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Torque Algorithms: The Permanent Multipole and Induced Dipole Vector Contributions in a Set of Charge Distributions

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Two algorithms for the permanent multipole contribution to the mutual torques in a set of charge distributions are presented. The first is in the conventional Newtonian formulation; the second is in terms of generalized forces. Both noncooperative and cooperative algorithms for the induced dipole vector contribution are given. The algorithms are based on earlier algorithms for the permanent multipole and induced dipole vector contributions to the energy in the Maxwell Invariant Form.

1. INTRODUCTION

An algorithm has been developed for the calculation of the torque experienced by each of a system of polarizable, nonoverlapping charge distributions,

$$D_1, \ldots, D_d, \tag{1}$$

where each D_j is characterized by

$\rho(\mathbf{r}_j)$: the charge density of D_j when it is isolated from all other D_k; (2a)

$\alpha_k^i(j)$: the ordinary dipole polarizability tensor for D_j. (2b)

The contribution of the polarization to the torque has been approximated by the induced dipole vector contributions $\mathbf{I}(j)$,

$$I^i(j) = \alpha_k^i(j)\, E^k(D_j); \tag{3a}$$

$\mathbf{E}(\mathbf{O}_j)$, the electric field experienced by D_j at its center of mass $\mathbf{O}_j$. (3b)

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The contribution of the field derivatives to the induced dipole vectors as well as induced multipole contributions will be considered in a later article with an algorithm for induced multipole moments and energies.

The proposed algorithm is based upon a multipole expansion, and makes use of the Maxwell invariant form (vide infra). Algorithms have been developed for this form for the calculation of the energies, electric fields, and induced dipole vectors in crystal lattices [1–3] and finite sets of distributions [4–6], and have been applied to both $(H_2O)_n$ [7, 8] and to ices Ih, II, IX [9]. Following the derivation of the fundamental equations, the steps in this torque algorithm will be given, making use of the previously published algorithms.

2. Calculation Using the Conventional Newtonian Definition: The Contribution of the $\rho(\mathbf{r}_j)$ to the Torque

Let us define the following:

$$\rho(\mathbf{r}_j): \quad \text{the permanent charge density of } D_j; \tag{4a}$$

$$\mathbf{T}(\langle j, \mathbf{O}_t\rangle): \quad \text{the torque exerted on } D_t \text{ about its center of mass, } \mathbf{O}_t, \text{ by } \rho(\mathbf{r}_j); \tag{4b}$$

$$\mathbf{E}(\langle j, \mathbf{r}_t\rangle): \quad \text{the electric field at } \mathbf{r}_t \text{ defined by } \rho(\mathbf{r}_j). \tag{4c}$$

Then the conventional Newtonian definition of the torque about the center of mass in orthogonal coordinate systems in SI units becomes:

$$\mathbf{T}(\langle j, \mathbf{O}_t\rangle) = \int (\mathbf{r}_t - \mathbf{O}_t) \times \mathbf{E}(\langle j, \mathbf{r}_t\rangle)\, \rho(\mathbf{r}_t)\, d\mathbf{r}_t; \tag{5a}$$

$$\begin{aligned}\mathbf{E}(\langle j, \mathbf{r}_t\rangle) &= -\nabla^{(t)}\{(4\pi\varepsilon_0)^{-1}\} \int \rho(\mathbf{r}_j)\, \|\mathbf{r}_t - \mathbf{r}_j\|^{-1}\, d\mathbf{r}_j \\ &= (4\pi\varepsilon_0)^{-1} \int \rho(\mathbf{r}_j)\, \nabla^{(j)} \|\mathbf{r}_t - \mathbf{r}_j\|^{-1}\, d\mathbf{r}_j;\end{aligned} \tag{5b}$$

$$\nabla^{(j)} \equiv \langle \partial/\partial r_j^1, \partial/\partial r_j^2, \partial/\partial r_j^3\rangle = -\nabla^{(t)}. \tag{5c}$$

In Section 3, use will be made of nonorthogonal frames and a tensor generalization of the definition of Eq. (5). Since the components of vectors transform by the contravariant law, the appropriate generalization to nonorthogonal frames which is consistent with the Newtonian definition for orthogonal frames, where the covariant and contravariant components of $\mathbf{r}$ and $\mathbf{E}$ are identical, is what Brillouin [10a] has called *une densité contravariante tensorielle.* In the convenient notation of McConnell

[11a],[1] this is a relative contravariant vector of weight +1 (in the implicit tensor summation convention),

$$T^i(\langle j, \mathbf{O}_t\rangle) = e^{ikl} T_{kl}(\langle j, \mathbf{O}_t\rangle), \tag{6a}$$

$$T_{kl}(\langle j, \mathbf{O}_t\rangle) = \int (r_k(t) - O_k(t))\, E_l(\langle j, \mathbf{r}_t\rangle)\, \rho(\mathbf{r}_t)\, d\mathbf{r}_t. \tag{6b}$$

In Eq. (6a), the e^{ikl} form a completely antisymmetric relative tensor of weight +1, with the transformation law from frame B to frame A

$$e^{ikl}(A) = |M(B \to A)|\, M(A \to B)^i_m M(A \to B)^k_n M(A \to B)^l_p e^{mnp}(B), \tag{7a}$$

when the basis vectors between the two frames are related by the matrix equation

$$(\mathbf{e}_1(A), \mathbf{e}_2(A), \mathbf{e}_3(A)) = (\mathbf{e}_1(B), \mathbf{e}_2(B), \mathbf{e}_3(B))\, M(B \to A), \tag{7b}$$

and

$$|M(B \to A)|\text{: the determinant;} \qquad M(A \to B) = M(B \to A)^{-1}. \tag{7c}$$

Then, in every frame,

$$\begin{aligned} e^{ikl}(A) &= e^{ikl}(B) \\ &= +1, \quad \text{if } \langle i, k, l\rangle \text{ is a cyclic permutation of } \langle 1, 2, 3\rangle; \\ &= -1, \quad \text{if } \langle i, k, l\rangle \text{ is a permutation of } \langle 1, 2, 3\rangle \text{ which is not cyclic;} \\ &= 0, \quad \text{if } \{i, k, l\} \neq \{1, 2, 3\}. \end{aligned} \tag{7d}$$

In this notation, the transformation law for the contravariant components of the torque relative vector is

$$T^i(\langle j, \mathbf{O}_t\rangle, A) = |M(B \to A)|\, M(A \to B)^i_m T^m(\langle j, \mathbf{O}_t\rangle, B). \tag{8}$$

The initial step in the algorithm is a Taylor series expansion of $\|\mathbf{r}_t - \mathbf{r}_j\|^{-1}$ in the integral for the potential energy of D_j at $\mathbf{r}_t$, $U(\langle j, \mathbf{r}_t\rangle)$,

$$U(\langle j, \mathbf{r}_t\rangle) = (4\pi\varepsilon_0)^{-1} \int \rho(\mathbf{r}_j)\, \|\mathbf{r}_t - \mathbf{r}_j\|^{-1}\, d\mathbf{r}_j, \tag{9}$$

[1] In contrast to Brillouin [10b], who used a generalization of axial vectors consistent with the conventional definition upon inversion of frames, McConnell [11b] uses a generalization as a true tensor, which is not consistent with the conventional definition upon inversion.

about a suitable $\mathbf{O}_j$ in D_j. Since the torque exerted on D_j will also be calculated, this will be the center of mass. This introduces the Nth-order *Taylor moments* about $\mathbf{O}_j$,

$$M(\langle n_1, n_2, n_3\rangle, \mathbf{O}_j) \equiv \int \prod_{q=1}^{3} (r^q(j) - O^q(j))^{n_q} \rho(\mathbf{r}_j)\, d\mathbf{r}_j; \tag{10a}$$

$$N = n_1 + n_2 + n_3. \tag{10b}$$

These *Taylor moments* are used in a published algorithm [4] to determine:

(i) the components of characteristic directions,

$$\mathbf{s}(\langle j, N\rangle, 1), \ldots, \mathbf{s}(\langle j, N\rangle, N), \tag{11a}$$

$$\|\mathbf{s}(\langle j, N\rangle, q)\| = 1, \qquad 1 \leqslant q \leqslant N, \tag{11b}$$

with respect to an intrinsic reference frame L_j for distribution D_j;

(ii) the scalar Nth-order multipole moment in the Maxwell invariant form [4], $P^{(N)}(j)$, for the spherical harmonic defined by the Nth-order terms in the Taylor series. Then the mth covariant component of the field for a finite set of distributions is given by the multipole expansion in the Maxwell invariant form as,

$$E_m(\langle j, \mathbf{r}_t\rangle) = (4\pi\varepsilon_0)^{-1} \sum_{N=0}^{\infty} (N!)^{-1} P^{(N)}(j) \prod_{q=1}^{N+1} (\mathbf{s}(\langle j, N\rangle, q) \cdot \boldsymbol{\nabla}^{(j)}) \|\mathbf{r}_t - \mathbf{r}_j\|^{-1} \Big|_{\mathbf{r}_j = \mathbf{O}_j}, \tag{12a}$$

where, for *formal* use of the algorithm, the $(N+1)$th characteristic direction is taken to be the mth unit basis vector of the coordinate frame,

$$\mathbf{s}(\langle j, N\rangle, N+1) \equiv \mathbf{e}_m. \tag{12b}$$

For crystals, $\|\mathbf{r}_t - \mathbf{r}_j\|^{-1}$ is replaced by another function of a vector magnitude. After substitution of Eq. (12a) into Eq. (6), the order of differentiation using $\boldsymbol{\nabla}^{(j)}$ and of integration over $\mathbf{r}_t$ can be inverted so that it is only necessary to evaluate integrals of the form

$$\int (r_t^k - O_t^k)\, \rho(\mathbf{r}_t) \|\mathbf{r}_t - \mathbf{r}_j\|^{-1}\, d\mathbf{r}_t. \tag{13}$$

For this purpose, let $\rho^k(\mathbf{r}_t)$ be defined as the pseudodensity function,

$$\rho^k(\mathbf{r}_t) \equiv (r_t^k - O_t^k)\, \rho(\mathbf{r}_t). \tag{14}$$

Then a Taylor series expansion of $\|\mathbf{r}_t - \mathbf{r}_j\|^{-1}$ about $\mathbf{r}_t = \mathbf{O}_t$ in the integral,

$$\int \rho^k(\mathbf{r}_t) \|\mathbf{r}_t - \mathbf{r}_j\|^{-1}\, d\mathbf{r}_t, \tag{15}$$

yields the Nth-order *Taylor moments*,

$$M(\langle n_1, n_2, n_3\rangle, \mathbf{O}_t, k) = \int \prod_{q=1}^{3} (r^q(t) - O^q(t))^{n_q} \rho^k(\mathbf{r}_t)\, d\mathbf{r}_t = M(\langle n_1 + \delta_k^1, n_2 + \delta_k^2, n_3 + \delta_k^3\rangle, \mathbf{O}_t). \tag{16}$$

Thus each Nth-order *Taylor moment* for the pseudodensity $\rho^k(\mathbf{r}_t)$ is an $(N+1)$th-order *Taylor moment* for $\rho(\mathbf{r}_t)$, which must be evaluated to determine the characteristic directions for both the calculation of the interaction energy between D_j and D_t as well as the field which D_t exerts on D_j.

The relation between the Maxwell invariant forms for $\rho(\mathbf{r}_t)$ and for $\rho^k(\mathbf{r}_t)$ is shown clearly by the construction of the zeroth- and first-order terms for the latter. Let

$$\{\mathbf{s}(\langle t, N\rangle, q, k), 1 \leqslant q \leqslant N\} \equiv \text{set of characteristic directions in the Maxwell invariant form for the } N\text{th-order spherical harmonic in the expansion of Eq. (15) for the pseudodensity; and} \tag{17a}$$

$$P^{(N)}(\langle t, k\rangle)\text{: the scalar multipole moment.} \tag{17b}$$

Whereas the expansion of $\|\mathbf{r}_t - \mathbf{r}_j\|^{-1}$ in the integral defining the potential has no constant term when $\rho(\mathbf{r}_t)$ is the density for a neutral distribution, the expansion in Eq. (15) for the pseudodensity $\rho^k(\mathbf{r}_t)$ contains a constant term, the contribution of a pseudocharge, which is one of the first-order *Taylor moments* of $\rho(\mathbf{r}_t)$,

$$M(\delta_k^1, \delta_k^2, \delta_k^3)\, \|\mathbf{O}_t - \mathbf{r}_j\|^{-1}. \tag{18a}$$

The characteristic direction defined by the first-order spherical harmonic for $\rho^k(\mathbf{r}_t)$ is determined by three of the six second-order *Taylor moments* of $\rho(\mathbf{r}_t)$,

$$\boldsymbol{\mu} = \langle M\langle 1 + \delta_k^1, \delta_k^2, \delta_k^3\rangle, \mathbf{O}_t), M(\langle \delta_k^1, 1 + \delta_k^2, \delta_k^3\rangle, \mathbf{O}_t), M(\langle \delta_k^1, \delta_k^2, 1 + \delta_k^3\rangle, \mathbf{O}_t)\rangle, \tag{18b}$$

$$\mathbf{s}(\langle t, 1\rangle, 1, k) = \boldsymbol{\mu}\, \|\boldsymbol{\mu}\|^{-1}, \qquad P^{(1)}(\langle t, k\rangle) = \|\boldsymbol{\mu}\|. \tag{18c}$$

Thus the steps in the calculation are: *Step* I. For each distribution D_j, calculate the *Taylor moments* about $\mathbf{O}_j$, the $M(\langle n_1, n_2, n_3\rangle, \mathbf{O}_j)$ of Eq. (10). When $\rho(\mathbf{r}_j)$ is the density defined by a single determinant wave function consisting of an LCGO, a tested program is available on request. *Step* II. Use the *Taylor moments* from Step I and the published algorithm [4] to determine the characteristic directions, $\mathbf{s}(\langle j, N\rangle, q)$, $1 \leqslant q \leqslant N$, and multipole moments, $P^{(N)}(j)$ of Eq. (11) for $\rho(\mathbf{r}_j)$ and a set of characteristic directions, $\mathbf{s}(\langle t, N\rangle, q, k)$, $1 \leqslant q \leqslant N$, and multipole moments, $P^{(N)}(\langle t, k\rangle)$, of Eq. (17) for each of the three pseudodensities, $\rho^k(\mathbf{r}_t)$, $1 \leqslant k \leqslant 3$. *Step* III. For any desired set of positions and orientations, use one of the algorithms for crystals [1, 3] or for $(H_2O)_n$ [5] to evaluate the expansions for the integrals of Eq. (6) (in SI units)

$$T_{kl}(\langle j, \mathbf{O}_t\rangle) = (4\pi\varepsilon_0)^{-1} \sum_{N_j} \sum_{N_t^k} (N_j!\, N_t^k!)^{-1} P^{(N_j)}(j)\, P^{(N_t^k)}(\langle t, k\rangle)(-1)^{N_t^k}$$
$$\times \prod_{q=1}^{N_j+1} (\mathbf{s}(\langle j, N_j\rangle, q) \cdot \nabla_j)$$
$$\times \prod_{m=1}^{N_t^k} (\mathbf{s}(\langle t, N_t^k\rangle, m, k) \cdot \nabla_j) \|\mathbf{O}_t - \mathbf{r}_j\|^{-1} \Big|_{\mathbf{r}_j = \mathbf{O}_j}; \quad (19)$$
$$\mathbf{s}(\langle j, N_j\rangle, N_j + 1) = \mathbf{e}_e.$$

For crystals, the lattice sums replace $\|\mathbf{O}_t - \mathbf{r}_j\|^{-1}$ by functions $f(\|\mathbf{O}_t - \mathbf{r}_j\|)$ [1, 3].

3. Calculation of the Torque on D_t from Generalized Forces: The Induced Dipole Vector Contribution and an Alternative Algorithm for the Contribution of the $\rho(\mathbf{r}_j)$

Let

$U(\{q_k\})$: potential energy as a function of generalized coordinates, $\{q_k\}$; (20a)

χ: a generalized coordinate which is an angle of rotation about an axis, $\mathbf{n}$. (20b)

The calculation of the induced dipole vector contribution must be based on the result that the generalized force with respect to χ, $-\partial U(\{q_k\})/\partial\chi$, is the projection of the conventional Newtonian torque $\mathbf{T}$ upon $\mathbf{n}$ (see, e.g., [12])

$$(\mathbf{T} \cdot \mathbf{n}) = -\partial U(\{q_k\})/\partial\chi. \quad (21)$$

The potential energy for this system is given by

$$U = U_{\text{perm}} + U_{\text{ind}}. \quad (22a)$$

The contribution of the $\rho(\mathbf{r}_j)$ to U_{perm} is given by a multipole expansion as

$$U_{\text{perm}} = \sum_{\{A,B\}} \sum_{N_A=0}^{\infty} \sum_{N_B=0}^{\infty} U(N_A, N_B), \quad (22b)$$

$$U(N_A, N_B) = (-1)^{N_B}\{(N_A!\, N_B!)^{-1} P^{N_A}(A)\, P^{N_B}(B)\} \prod_{q=1}^{N_A} (\mathbf{s}(\langle A, N_A\rangle, q) \cdot \nabla^{(A)})$$
$$\times \prod_{m=1}^{N_B} (\mathbf{s}(\langle B, N_B\rangle, m) \cdot \nabla^{(A)}) \|\mathbf{r}_B - \mathbf{r}_A\|^{-1}_{\langle \mathbf{r}_A, \mathbf{r}_B\rangle = \langle \mathbf{O}_A, \mathbf{O}_B\rangle}. \quad (22c)$$

For crystals, the lattice sums replace $\|\mathbf{r}_B - \mathbf{r}_A\|^{-1}$ by functions $f(\|\mathbf{r}_B - \mathbf{r}_A\|)$ [1, 3]. The moments and characteristic directions are those of Eq. (11). The potential energy

involving the induced dipoles of Eq. (3) is given by an extension to multipole fields [7] of the equation of Mandel and Mazur for dipole fields [13]

$$U_{\text{ind}} = -\tfrac{1}{2} \sum_{k} \sum_{j \neq k} I^m(k)\, E_m(\langle j, \mathbf{O}_k \rangle); \tag{23a}$$

$\mathbf{E}(\langle j, \mathbf{O}_k \rangle)$: the electric field at the center of mass $\mathbf{O}_k$ of D_k defined by the permanent charge density $\rho(\mathbf{r}_j)$ of D_j. (23b)

Let

χ_t: one of the three Eulerian angles for D_t; (24a)

$\mathbf{n}(\chi_t)$: the unit vector along the directed invariant axis for χ_t. (24b)

Then, the projection of the torque along $\mathbf{n}(\chi_t)$ is given by

$$T(\chi_t) = T_{\text{perm}}(\chi_t) + T_{\text{ind}}(\chi_t), \tag{25a}$$

$$T_{\text{perm}}(\chi_t) = \sum_{\{A,B\}} \sum_{N_A=0}^{\infty} \sum_{N_B=0}^{\infty} T_{\text{perm}}(\chi_t, N_A, N_B), \tag{25b}$$

$$\begin{aligned} T_{\text{perm}}(\chi_t, N_A, N_B) = {} & (-1)^{N_B} \{N_A!\, N_B!\}^{-1} P^{(N_A)}(A)\, P^{(N_B)}(B)\} \\ & \times \left(\frac{-\partial}{\partial \chi_t}\right) \left\{ \prod_{q=1}^{N_A} (\mathbf{s}(\langle A, N_A \rangle, q) \cdot \boldsymbol{\nabla}^{(A)}) \right. \\ & \left. \times \prod_{m=1}^{N_B} (\mathbf{s}(\langle B, N_B \rangle, m) \cdot \boldsymbol{\nabla}^{(A)}) \, \| \mathbf{r}_B - \mathbf{r}_A \|^{-1} \right\}_{\langle \mathbf{r}_A, \mathbf{r}_B \rangle = \langle \mathbf{O}_A, \mathbf{O}_B \rangle}, \end{aligned} \tag{25c}$$

$$\begin{aligned} T_{\text{ind}}(\chi_t) = {} & \tfrac{1}{2} \sum_{k} \sum_{j \neq k} \left(\frac{\partial I^m(k)}{\partial \chi_t}\right) E_m(\langle j, \mathbf{O}_k \rangle) \\ & + \tfrac{1}{2} \sum_{k \neq t} I^m(k) \left\{ \frac{\partial E_m(\langle t, \mathbf{O}_k \rangle)}{\partial \chi_t} \right\}. \end{aligned} \tag{25d}$$

The algorithm depends upon the transformation between the following frames for each distribution:

L_j: an intrinsic frame in which the components of the characteristic directions of Eq. (11) are computed; (26a)

G: a global frame for $\{D_k\}$. (26b)

The orientation of L_j in $\{D_k\}$ is defined by the matrix $M(G \to L_j)$ for the basis vector transformation:

$$(\mathbf{e}_1(L_j), \mathbf{e}_2(L_j), \mathbf{e}_3(L_j)) = (\mathbf{e}_1(G), \mathbf{e}_2(G), \mathbf{e}_3(G))\, M(G \to L_j). \tag{26c}$$

According to Eqs. (12), (25c), the partial derivative of both U_{perm} and of the field components are defined by partial derivatives of Maxwell invariant forms,

$$(\partial/\partial\chi_t) \prod_{q=1}^{M} (\mathbf{s}(\langle i, N\rangle, q) \cdot \nabla^{(k)}) \|\mathbf{r}_m - \mathbf{r}_k\|^{-1}; \tag{27a}$$

$$\text{for field components:} \quad i = k \text{ for all } q: \tag{27b}$$

$$\text{for permanent multipole energies:} \quad i = k \text{ for some } q, \text{ and} \tag{27c}$$

$$= m \text{ for the remainder;}$$

$$\partial/\partial\chi_t(\mathbf{s}(\langle i, N\rangle, q) \cdot \nabla^k) \|\mathbf{r}_m - \mathbf{r}_k\|^{-1} = 0, \qquad \text{when} \quad i \neq t. \tag{27d}$$

The algorithms for the Eulerian angle partial derivatives of the Maxwell invariant forms will be given in Section 3A, and those of the induced dipole vector components in Section 3B.

3A. *The Eulerian Angle Partial Derivatives of the Maxwell Invariant Form*

Since the components of the ∇ operator are taken in frame G, it is necessary to use the partials of the G frame components given by the matrix equations, $1 \leqslant q \leqslant M$:

$$i \neq t: \qquad 0; \tag{28a}$$

$$i = t: \qquad \begin{bmatrix} \partial s^1(\langle i, M\rangle, q, G)/\partial\chi_t \\ \partial s^2(\langle i, M\rangle, q, G)/\partial\chi_t \\ \partial s^3(\langle i, M\rangle, q, G)/\partial\chi_t \end{bmatrix} = M\chi_t(G \to L_t) \begin{bmatrix} s^1(\langle i, M\rangle, q, L_i) \\ s^2(\langle i, M\rangle, q, L_i) \\ s^3(\langle i, M\rangle, q, L_i) \end{bmatrix}; \tag{28b}$$

$$M\chi_t(G \to L_t): \quad \text{the partial derivative of the matrix } M(G \to L_t) \text{ with respect to the Eulerian angle } \chi_t. \tag{28c}$$

The algorithms for the partial derivatives of Maxwell invariant forms of differentiable functions $f(R)$ are simple extensions of the following algorithms for the invariant forms themselves: (i) efficient recursive algorithms for general $f(R)$ [5, Method III], and for $f(R) = R^{-1}$, as in Eq. (27) for a finite set of D_j [5, Method IV]; and (ii) an efficient algorithm for lattice sums in crystals [5, Method II], which has been trivially extended to nonperiodic systems [5], and for which we have developed a similar recursive construction. (We have applied Method IV to nonperiodic systems and Method II to crystals extensively.) Consider, for example, Method IV for a finite set of distributions so that

$$f(R) = R^{-1}. \tag{29}$$

It has been shown (cf. [5, Eq. (8)]) that

$$\prod_{q=1}^{n-1} (\mathbf{s}(\langle i, N\rangle, q) \cdot \nabla) R^{-1} = R^{-(2n-1)} \sum_{N(n-1)} d(\mathbf{v}, \mathscr{S}_{n-1}) \prod_{i=1}^{3} x_i^{v_i}; \tag{30a}$$

$$N(n-1) = \{\mathbf{v}, v_i \text{ is a nonnegative integer and } v_1 + v_2 + v_3 = n - 1, n \geqslant 2\}. \tag{30b}$$

This can be evaluated by the efficient recursion given by [5, Eq. (9)]. Partial derivatives of such invariant forms have an analogous development:

$$\frac{\partial}{\partial t}\prod_{q=1}^{n-1}(\mathbf{s}(\langle i,N\rangle,q)\cdot\nabla)R^{-1}=0, \qquad \text{if} \quad i\neq t \quad 1\leqslant q\leqslant n-1,$$
$$=R^{-(2n-1)}\sum_{N(n-1)} d(\mathbf{v},\mathscr{S}_{n-1}(\chi_t))\prod_{i=1}^{3}x_i^{v_i}, \tag{31a}$$
$$\text{otherwise;}$$

$$N(n-1)=\{\mathbf{v}, v_i \text{ is a nonnegative integer and } v_1+v_2+v_3=n-1, n\geqslant 2\}. \tag{31b}$$

The $d(\mathbf{v},\mathscr{S}_{n-1}(\chi_t))$ can be calculated by the following recursion analogous to that for the $d(\mathbf{v},\mathscr{S}_{n-1})$: Let the characteristic directions be ordered so that $i=t$ for $q=1$. Then,

$$N(1)=\{\mathbf{e}_m : \boldsymbol{e}_m=\langle\delta_m^1,\delta_m^2,\delta_m^3\rangle, m=1,2,3\}; \tag{32a}$$

$$\mathscr{S}_1(\chi_t)=\{\partial\mathbf{s}(\langle t,N\rangle,1)/\partial\chi_t\}; \tag{32b}$$

$$d(\mathbf{e}_m,\mathscr{S}_1(\chi_t))=\partial s^m(\langle t,N\rangle,1)/\partial\chi_t. \tag{32c}$$

For $n>1$, each $d(\mathbf{v},\mathscr{S}_{n-1})$, computed from the recursion [5, Eq. (9)], yields the following 12 additions to the accumulators for the $d(\mathbf{v},\mathscr{S}_n(\chi_t))$ when $i=t$ for $q=n$:

$$A[d(\mathbf{v}+\mathbf{e}_k,\mathscr{S}_n(\chi_t))]-(2n-1)\,\partial s^k(\langle t,N\rangle,n)/\partial\chi_t\, d(\mathbf{v},\mathscr{S}_{n-1}), \qquad 1\leqslant k\leqslant 3,$$
$$A[d(\mathbf{v}+2\mathbf{e}_k-\mathbf{e}_m,\mathscr{S}_n(\chi_t))]+v_m(\partial s^m(\langle t,N\rangle,n)/\partial\chi_t)\,d(\mathbf{v},\mathscr{S}_{n-1}), \tag{32d}$$
$$1\leqslant k\leqslant 3, \quad 1\leqslant m\leqslant 3.$$

Each $d(\mathbf{v},\mathscr{S}_{n-1}(\chi_t))$ always yields another 12 additions to the accumulators for the $d(\mathbf{v},\mathscr{S}_n(\chi_t))$,

$$A[d(\mathbf{v}+\mathbf{e}_k,\mathscr{S}_n(\chi_t))]-(2n-1)\,s^k(\langle t,N\rangle,n)\,d(\mathbf{v},\mathscr{S}_{n-1}(\chi_t)), \qquad 1\leqslant k\leqslant 3,$$
$$A[d(\mathbf{v}+2\mathbf{e}_k-\mathbf{e}_m,\mathscr{S}_n(\chi_t))]+v_m s^m(\langle t,N\rangle,n)\,d(\mathbf{v},\mathscr{S}_{n-1}(\chi_t)), \tag{32e}$$
$$1\leqslant k\leqslant 3, \quad 1\leqslant m\leqslant 3.$$

Finally, each $d(\mathbf{v},\mathscr{S}_{n-1})$ yields the 12 additions [5, Eq. (9)] for use in Eq. (32d) for the next step, $n+1$, of the recursion.

3B. *Eulerian Angle Derivatives of the Induced Dipole Vector Components*

3B1. *The Noncooperative Approximation*

In the noncooperative approximation, the electric field at a site k is given by the contribution of $\rho(j)$, i.e., the contribution of the $\mathbf{I}(j)$, $j\neq k$, is omitted. Then, in the global reference frame G,

$$I^m(k, G) = \alpha_q^m(\langle k, G\rangle) \sum_{j \neq k} E^q(\langle j, \mathbf{O}_k\rangle, G), \tag{33a}$$

$$\partial I^m(\langle k, G\rangle)/\partial\chi_t = (1 - \delta_t^k)\, \alpha_q^m(\langle k, G\rangle)\, \partial E^q(\langle t, \mathbf{O}_k\rangle, G)/\partial\chi_t + \delta_t^k \sum_{j \neq t} \partial\alpha_q^m(\langle t, G\rangle)/\partial\chi_t E^q(\langle j, \mathbf{O}_t\rangle, G). \tag{33b}$$

Since the algorithm for the partial derivatives of the field components has been derived in Section 3A, it is only necessary to obtain those of the polarizability tensor. This is simplified if the intrinsic local frames L_j of Eq. (26a) are chosen as the principal axis frames for the polarizability tensors. Then

$$\begin{aligned} \alpha_q^m(\langle t, G\rangle) &= \sum_{c=1}^{3} M(G \to L_t)_c^m \alpha_c^c(\langle t, L_t\rangle)\, M^{-1}(G \to L_t)_q^c \\ &= \sum_{c=1}^{3} M(G \to L_t)_c^m M(G \to L_t)_c^q \alpha_c^c(\langle t, L_t\rangle), \end{aligned} \tag{34}$$

$$\begin{aligned} \partial\alpha_q^m(\langle t, G\rangle)/\partial\chi_t = \sum_{c=1}^{3} \{&[\partial M(G \to L_t)_c^m/\partial\chi_t]\, M(G \to L_t)_c^q \\ &+ M(G \to L_t)_c^m [\partial M(G \to L_t)_c^q/\partial\chi_t]\}\, \alpha_c^c(\langle t, L_t\rangle). \end{aligned} \tag{35}$$

3B2. *The Cooperative Approximation*

In the cooperative approximation, it has been shown [2] that the components of the induced dipole vectors (when all terms in the equation for the energy involving either field derivatives or higher than quadratic products of field components are excluded [14]) are given as the solution to a set of simultaneous linear equations

$$\sum_h C_{3h+s-3}^{3j+i-3} I^s(h) = C_0^{3j+i-3}. \tag{36a}$$

The constant terms are

$$C_0^{3j+i-3} = \alpha_q^i(j) \sum_{h \neq j} E^q(\langle h, \mathbf{O}_j\rangle). \tag{36b}$$

For the noncrystalline case ($f(R) = R^{-1}$, cf. Eq. (29)),

$$C_{3h+s-3}^{3j+i-3} = \delta_h^j \delta_s^i + (4\pi\varepsilon_0)^{-1}(1 - \delta_h^j) \|\mathbf{O}_j - \mathbf{O}_h\|^{-3} \times \{\alpha_s^i(j) - 3n_s(\langle h, j\rangle)\, \alpha_m^i(j)\, n^m(\langle h, j\rangle)\}, \tag{36c}$$

$$\mathbf{n}(\langle h, j\rangle) \equiv (\mathbf{O}_j - \mathbf{O}_h) \|\mathbf{O}_j - \mathbf{O}_h\|^{-1}. \tag{36d}$$

Partial differentiation of Eq. (36) with respect to each of the $3N$ different χ_t gives the following set of linear equations for the partial derivatives:

$$\sum_h P_{3h+s-3}^{3j+i-3}\, \partial I^s(h)/\partial\chi_t = P_0^{3j+i-3}. \tag{37a}$$

In this case,

$$P^{3j+i-3}_{3h+s-3} = C^{3j+i-3}_{3h+s-3}, \tag{37b}$$

$$\begin{aligned} P^{3j+i-3}_{0} = {} & \delta^j_t\, \partial\alpha^i_s(t)/\partial\chi_t \sum_{h\neq t} E^s(\langle h, \mathbf{O}_t\rangle) \\ & + (1-\delta^j_t)\, \alpha^i_s(j)\, \partial E^s(\langle t, \mathbf{O}_j\rangle)/\partial\chi_t \\ & - \delta^j_t (4\pi\varepsilon_0)^{-1} \sum_h (1-\delta^h_t) \|\mathbf{O}_t - \mathbf{O}_h\|^{-3} \\ & \times \{\partial\alpha^i_s(t)/\partial\chi_t - 3n_s(\langle h, t\rangle)[\partial\alpha^i_m(t)/\partial\chi_t]\, n^m(\langle h, t\rangle)\}\, I^s(h). \end{aligned} \tag{37c}$$

Since the $3N$ sets of Eqs. (37a) for the $\partial\mathbf{I}/\partial\chi_t$ have a common coefficient matrix, they need not be solved explicitly and multiplications with a $3N \times 3N$ matrix can be avoided by regrouping the terms in the substitution in torque Eq. (25d) of the formal matrix solutions

$$[\partial\mathbf{I}/\partial\chi_t] = C^{-1}[P_0(\chi_t)]; \tag{37d}$$

$[\mathbf{I}]$: the $[3N \times 1]$ matrix whose element in row $(3h + s - 3)$ is $I^s(h)$; (37e)

$[P_0(\chi_t)]$: the $[3N \times 1]$ constant matrices of equation systems (37a); (37f)

C: the common $(3N \times 3N)$ coefficient matrix of equation systems (36a), (37a). (37g)

The first term of Eq. (25d) becomes

$$\tfrac{1}{2}(\mathbf{E})[\partial\mathbf{I}/\partial\chi_t] = \tfrac{1}{2}(\mathbf{E})C^{-1}[P_0(\chi_t)], \tag{37h}$$

where

(**E**): the $(1 \times 3N)$ matrix whose element in column $3k + m - 3$ is $\sum_{j\neq k} E_m(\langle j, \mathbf{O}_k\rangle)$. (37i)

The algorithm proceeds in the following order: *Step* I. Solve the set of $3N$ linear equations (36) for the induced dipole vector components which enter the constants in the partial derivative equations. *Step* II. Solve a single set of $3N \times 3N$ linear equations which is independent of χ_t.

$$(x)C = (\mathbf{E}). \tag{38a}$$

Use the solution to compute the first term of Eq. (25d)

$$\tfrac{1}{2}(\mathbf{E})[\partial\mathbf{I}/\partial\chi_t] = (x)[P_0(\chi_t)]. \tag{38b}$$

Stillinger [15] derived an algorithm for the mutual forces exerted for the special case of spherically symmetric polarizable systems from a variational problem. It can be

shown that his result can be written as the analog of Eqs. (38a), (38b) for such systems.

As an alternative to the direct solution of the linear equations, iterative solutions of Eqs. (36) can be constructed using the noncooperative approximation of Eq. (33a) as the initial (0) approximation in Step I.

It should be noted that any convergence difficulties in the iteration arise solely from the iteration itself and are not intrinsic to the physical problem.

The foregoing generalized forces can be simply related to the conventional Newtonian definition as follows: Let

$$\chi_t^1, \chi_t^2, \chi_t^3: \quad \text{the three Eulerian angles for } D_t; \tag{39a}$$

$$\mathbf{n}(\langle t, k\rangle): \quad \text{the unit vector along the directed axis for } \chi_t^k; \tag{39b}$$

$$T^i(\mathbf{O}_t) = \sum_{j \neq t} T^i(\langle j, \mathbf{O}_t\rangle);$$
$$T^i(\langle j, \mathbf{O}_t\rangle): \quad \text{cf. Eq. (6).} \tag{39c}$$

According to Eq. (21), the contravariant components of $\mathbf{T}(\mathbf{O}_t)$ with respect to the nonorthogonal bases set $\{\mathbf{n}(\langle t, k\rangle)\}$ can be computed by inversion of the equation

$$-\partial U/\partial \chi_t^k = (\mathbf{T}(\mathbf{O}_t) \cdot \mathbf{n}(\langle t, k\rangle)) = \sum_{i=1}^{3} T^i(\mathbf{O}_t)(\mathbf{n}(\langle t, k\rangle) \cdot \mathbf{n}(\langle t, i\rangle)). \tag{40}$$

4. Summary

The following considerations provide a basis for a choice between the two alternative algorithms for the permanent multipole contribution to the torque (with the direct Newtonian formulation (Sect. 2); with the generalized force formulation (Sect. 3)) for different applications.

Case I. Only the permanent multipole contribution to the torque is calculated.

(i) The algorithm in the direct Newtonian formulation requires the determination of three additional sets of characteristic directions in a local intrinsic frame prior to the calculation.

(ii) Whereas the Newtonian formulation minimizes coding and debugging costs by using the same principal subroutines required by the permanent multipole energy calculation, the generalized force formulation requires a completely different code.

(iii) The relative number of operations required by the two algorithms for each set of orientations of the charge distribution is close enough that, in applications, which algorithm proves to be more economical will depend less upon intrinsic differences than upon the relative effectiveness with which intermediate results are used, vanishing terms recognized, etc., in particular codes.

Case II. The induced dipole vector contribution is included. Since the generalized force algorithm must be coded and used for the induced dipole vector contribution, point (ii) does not apply, and only (i) and (iii) remain. Note also that the required recursions are simple extensions of efficient algorithms developed for and extensively tested in permanent multipole energy calculations.

The range of applicability of the multipole calculation has been discussed in previous publications [5, 6, 9].

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