examples of the Formulas

The even and odd illustrations of the expression of the directional derivative for $n = 4, 5$ are given. These show all the essential features of the general formulas. The numbers at left identify the general equation in the text.

(2c) $n = 4$: $q = 2$; $n = 5$: $q = 3$; (A1)

(2b) $n = 4$: $2 = q \leqslant j \leqslant 4$; $n = 5$: $3 = q \leqslant j \leqslant 5$; (A2)

$n = 4, j = 2$.

(2f) Each partition has $n - j + 1 = 3$ sets and there are 3 such partitions: (A3)

(2g.1, 2)

$$1 \leqslant g \leqslant n - j = 2 \qquad g = n - j + 1 = 3$$

$$\begin{aligned} (D_2^4)_1 &: \{C_1 = \{1, 2\}, C_2 = \{3, 4\}\}, && C_3 = \text{empty set}; \\ (D_2^4)_2 &: \{C_1 = \{1, 3\}, C_2 = \{2, 4\}\}, && C_3 = \text{empty set}; \\ (D_2^4)_3 &: \{C_1 = \{1, 4\}, C_2 = \{2, 3\}\}, && C_3 = \text{empty set}; \end{aligned} \tag{A4}$$

$n = 4, j = 3.$

(2f) Each partition has $n - j + 1 = 2$ sets and there are six such partitions: (A5)

(2g.1, 2)

$$\begin{array}{ll} 1 \leqslant g \leqslant n - j = 1 & g = n - j + 1 = 2 \\ (D_3^4)_1 : C_1 = \{1, 2\}, & C_2 = \{3, 4\}; \\ (D_3^4)_2 : C_1 = \{1, 3\}, & C_2 = \{2, 4\}; \\ (D_3^4)_3 : C_1 = \{1, 4\}, & C_2 = \{2, 3\}; \\ (D_3^4)_4 : C_1 = \{2, 3\}, & C_2 = \{1, 4\}; \\ (D_3^4)_5 : C_1 = \{2, 4\}, & C_2 = \{1, 3\}; \\ (D_3^4)_6 : C_1 = \{3, 4\}, & C_2 = \{1, 2\}. \end{array} \tag{A6}$$

$n = 4, j = 4.$

(2g.3) $(D_4^4)_1 : C_1 = \{1, 2, 3, 4\}.$ (A7)

$n = 5, j = 3.$

(2f) Each partition has $n - j + 1 = 3$ sets and there are 15 such partitions: (A8)

(2g.1, 2)

$$\begin{array}{ll} 1 \leqslant g \leqslant n - j = 2 & g = n - j + 1 = 3 \\ (D_3^5)_1 : \{C_1 = \{1, 2\}, C_2 = \{3, 4\}\}, & C_3 = \{5\}; \\ (D_3^5)_2 : \{C_1 = \{1, 3\}, C_2 = \{2, 4\}\}, & C_3 = \{5\}; \\ (D_3^5)_3 : \{C_1 = \{2, 3\}, C_2 = \{1, 4\}\}, & C_3 = \{5\}; \\ (D_3^5)_4 : \{C_1 = \{1, 2\}, C_2 = \{3, 5\}\}, & C_3 = \{4\}; \\ (D_3^5)_5 : \{C_1 = \{1, 3\}, C_2 = \{2, 5\}\}, & C_3 = \{4\}; \\ (D_3^5)_6 : \{C_1 = \{1, 5\}, C_2 = \{2, 3\}\}, & C_3 = \{4\}; \\ (D_3^5)_7 : \{C_1 = \{1, 2\}, C_2 = \{4, 5\}\}, & C_3 = \{3\}; \\ (D_3^5)_8 : \{C_1 = \{1, 4\}, C_2 = \{2, 5\}\}, & C_3 = \{3\}; \\ (D_3^5)_9 : \{C_1 = \{1, 5\}, C_2 = \{2, 4\}\}, & C_3 = \{3\}; \\ (D_3^5)_{10} : \{C_1 = \{1, 3\}, C_2 = \{4, 5\}\}, & C_3 = \{2\}; \\ (D_3^5)_{11} : \{C_1 = \{1, 4\}, C_2 = \{3, 5\}\}, & C_3 = \{2\}; \\ (D_3^5)_{12} : \{C_1 = \{1, 5\}, C_2 = \{3, 4\}\}, & C_3 = \{2\}; \\ (D_3^5)_{13} : \{C_1 = \{2, 3\}, C_2 = \{4, 5\}\}, & C_3 = \{1\}; \\ (D_3^5)_{14} : \{C_1 = \{2, 4\}, C_2 = \{3, 5\}\}, & C_3 = \{1\}; \\ (D_3^5)_{15} : \{C_1 = \{2, 5\}, C_2 = \{3, 4\}\}, & C_3 = \{1\}; \end{array} \tag{A9}$$

$n = 5, j = 4.$

(2f) Each partition has $n - j + 1 = 2$ sets and there are 10 such partitions: (A10)

(2g.1, 2)

$$
\begin{aligned}
(D_4^5)_1 &: C_1 = \{1, 2\}, \quad C_2 = \{3, 4, 5\};\\
(D_4^5)_2 &: C_1 = \{1, 3\}, \quad C_2 = \{2, 4, 5\};\\
(D_4^5)_3 &: C_1 = \{1, 4\}, \quad C_2 = \{2, 3, 5\};\\
(D_4^5)_4 &: C_1 = \{1, 5\}, \quad C_2 = \{2, 3, 4\};\\
(D_4^5)_5 &: C_1 = \{2, 3\}, \quad C_2 = \{1, 4, 5\};\\
(D_4^5)_6 &: C_1 = \{2, 4\}, \quad C_2 = \{1, 3, 5\};\\
(D_4^5)_7 &: C_1 = \{2, 5\}, \quad C_2 = \{1, 3, 4\};\\
(D_4^5)_8 &: C_1 = \{3, 4\}, \quad C_2 = \{1, 2, 5\};\\
(D_4^5)_9 &: C_1 = \{3, 5\}, \quad C_2 = \{1, 2, 4\};\\
(D_4^5)_{10} &: C_1 = \{4, 5\}, \quad C_2 = \{1, 2, 3\};
\end{aligned}
\tag{A11}
$$

$n = 5, j = 5.$

(2g.3) $(D_5^5)_1 : C_1 = \{1, 2, 3, 4, 5\}.$ (A12)

Appendix B

Although [4, Eq. (39)] (which summarizes the computational steps for Method II) is stated in terms of the specifics of a generalization of the Ewald method for lattice sums, for other applications, the equation need only be modified as follows. The $g(R)$ of [4, Eq. (15)] is any function of R with the required number of derivatives instead of $g(R) = G(\epsilon R)/R$. The remaining reference to lattice sums can be removed when the definition of [4, Eq. (31)] is noted.

References

1. E. W. Hobson, "The Theory of Spherical and Ellipsoidal Harmonics," pp. 124–32, Cambridge Univ. Press, Cambridge, England, 1931.
2. M. Mezei and E. S. Campbell, *J. Comput. Phys.* **20** (1976), 110–116.
3. E. S. Campbell, *Helvetica Physica Acta* **40** (1967), 387–388.
4. E. S. Campbell, *J. Phys. Chem. Solids* **26** (1965), 1395–1408; (4a), 1397–8.

5. R. S. MULLIKEN, *J. Chem. Phys.* **61** (1964), 20 (cf. p. 75).
6. G. R. PACK, HSIN-YU WANG, AND R. REIN, *Chem. Phys. Lett.* **17** (1972), 381–4; (6a) Tables I and II.
7. E. S. CAMPBELL, G. GELERNTER, H. HEINEN, AND V. R. G. MOORTI, *J. Chem. Phys.* **46** (1967), 2690–2707; (7a) 2699–700, 2705; (7b) 2699–2703.

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