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The Construction of the Maxwell Representation for a Cylindrically Symmetric Spherical Harmonic of Arbitrary Order

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The general structure of the sets of characteristic directions in the Maxwell invariant representation (vide infra) of spherical harmonics which have the symmetry of those defined by the moments of a cylindrically symmetric distribution has been determined. These results, valid for arbitrary orders, have been used to derive an algorithm for the construction of the characteristic directions. The calculations in the new algorithm are significantly simpler than those in the algorithm for the general spherical harmonic and in test calculations comparing the two algorithms the new one gave more accurate sets of characteristic directions. Previous work has established the convenience of the invariant representation for: (i) the calculation of the interaction energy of either a finite set or a crystal lattice of charge distributions; (ii) the construction of algorithms for problems which require partial derivatives of the electric field (e.g., mutual torques or induced multipoles and their contribution to the net electrostatic energy). © 1989 Academic Press, Inc.

1. INTRODUCTION

Consider the Cartesian representation of a general spherical harmonic of order N,

$$S_N(\mathbf{x}) = \|\mathbf{x}\|^{-(2N+1)} Y_N(\mathbf{x}), \tag{1a}$$

$$Y_N(\mathbf{x}) = \sum_{\{\mathbf{n} \mid n_1+n_2+n_3=N\}} C(\mathbf{n}) \prod_{i=1}^{3} x_i^{n_i}, \tag{1b}$$

where $Y_N(\mathbf{x})$ is a homogeneous Nth order polynomial which is a solution of Laplace's equation, and is, therefore, a surface spherical harmonic in the sense defined by Hobson [1a]. Hobson has shown [1b] that $Y_N(\mathbf{x})$ defines a set of N unit vectors (characteristic directions) and a scalar multiple (the Nth order moment) in the Maxwell invariant representation of the spherical harmonic:

$$S_N(\mathbf{x}) = P^{(N)} \prod_{i=1}^{3} (\mathbf{s}_i^{(N)} \cdot \boldsymbol{\nabla})(1/\|\mathbf{x}\|); \tag{2a}$$

$$\boldsymbol{\nabla} \equiv \langle \partial/\partial x_1, \partial/\partial x_2, \partial/\partial x_3 \rangle. \tag{2b}$$

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His theorem [1b] shows that the characteristic directions, which are unique (except for sign), can be determined as follows. Let:

$$\mathbf{x}_{(j)} = \langle x_{1(j)}, x_{2(j)}, x_{3(j)} \rangle \text{ be } j\text{th simultaneous root of Eqs. (3b), (3c)} \tag{3a}$$

$$x_1^2 + x_2^2 + x_3^2 = 0; \tag{3b}$$

$$Y_N(\mathbf{x}) = 0. \tag{3c}$$

It is clear that each $x_{(j)}$ is complex. Then,

$$\mathbf{s}_j = \mathbf{V}_{(j)}/i\,\|\mathbf{V}_{(j)}\|; \tag{4a}$$

$$\mathbf{V}_{(j)} = \begin{vmatrix} \mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3 \\ x_{1(j)} & x_{2(j)} & x_{3(j)} \\ x_{1(j)}^* & x_{2(j)}^* & x_{3(j)}^* \end{vmatrix}.^{1} \tag{4b}$$

A general algorithm [2] for the construction of the characteristic directions for an arbitrary Nth order spherical harmonic requires the determination of the complex roots of a homogeneous polynomial of either order N or $2N$ in a single variable. This paper presents a significant simplification of this algorithm and establishes general forms for arbitrary order for the special case in which the coefficients $C(\mathbf{n})$ of the spherical harmonic, Eqs. (1), have the symmetry of harmonics defined by the moments of a cylindrically symmetric distribution. This algorithm is simple to program and is considerably more efficient. Furthermore, it gave more accurate sets of characteristic directions than the general algorithm [2] did for the spherical harmonics in the following practically important problem (the results will be briefly summarized in Section 3). Consider the calculation of the electrostatic potential $U(\mathbf{R})$ defined by an unpolarized charge density $\rho(\mathbf{r})$. In SI units,

$$U(\mathbf{R}) = (4\pi\varepsilon_0)^{-1} \int \rho(\mathbf{r}) \|\mathbf{R} - \mathbf{r}\|^{-1}\, d\mathbf{r}. \tag{5}$$

A Taylor series expansion about $\mathbf{r} = \mathbf{0}$ gives a series which converges absolutely and uniformly for $\mathbf{R}$ exterior to any sphere containing $\rho(\mathbf{r})$. (In molecular problems, since the isolated molecular charge density decreases exponentially with distance, this Taylor series (permanent multipole expansion) still converges asymptotically.) Since

$$\partial/\partial r_j \|\mathbf{R} - \mathbf{r}\|^{-1}|_{\mathbf{r}=\mathbf{0}} = -\partial/\partial R_j \|\mathbf{R} - \mathbf{0}\|^{-1}, \tag{6}$$

[1] It is clear that V_j has purely imaginary components. Nevertheless, the factor i was omitted both in Hobson's book [1] and in a paper giving a general algorithm for the construction of the $\mathbf{s}_j$ [2].

The series can be written in the form:

$$U(\mathbf{R}) = (4\pi\varepsilon_0)^{-1} \sum_{N=0} U_N(\mathbf{R}, \mathbf{0}); \tag{7a}$$

$$U_N(\mathbf{R}, \mathbf{0}) = (-1)^N \sum_{\{\mathbf{n} \mid n_1+n_2+n_3=N\}} M(\mathbf{n}, \mathbf{0}) \left(\prod_{j=1}^{3} n_j! \right)^{-1} \prod_{j=1}^{3} (\partial/\partial R_j)^{n_j} \|\mathbf{R}-\mathbf{0}\|^{-1}; \tag{7b}$$

$$M(\mathbf{n}, \mathbf{0}) = \int \prod_{j=1}^{3} (r_j - o_j)^{n_j} \rho(\mathbf{r})\, d\mathbf{r}. \tag{7c}$$

Since $\|\mathbf{R}-\mathbf{0}\|^{-1}$ is a solution of LaPlace's equation for $\mathbf{R} \neq \mathbf{0}$, each partial derivative is also a solution. This linear combination of spherical harmonics defines the coefficients in the surface spherical harmonic of Eq. (1b) for which the characteristic directions were determined:

$$(-1)^N U_N(\mathbf{R}, \mathbf{0}) = \|\mathbf{x}\|^{-(2N+1)} Y_N(\mathbf{x}) = P^{(N)}(\mathbf{0}) \prod_{j=1}^{N} (\mathbf{s}_j \cdot \nabla_{\mathbf{R}}) \|\mathbf{R}-\mathbf{0}\|^{-1}; \tag{8a}$$

$$\mathbf{x} \equiv \mathbf{R} - \mathbf{0}; \tag{8b}$$

$$\nabla_{\mathbf{R}} \equiv \langle \partial/\partial R_1, \partial/\partial R_2, \partial/\partial R_3 \rangle. \tag{8c}$$

Section 2 outlines the general construction of the polynomials in a single variable whose roots define the characteristic directions of Eqs. (2)–(4). It establishes general results about the form of the polynomials and the sets of characteristic directions. It is shown that for any order $N = 4Q + k$, $0 \leqslant k \leqslant 3$, k directions lie along the symmetry axis and the remaining $4Q$ directions occur in Q sets of four characteristic directions each, where each set of directions is determined from the roots of a quadratic equation. Each quadratic has the same form with only one variable coefficient. The unknown Q coefficients are given by the roots of a Qth order polynomial. A simple recursive construction of the polynomial from the known coefficients of the spherical harmonic is given. Section 3 summarizes the computational steps in the new algorithm for the determination of the $\mathbf{s}_j$ and tests of the comparative accuracy of the general and the simplifying algorithms.

2. A Simplified Algorithm for Cylindrically Symmetric Spherical Harmonics

The standard spectroscopic convention that $\mathbf{e}_3$ lies along the rotation axis of highest symmetry has been adopted. Then the coefficients $C(\mathbf{n})$ of the spherical harmonic of Eq. (1) satisfy the conditions:

$$(n_1 \text{ or } n_2 \text{ odd}) \rightarrow C(\mathbf{n}) = 0; \tag{9a}$$

$$(N = 2P) \rightarrow n_3 \text{ is even}; \qquad (N = 2P + 1) \rightarrow n_3 \text{ is odd}; \tag{9b}$$

$$(q_1 = n_2, q_2 = n_1, q_3 = n_3) \rightarrow C(\mathbf{n}) = C(\mathbf{q}). \tag{9c}$$

The first part of the construction of the algorithm for the Nth order spherical harmonic replaces the simultaneous solution of the Nth order polynomial in $\langle x_1, x_2, x_3 \rangle$ (Eqs. (3c), (1b)) and Eq. (3b) with the determination of the roots of a polynomial in a single variable of order equal to the greatest integer $\leqslant N/2$ in the following steps. Suppose N is odd. Let

$$N = 2P + 1. \tag{10}$$

Then the symmetry requirements of Eq. (9a), (9b) imply that a $C(\mathbf{n})$ of Eq. (1b) vanishes unless

$$\mathbf{n} = 2\mathbf{p} + \mathbf{e}_3 = \langle 2p_1, 2p_2, 2p_3 + 1 \rangle, \qquad p_1 + p_2 + p_3 = P. \tag{11}$$

This implies that Eq. (3c) has a root $\mathbf{x}$ for which $x_3 = 0$. The existence of such a root and Eqs. (3b), (4) imply that one characteristic direction lies along the symmetry axis:

$$\exists_j (\mathbf{s}_j = \pm \mathbf{e}_3) \tag{12a}$$

and

$$0 = Y_{2P+1}(\mathbf{x})/x_3 = \sum_{\{\mathbf{p} \mid p_1 + p_2 + p_3 = P\}} \kappa(2\mathbf{p}) \prod_{j=1}^{3} x_j^{2p_j}, \tag{12b}$$

$$\kappa(2\mathbf{p}) = C(2\mathbf{p} + \mathbf{e}_3). \tag{12c}$$

Conversely, suppose N is even:

$$N = 2P. \tag{13a}$$

Then the symmetry requirements of Eq. (9a), (9b) imply that a $C(\mathbf{n})$ of Eq. (1b) vanishes unless

$$\mathbf{n} = 2\mathbf{p} = \langle 2p_1, 2p_2, 2p_3 \rangle, \qquad p_1 + p_2 + p_3 = P. \tag{13b}$$

Thus the equation for an even order has the same form (with a different definition of $\kappa(2\mathbf{p})$):

$$Y_{2P}(\mathbf{x}) = \sum_{\{\mathbf{p} \mid p_1 + p_2 + p_3 = P\}} \kappa(2\mathbf{p}) \prod_{j=1}^{3} x_j^{2P_j} = 0; \tag{14a}$$

$$\kappa(2\mathbf{p}) = C(2\mathbf{p}). \tag{14b}$$

Therefore, for both even and odd N it is convenient to define

$$d_j \equiv x_j^2, \qquad j = 1, 2, 3. \tag{15}$$

Then in both cases the two polynomials Eqs. (3b), (3c) can be replaced by a single Pth order polynomial in d_1 and d_2,

$$Y_P(\langle d_1, d_2\rangle) = \sum_{\{\langle p_1, p_2\rangle \mid p_1+p_2=P\}} C(\langle p_1, p_2\rangle)\, d_1^{p_1} d_2^{p_2} = 0; \tag{16a}$$

$$\{C(\langle p_1, p_2\rangle) \quad \text{(cf. Appendix A for their construction from the } \kappa(2\mathbf{p})). \tag{16b}$$

Since by symmetry no $C(\langle p_1, p_2\rangle)$ vanishes, the only root of Eq. (16a) such that $d_1 = 0$ or $d_2 = 0$ is the trivial root $\langle d_1, d_2\rangle = \langle 0, 0\rangle$. Therefore, Eq. (16) can be replaced by the following Pth order polynomial equation in the variable R_1:

$$R_1 \equiv d_1/d_2; \tag{17a}$$

$$0 = Y_P(R_1) = Y_P(\langle d_1, d_2\rangle)/d_2^P = \sum_{k=0}^{P} C(\langle k, P-k\rangle)\, R_1^k. \tag{17b}$$

The symmetry of the coefficients in the spherical harmonics defined by a cylindrically symmetric distribution (Eq. (9)) implies the following relations between the coefficients of $Y_P(R_1)$, which simplify the solution for the characteristic directions:

$$\text{even } P\ (P=2Q):\ [0 \leqslant k \leqslant Q-1,\ C_k \equiv C(\langle k, P-k\rangle) = C(\langle P-k, k\rangle)],$$
$$C_Q \equiv C(\langle Q, Q\rangle); \tag{18a}$$

$$\text{odd } P\ (P=2Q+1):\ [0 \leqslant k \leqslant Q,\ C_k \equiv C(\langle k, P-k\rangle) = C(\langle P-k, k\rangle). \tag{18b}$$

Thus the normalized Eq. (17) has the convenient symmetry:

$$0 = Y_P(R_1)/C_0 =$$

$$P = 2Q,\ R_1^P + 1 + \gamma_Q(2Q)\, R_1^Q + \sum_{k=1}^{Q-1} \gamma_k(2Q)(R_1^{P-k} + R_1^k); \tag{19a}$$

$$P = 2Q+1,\ R_1^P + 1 + \sum_{k=1}^{Q} \gamma_k(2Q+1)(R_1^{P-k} + R_1^k); \tag{19b}$$

$$1 \leqslant k \leqslant Q, \qquad \gamma_k \equiv C_k/C_0. \tag{19c}$$

It can easily be verified that for odd $P = 2Q+1$, $R_1 = -1$ is a root of the normalized equation (19). Now each root of Eq. (19) defines a simultaneous root of Eqs. (3.b), (3c):

$$\langle x_1, x_2, x_3\rangle = c\langle R_1^{1/2}, 1, [-(1+R_1)]^{1/2}\rangle; \tag{20a}$$

$$c\text{: any arbitrary constant.} \tag{20b}$$

Therefore, Eq. (4) implies that for odd P, this root $R_1 = -1$ yields $2\mathbf{s}_j$ along the symmetry axis $\mathbf{e}_3$. Removal of this root gives a polynomial for the remaining roots of $Y_{2Q+1}(R_1)$ which has the same form as Eq. (19a) for even P:

$$Y'_{2Q}(R_1) \equiv Y_{2Q+1}(R_1)/(R_1+1) = R_1^{2Q} + 1 + \gamma'_Q(2Q)\, R_1^Q + \sum_{k=1}^{Q-1} \gamma'_k(2Q)(R_1^{P'-k} + R_1^k); \tag{21a}$$

$$1 \leqslant k \leqslant Q, \qquad \gamma'_k = \gamma_k - \delta_1^k - (1-\delta_1^k)\, \gamma'_{k-1}; \qquad P' \equiv 2Q. \tag{21b}$$

Thus, Eq. (12a) and the above argument show that for a spherical harmonic of arbitrary order $N = 4Q + k$, $0 \leqslant k \leqslant 3$, k characteristic directions lie along the symmetry axis and the remaining $4Q$ are determined by the roots of the $2Q$th order polynomials which have the symmetry of Eqs. (19a), (19c), (21a), (21b). Furthermore, a mathematical induction argument in Appendix B proves that for arbitrary Q, a product of Q quadratics of identical form,

$$P_Q \equiv \prod_{k=1}^{Q} (1 + e_1^k R_1 + R_1^2), \tag{22}$$

has this symmetry. It only remains to show that coefficients $e_1^1, ..., e_1^Q$ can be determined such that for an arbitrary polynomial having the symmetry of Eqs. (19a), (19c), (21a), (21b):

$$P_Q = Y_{2Q}(R_1) \qquad (\text{or } Y'_{2Q}(R_1)). \tag{23}$$

The following simple argument shows that Eq. (23) has a unique solution for the $e_1^1, ..., e_1^Q$ by giving a recursive construction of a Qth-order polynomial whose roots are the desired coefficients of P_Q for an arbitrary polynomial of the form of $Y_{2Q}(R_1)$.

As shown in Appendix B, the $(Q-1)$th-order product

$$P_{Q-1} \equiv \prod_{k=1}^{Q-1} (1 + e_1^k R_1 + R_1^2) \tag{24a}$$

is a polynomial of the form:

$$P_{Q-1} = R_1^{2(Q-1)} + 1 + \alpha_{Q-1}(2[Q-1])\, R_1^{Q-1} + \sum_{j=1}^{Q-2} \alpha_j(2[Q-1])(R_1^{2[Q-1]-j} + R_1^j). \tag{24b}$$

Therefore, Eq. (23) has the form:

$$P_Q = (1 + e_1 R_1 + R_1^2)\Big(R_1^{2(Q-1)} + 1 + \alpha_{Q-1}(2[Q-1])\, R_1^{Q-1} + \sum_{j=1}^{Q-2} \alpha_j(2[Q-1])(R_1^{2[Q-1]-j} + R_1^j)\Big) = R_1^{2Q} + 1 + \gamma_Q(2Q)\, R_1^Q + \sum_{k=1}^{Q-1} \gamma_k(2Q)(R_1^{2Q-k} + R_1^k). \tag{25}$$

Equating coefficients of R_1^k yields the following identities. The first $(Q-1)$ provide a recursive construction of the α_k as kth-order polynomials in e_1: The Q-th gives the Q-th order polynomial.

$$k=1, \qquad \alpha_1(2[Q-1]) = \gamma_1(2Q) - e_1; \tag{26a}$$

$$k=2=Q, \qquad \gamma_2(2[2]) = 2 + \gamma_1(2[2])\, e_1 - e_1^2; \tag{26b}$$

$$2 \leqslant k \leqslant Q-1, \qquad \alpha_k(2[Q-1]) = \gamma_k(2Q) - e_1 \alpha_{Q-1}(2[Q-1]) - [\alpha_{k-2}(2[Q-1]) \cdot (1-\delta_k^2) + \delta_k^2]. \tag{26c}$$

Thus recursive substitution of the identities for $1 \leqslant p \leqslant Q-1$ yields successively each $\alpha_k(2[Q-1])$ as a kth order polynomial in e_1 whose coefficients are given as functions of $\gamma_1(2Q), ..., \gamma_{Q-1}(2Q)$. Then the desired Qth-order polynomial is the identity:

$$k = Q > 2, \qquad e_1 \alpha_{k-1}(2[Q-1]) + 2\alpha_{Q-2}(2[Q-1]) - \gamma_Q(2Q) = 0. \tag{27}$$

This shows that the order of the polynomial whose roots must be determined has been reduced by at least a factor of 4. Specifically, for any spherical harmonic of order $N = 4Q + k$, $0 \leqslant k \leqslant 3$, instead of solving for the roots of an Nth order polynomial for even N or an $(N-1)$th-order polynomial for odd N, it is only necessary to solve for the roots $[e_1^k, 1 \leqslant 1 \leqslant Q]$ of the Qth order polynomial of Eq. (27) and the roots of Q quadratic equations:

$$1 \leqslant k \leqslant Q, \qquad R_1^k = \{-e_1^k \pm [(e_1^k)^2 - 4]^{1/2}\}/2. \tag{28}$$

Thus for all orders $\leqslant 19$ the numerical determination of roots has been eliminated and the roots can be calculated explicitly using known functions. Note that for all orders $\leqslant 11$ the solution uses only quadratic equations.

The conditions under which one of the four characterstic directions defined by the solution to one of the quadratic equations exactly lies along the symmetry axis have a simple interpretation when $N = 4$ (i.e., $Q = 1$). Equations (4), (20) imply that a characteristic direction defined by a root R_1^k lies exactly on the symmetry axis $\leftrightarrow R_1^k = -1$. By Eq. (28) this is true $\leftrightarrow e_1^k = 2 \leftrightarrow R_1^k = -1$ is a double root and each of the four lies along the axis. For $N = 4$, $e_1 = 2$ only when the moments of the density ρ satisfy an equation which would hold if ρ were spherically symmetric about the expansion center.

The next section summarizes the computational steps for this simplified algorithm and compares the accuracy of the general [2] and this simplified algorithm in test calculations.

3. Summary of the Steps in the Algorithm: Results of Test Calculations

The input for the algorithm is the set of constants $C(\mathbf{n})$ which define the surface spherical harmonic of Eq. (1) and which satisfy the symmetry conditions of Eq. (9). (A Fortran program is available on request which generates the $C(\mathbf{n})$ for a charge density $\rho(\mathbf{r})$ defined by a single determinant wave function over a contracted Gaussian basis set.) The algorithm uses the following computational steps: (i) For any even order $N=2P$ use the $\kappa(2p)$ of Eq. (14b) or for any odd order $N=2P+1$ use the $\kappa(2p)$ of Eq. (12c) to construct the coefficients $C(\langle p_1, p_2\rangle)$ for the Pth order polynomials in 2 variables of Eq. (16) by Appendix A. (ii) When P is even ($P=2Q$) calculate the Q independent coefficients γ_k of Eqs. (19a), (19c); when P is odd ($P=2Q+1$), calculate the Q independent coefficients γ'_k of Eq. (21); (iii) For any order $N=4Q+k$, $0\leqslant k\leqslant 3$, $Q\geqslant 0$, it has been shown that k characteristic directions lie along the symmetry axis $\mathbf{e}_3$ and that the polynomial of order $2Q$ is a product of Q quadratic factors (cf. Eqs. (22), (23)). For $Q\geqslant 2$ construct the Qth order polynomial whose roots are $e_1^1, ..., e_1^Q$, by the Q step recursion of Eqs. (26), (27) and calculate its roots. (iv) For each e_1^k, compute R_1^k by Eq. (28). Then calculate $\langle x_1, x_2, x_3\rangle$ by Eq. (20) and the characteristic directions by Eq. (4). Note that if e_1^k and e_1^j are complex conjugate, only one of the conjugates must be considered explicitly, since the other necessarily yields the complex conjugate for a pair of roots of Eq. (4).

Not only is the new algorithm far simpler, but in each of four test calculations it gave more accurate sets of characteristic directions. The tests involved the determination of the characteristic directions of Eq. (8a) for the moments of Eq. (7c) of the charge density defined by wave functions for the cylindrically symmetric HF molecule. Wave functions both with and without polarization functions in their basis sets were used and characteristic directions were calculated for both single- and two-center expansions [3]. Whereas, it has been shown that for any spherical harmonic of order $N=4Q+k$, $0\leqslant k\leqslant 3$, k characteristic directions lie along the symmetry axis, the error in the root $R_1=-1$ extracted from the higher order polynomials in the general algorithm in several case gave significant off-axis components in two characteristic directions (when $k=2$ or 3). In one case, this was already true at order $N=6$ and in another, at $N=7$. In every case, two were off axis at $N=10$, 11 ($Q=2$; $k=2, 3$), and at $N=14$ ($Q=3$, $k=2$). In one case the off-axis components were in the second decimal (at $N=10$) and in all other cases, in the third decimal.

Consider next the remaining characteristic directions, which do not in general lie along the symmetry axis (those in the Q sets of four characteristic directions each). Comparison of those generated by the new and by the general algorithm also showed significant differences in some cases. Since there was no a priori basis for concluding which of the two sets was more accurate, some check calculations were made for some of the discrepancies. These verified that in the test cases the characteristic directions generated by the new algorithm were more accurate. As might be expected, apparently errors in the determination of the roots $R_1 \neq -1$ were similar to those for $R_1 = -1$ and these gave similar errors in the corresponding characteristic directions. Thus errors in the second and third decimal occurred at $N = 8$.

This algorithm can provide input for the following general algorithms based on the Maxwell invariant representation of the spherical harmonics defined by a charge distribution: (i) the calculation of the electrostatic potential or the electrostatic interaction energy of either a crystal lattice [4a] or a finite collection [4b] of unpolarized charge distributions; (ii) the calculation of induced multipole moments and the contribution of polarization to the net electrostatic energy [4c, d] in both cases; (iii) the calculation of mutual torques (including the induced dipole contribution) in both cases [4e].

Appendix A: Construction of the $C(\langle p_1, p_2 \rangle)$

Both even ($N = 2P$) and odd order ($N = 2P + 1$) spherical harmonics give rise to a polynomial of the form:

$$Y_{2P}(\mathbf{x}) = \sum_{\{\mathbf{p} \mid p_1 + p_2 + p_3 = P\}} \kappa(2\mathbf{p}) \prod_{j=1}^{3} x_j^{2p_j}. \tag{A.1}$$

After substitution of the definition of Eq. (15), this becomes:

$$Y_P(\mathbf{d}) = \sum_{\{\mathbf{p} \mid p_1 + p_2 + p_3 = P\}} \kappa(2\mathbf{p}) \prod_{j=1}^{3} d_j^{p_j}. \tag{A.2}$$

For $N = 2P + 1$, the $\kappa(2\mathbf{p})$ are given by Eq. (12c) and for $N = 2P$, by Eq. (14b). After substitution of the definition of Eq. (15), Eq. (3b) yields $d_3 = -(d_1 + d_2)$. Substitution of $d_3(d_1, d_3)$ in Eq. (A.2) and use of the binomial expansion show that $C(\langle p_1, p_2 \rangle)$ can be constructed in the following steps:

Step 1. For each $\langle p_1, p_2 \rangle$ such that $p_1 + p_2 = P$, set an accumulator $A(\langle p_1, p_2 \rangle) = \kappa(\langle 2p_1, 2p_2, 0 \rangle)$.

Step 2. For each of the remaining $\langle p'_1, p'_2, p'_3 \rangle$ such that $p'_1 + p'_2 + p'_3 = P$ and $p'_3 \neq 0$, make the following additions to the accumulators: For each t_3, $0 \leqslant t_3 \leqslant p'_3$, make the addition to the accumulator $A(\langle p_1, p_2 \rangle)$, where

$$p_1 = p'_1 + p'_3 - t_3 \quad \text{and} \quad p_2 = p'_2 + t_3: \tag{A.3a}$$

$$A(\langle p_1, p_2 \rangle) = (-1)^{p'_3} \{p'_3!/[t_3!(p'_3 - t_3)!]\} \, \kappa(\langle 2p'_1, 2p'_2, 2p'_3 \rangle) + A(\langle p_1, p_2 \rangle). \tag{A.3b}$$

APPENDIX B: Proof that a Product of a Q Quadratics of the Form of Eq. (22) Is a $2Q$th-order Polynomial of the Form of Eqs. (19a), (19b), (21)

Since this is immediate for $Q=1$ (and can be trivially verified for $Q=2$ as well), it is only necessary to show that the induction hypothesis for $Q=Q'$ implies it is true for $Q=Q'+1$. Thus it is necessary to show that the product

$$P=[1+e_1^{Q'+1}R_1+R_1^2][R_1^{2Q'}+1+\gamma_{Q'}(2Q')\,R_1^{Q'} + \sum_{i=1}^{Q'-1} \gamma_i(2Q')(R_1^{2Q'-i}+R_1^i) \tag{B.1a}$$

has the form

$$R_1^{2(Q'+1)}+1+\gamma_{(Q+1)}(2[Q'+1])\,R_1^{(Q'+1)}+\sum_{k=1}^{Q'} \gamma_k(2[Q'+1])(R_1^{2(Q'+1)-k}+R_1^k). \tag{B.1b}$$

For this purpose it is convenient to regroup the terms in 1 and R_1^2 times the summation and to use the grouping

$$\begin{aligned} P = {} & R_1^{2(Q'+1)}+1+[R_1^{2Q'}+R_1^2] \\ & +[e_1^{Q'+1}(R_1^{2Q'+1}+R_1+\gamma_{Q'}(2Q')\,R_1^{Q'+1})]+[\gamma_{Q'}(2Q')(R_1^{Q'}+R_1^{Q'+2})] \\ & +e_1^{Q'+1}\sum_{i=1}^{Q'-1} \gamma_i(2Q')(R_1^{2(Q'+1)-(i+1)}+R_1^{i+1}) \\ & +\sum_{i=1}^{Q'-1} \gamma_i(2Q')(R_1^{2(Q'+1)-(i+2)}+R_1^{i+2}) \\ & +\sum_{i=1}^{Q'-1} \gamma_i(2Q')(R_1^{2(Q'+1)-i}+R_1^i). \end{aligned} \tag{B.2}$$

In the second summation of Eq. (B.2), separate out the term for $i=Q'-1$ and transform the summation index to $j\equiv i+2$ to obtain

$$2\gamma_{Q'-1}(2Q')\,R_1^{Q'+1}+\sum_{j=3}^{Q'} \gamma_{j-2}(2Q')(R_1^{2(Q'+1)-j}+R_1^j). \tag{B.3}$$

Addition of the first [ ] of Eq. (B.2) to Eq. (B.3) gives:

$$2\gamma_{Q'-1}(2Q')\,R_1^{Q'+1}+\sum_{j=2}^{Q'} (\delta_j^2+(1-\delta_j^2)\,\gamma_{j-2}(2Q'))(R_1^{(2Q'+1)-j}+R_1^j). \tag{B.4}$$

Add the third square bracket and the third summation of Eq. (B.2) to obtain:

$$\sum_{i=1}^{Q'} \gamma_i(2Q')(R_1^{2(Q'+1)-i} + R_1^i). \tag{B.5}$$

In the first summation of Eq. (B.2) use the index transformation $j = i + 1$, then add the second square bracket of the same equation to obtain:

$$e_1^{Q'+1}\gamma_{Q'}(2Q')\, R_1^{Q'+1} + \sum_{j=1}^{Q'} [e_1^{Q'+1}\delta_j^1 + (1-\delta_j^1)\, e_1^{Q'+1}\gamma_{j-1}(2Q')](R_1^{2(Q'+1)-j} + R_1^j). \tag{B.6}$$

Thus the product P has the form of Eq. (B.1b) with

$$\gamma_{Q'+1}(2[Q'+1]) = 2\gamma_{Q'-1}(2Q') + e_1^{Q'+1}\gamma_{Q'}(2Q'); \tag{B.7a}$$

$$1 \leqslant k \leqslant Q': \qquad \gamma_k(2[Q'+1]) = e_1^{Q'+1}\,\delta_k^1 + e_1^{Q'+1}\gamma_{k-1}(2Q')(1-\delta_k^1) + \gamma_k(2Q') + (1-\delta_k^1)[\delta_k^2 + (1-\delta_k^2)\,\gamma_{k-2}(2Q')]. \tag{B.7b}$$

References

1. E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Cambridge Univ. Press, London/New York, 1931); (a) p. 119; (b) pp.127, 135–137.
2. M. Mezei and E. S. Campbell, *J. Comput. Phys.* **20**, 110 (1976).
3. M. Mezei and E. S. Campbell, *Theor. Chim. Acta (Berlin)* **43**, 227 (1977).
4. (a) E. S. Campbell, *J. Phys. Chem. Solids* **26**, 1395 (1965); (b) E. S. Campbell and M. Mezei, *J. Comput. Phys.* **21**, 114 (1976); (c) E. S. Campbell, *Helv. Phys. Acta* **40**, 387 (1967); (d) E. S. Campbell and M. Mezei, *Mol. Phys.* **57**, 1201 (1986); (e) E. S. Campbell and M. Mezei, *J. Comput. Phys.* **47**, 245 (1982).