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LETTER TO THE EDITOR

Note on the multipole expansion in the spherical tensor form

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Abstract. Stone's cartesian-spherical transformation formalism is used for a simple, direct derivation of the multipole expansion in the spherical tensor form starting from the cartesian tensor form.

Suppose $\boldsymbol{r}_a$ is the position vector of particle a with respect to an arbitrary origin A and $\boldsymbol{r}_b$ the position vector of particle b with respect to origin B. Let $\boldsymbol{R}$ be the vector connecting the origins A and B, pointing from A to B, and let $\boldsymbol{r}_{ab} = \boldsymbol{R} - \boldsymbol{r}_a + \boldsymbol{r}_b$. One of the problems in several domains of theoretical physics and chemistry is to expand $r_{ab}^{-1} = |\boldsymbol{r}_{ab}|^{-1}$ as a power series in $R^{-1} = |\boldsymbol{R}|^{-1}$—the bipolar or multipole expansion. From the mathematical point of view the multipole expansion is simply a Taylor series of the form (Jansen 1957)

$$\begin{aligned} r_{ab}^{-1} &= \sum_{k=0}^{\infty} (k!)^{-1}[(\boldsymbol{r}_b - \boldsymbol{r}_a)\cdot\boldsymbol{\nabla}]^k (R^{-1}) \\ &= \sum_{l=0}^{\infty}\sum_{L=0}^{\infty} (-1)^l (l!L!)^{-1} (\boldsymbol{r}_a\cdot\boldsymbol{\nabla})^l (\boldsymbol{r}_b\cdot\boldsymbol{\nabla})^L (R^{-1}) \\ &= \sum_{l=0}^{\infty}\sum_{L=0}^{\infty} (-1)^l (l!L!)^{-1} \sum_{\substack{\alpha_1\ldots\alpha_l \\ \beta_1\ldots\beta_L}} r_{a\alpha_1}\times\ldots\times r_{a\alpha_l}\times r_{b\beta_1}\times\ldots\times r_{b\beta_L} \\ &\quad \times\nabla_{\alpha_1}\times\ldots\times\nabla_{\alpha_l}\times\nabla_{\beta_1}\times\ldots\times\nabla_{\beta_L}(R^{-1}); \end{aligned} \tag{1}$$

this series converges if and only if $|\boldsymbol{r}_b - \boldsymbol{r}_a| < R$ (see, e.g., Amos and Crispin 1976). Here $\boldsymbol{\nabla} = \partial/\partial\boldsymbol{R}$ and $r_{a\alpha}$, $r_{b\beta}$ and $\nabla_{\alpha(\beta)}$ are the cartesian components of the vectors $\boldsymbol{r}_a$, $\boldsymbol{r}_b$ and $\boldsymbol{\nabla}$. Many different forms of the series (1) may be found in the literature. Several authors use a similar multipole expansion in the cartesian tensor form (Jansen 1957, 1958, Buckingham 1959, 1967, Kielich 1965a, b, Stogryn 1971) but in many physical applications the spherical tensor form of the multipole series is much more convenient. For example, it can be helpful in the calculation of the molecular multi-centre integrals which appear in quantum chemistry (see, e.g., Steinborn and Ruedenberg 1973 and references therein) and it is very suitable for describing long-range electrostatic interactions between arbitrary charge distributions (Hirschfelder *et al* 1954, Rose 1958, Fontana 1961, Margenau and Kestner 1971, Wormer 1975, Gray 1976, Wormer *et al* 1977, van der Avoird *et al* 1980, Leavitt 1980, Piecuch 1984a, b, c, 1985a, b, Stone and Tough 1984). For our purpose we write the spherical tensor form of the multipole expansion as

$$r_{\mathrm{ab}}^{-1}=\sum_{l=0}^{\infty}\sum_{L=0}^{\infty}(-1)^{L}\binom{2l+2L}{2l}^{1/2}[\boldsymbol{R}_{l}(\boldsymbol{r}_{\mathrm{a}})\otimes\boldsymbol{R}_{L}(\boldsymbol{r}_{\mathrm{b}})]_{l+L}\cdot\boldsymbol{I}_{l+L}(\boldsymbol{R}) \tag{2}$$

where the irreducible tensor product between two sets of irreducible tensors $\boldsymbol{U}_{k_1}=\{U_{k_1q_1}: q_1=-k_1,\ldots,k_1\}$ and $\boldsymbol{V}_{k_2}=\{V_{k_2q_2}: q_2=-k_2,\ldots,k_2\}$ is defined (Fano and Racah 1959) by

$$[\boldsymbol{U}_{k_1}\otimes\boldsymbol{V}_{k_2}]_{kq}=\sum_{q_1q_2}U_{k_1q_1}V_{k_2q_2}\langle k_1q_1,k_2q_2|kq\rangle \tag{3}$$

(here $\langle k_1q_1, k_2q_2 \mid kq\rangle$ is a Clebsch-Gordan coefficient) while the scalar (inner) product is defined (Rose 1957) by

$$\boldsymbol{U}_k\cdot\boldsymbol{V}_k=\sum_q(-1)^qU_{kq}V_{k-q}. \tag{4}$$

Here $R_{lm}(\boldsymbol{r})$ and $I_{lm}(\boldsymbol{r})$ are the regular and irregular solid spherical harmonics defined respectively as

$$R_{lm}(\boldsymbol{r})=r^{l}C_{lm}(\vartheta,\varphi) \tag{5}$$

and

$$I_{lm}(\boldsymbol{r})=r^{-l-1}C_{lm}(\vartheta,\varphi) \tag{6}$$

where $C_{lm}(\vartheta,\varphi)$ is an unnormalised spherical harmonic (Brink and Satchler 1968) and (r,ϑ,φ) are the spherical coordinates of $\boldsymbol{r}$. In (2) we have used the fact that the sets $\boldsymbol{R}_l(\boldsymbol{r})=\{R_{lm}(\boldsymbol{r}): m=-l,\ldots,l\}$ and $\boldsymbol{I}_l(\boldsymbol{r})=\{I_{lm}(\boldsymbol{r}): m=-l,\ldots,-l\}$ form irreducible tensorial sets of order l.

Expression (2) or its special cases (e.g., for $\boldsymbol{R}$ parallel to the z axis of the coordinate system) has been obtained previously by several authors (Carlson and Rushbrooke 1950, Rose 1958, Fontana 1961, Steinborn 1969, Steinborn and Ruedenberg 1973, Wormer 1975, Gray 1976, Leavitt 1980, Stone and Tough 1984). However none of these derivations is achieved directly from the Taylor series (1), although this would seem to be the most natural way. Here we wish to derive the spherical tensor form of the multipole expansion (2) directly from the Taylor series (1). Our straightforward derivation is based on transforming (1) from the cartesian to the spherical tensorial form via the cartesian-spherical (CS) unitary transformation introduced by Stone (1975, 1976). We use Stone's notation within the Condon-Shortley phase convention.

We recall that the CS transformation is defined by

$$T_{\alpha_1\ldots\alpha_n}=\sum_{j_1\ldots j_nm}T_{j_1\ldots j_n;m}\langle j_1\ldots j_n;m\mid\alpha_1\ldots\alpha_n\rangle \tag{7a}$$

$$T_{j_1\ldots j_n;m}=\sum_{\alpha_1\ldots\alpha_n}T_{\alpha_1\ldots\alpha_n}\langle\alpha_1\ldots\alpha_n|j_1\ldots j_n;m\rangle \tag{7b}$$

and

$$\langle j_1\ldots j_n;m|\alpha_1\ldots\alpha_n\rangle=\langle\alpha_1\ldots\alpha_n|j_1\ldots j_n;m\rangle^* \tag{8}$$

where the $T_{j_1\ldots j_n;m}$ are the spherical components of spherical rank j_n of a cartesian tensor $T_{\alpha_1\ldots\alpha_n}$ of cartesian rank n. The subscripts $j_1,j_2,\ldots,j_{n-1}$ denote the intermediate quantum numbers which are required to distinguish between different spherical tensors with the same j_n. j_1 is always equal to one and $(j_{\sigma-1},1,j_\sigma)$ $(\sigma=2,\ldots,n)$ satisfy triangle conditions. As examples of relations (7) we can write (Tough and Stone 1977)

$$R_{lm}(\boldsymbol{r}) = [(2l)!/2^l]^{1/2}(l!)^{-1} \sum_{\alpha_1\ldots\alpha_l} r_{\alpha_1} \times \ldots \times r_{\alpha_l} \times \langle \alpha_1 \ldots \alpha_l | 12 \ldots l; m\rangle \tag{5a}$$

and

$$I_{lm}(\boldsymbol{r}) = (-1)^l [2^l/(2l)!]^{1/2} \sum_{\alpha_1\ldots\alpha_l} \nabla_{\alpha_l} \times \ldots \times \nabla_{\alpha_1}(r^{-1}) \times \langle \alpha_1 \ldots \alpha_l | 12 \ldots l; m\rangle. \tag{6a}$$

We consider the mixed scalar product of the three arbitrary cartesian tensors $A_{\alpha_1\ldots\alpha_r}$, $B_{\beta_1\ldots\beta_s}$ and $C_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s}$, i.e. the expression

$$S_{ABC} = \sum_{\substack{\alpha_1\ldots\alpha_r\\ \beta_1\ldots\beta_s}} A_{\alpha_1\ldots\alpha_r} B_{\beta_1\ldots\beta_s} C_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s}. \tag{9}$$

If $T_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s} = A_{\alpha_1\ldots\alpha_r} B_{\beta_1\ldots\beta_s}$ denotes the outer product of $A_{\alpha_1\ldots\alpha_r}$ and $B_{\beta_1\ldots\beta_s}$ then (Stone 1975, 1976)

$$T_{j_1\ldots j_t;m} = \sum_{k_1\ldots k_s} [\boldsymbol{A}_{j_1\ldots j_r} \otimes \boldsymbol{B}_{k_1\ldots k_s}]_{j_t m}$$

$$\times \prod_{\sigma=2}^{s} \{[(2k_\sigma+1)(2j_{r+\sigma-1}+1)]^{1/2} W(k_{\sigma-1} 1 j_r j_{r+\sigma}; k_\sigma j_{r+\sigma-1})\} \tag{10}$$

where $t = r+s$ and $W(\ldots)$ is a Racah coefficient (Rose 1957). Since

$$S_{ABC} = \sum_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s} T_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s} C_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s} \tag{11}$$

we have (Stone 1975, 1976)

$$S_{ABC} = \sum_{j_1\ldots j_t} (-1)^{t+j_t} \boldsymbol{T}_{j_1\ldots j_t} \cdot \boldsymbol{C}_{j_1\ldots j_t}. \tag{12}$$

Inserting (10) into (12) we obtain the following general result:

$$S_{ABC} = \sum_{\substack{j_1\ldots j_t\\ k_1\ldots k_s}} (-1)^{t+j_t} [\boldsymbol{A}_{j_1\ldots j_r} \otimes \boldsymbol{B}_{k_1\ldots k_s}]_{j_t} \cdot \boldsymbol{C}_{j_1\ldots j_t}$$

$$\times \prod_{\sigma=2}^{s} \{[(2k_\sigma+1)(2j_{r+\sigma-1}+1)]^{1/2} W(k_{\sigma-1} 1 j_r j_{r+\sigma}; k_\sigma j_{r+\sigma-1})\}_{t=r+s}. \tag{13}$$

As a special case of (13) we assume that the cartesian tensor $C_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s}$ of rank $t = r+s$ is symmetric and traceless in each pair of its indices. Tough and Stone (1977; appendix) have shown that the only non-vanishing spherical components of $C_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s}$ are $C_{12\ldots t;m}$ ($m = -t, \ldots, t$). Thus we have

$$S_{ABC} = \sum_{k_1\ldots k_s} [\boldsymbol{A}_{12\ldots r} \otimes \boldsymbol{B}_{k_1\ldots k_s}]_{r+s} \cdot \boldsymbol{C}_{12\ldots r+s}$$

$$\times \prod_{\sigma=2}^{s} \{[(2k_\sigma+1)(2r+2\sigma-1)]^{1/2} W(k_{\sigma-1} 1\, r\, r+\sigma; k_\sigma\, r+\sigma-1)\}. \tag{14}$$

From the definition of the irreducible tensor product (3) it follows that $[\boldsymbol{A}_{12\ldots r} \otimes \boldsymbol{B}_{k_1\ldots k_s}]_{r+s}$ does not vanish only if (r, k_s, $r+s$) satisfy the triangle conditions. This means that $k_s \geqslant s$. But $k_1 = 1$ and the ($k_{\sigma-1}$, 1, k_σ) ($\sigma = 2, \ldots, s$) triangle conditions require that $k_\sigma \leqslant \sigma$. Consequently the summation over $k_1, \ldots, k_s$ in equation (14) reduces to the single term satisfying $k_\sigma = \sigma$ ($\sigma = 1, 2, \ldots, s$). Since (Rose 1957)

$$W(\sigma-1\, 1\, r\, r+\sigma; \sigma\, r+\sigma-1) = [(2\sigma+1)(2r+2\sigma-1)]^{-1/2} \tag{15}$$

we get the following general expression for S_{ABC} when the cartesian tensor $C_{\alpha_1\ldots\alpha_r\beta_1\ldots\beta_s}$ is symmetric and traceless in each pair of its indices:

$$S_{ABC}=[\boldsymbol{A}_{12\ldots r}\otimes\boldsymbol{B}_{12\ldots s}]_{r+s}\cdot\boldsymbol{C}_{12\ldots r+s}. \tag{16}$$

Now we use our result (16) to derive (2) directly from (1). The Taylor series (1) can be rewritten as

$$r_{\mathrm{ab}}^{-1}=\sum_{l=0}^{\infty}\sum_{L=0}^{\infty}(-1)^l(l!\,L!)^{-1}S_{\tilde{A}\tilde{B}\tilde{C}} \tag{17}$$

where

$$\tilde{A}_{\alpha_1\ldots\alpha_l}=r_{\mathrm{a}\alpha_1}\times\ldots\times r_{\mathrm{a}\alpha_l}$$
$$\tilde{B}_{\beta_1\ldots\beta_L}=r_{\mathrm{b}\beta_1}\times\ldots\times r_{\mathrm{b}\beta_L}$$
$$\tilde{C}_{\alpha_1\ldots\alpha_l\beta_1\ldots\beta_L}=\nabla_{\alpha_1}\times\ldots\times\nabla_{\alpha_l}\times\nabla_{\beta_1}\times\ldots\times\nabla_{\beta_L}(R^{-1}).$$

The cartesian tensor $\nabla_{\alpha_1}\times\ldots\times\nabla_{\alpha_l}\times\nabla_{\beta_1}\times\ldots\times\nabla_{\beta_L}(R^{-1})$ is symmetric and traceless in each pair of its indices (because R^{-1} is the solution of Laplace's equation $\nabla^2 f=0$) so we can apply (16) to the quantities $S_{\tilde{A}\tilde{B}\tilde{C}}$ which appear in (17). From (5a) and (6a) it follows immediately that

$$\tilde{\boldsymbol{A}}_{12\ldots l}=l!\,[2^l/(2l)!]^{1/2}\boldsymbol{R}_l(\boldsymbol{r}_{\mathrm{a}}) \tag{18}$$

$$\tilde{\boldsymbol{B}}_{12\ldots L}=L!\,[2^L/(2L)!]^{1/2}\boldsymbol{R}_L(\boldsymbol{r}_{\mathrm{b}}) \tag{19}$$

$$\tilde{\boldsymbol{C}}_{12\ldots l+L}=(-1)^{l+L}[(2l+2L)!/2^{l+L}]^{1/2}\boldsymbol{I}_{l+L}(\boldsymbol{R}). \tag{20}$$

Substituting (18), (19) and (20) into (16) we obtain

$$S_{\tilde{A}\tilde{B}\tilde{C}}=(-1)^{l+L}l!\,L!\binom{2l+2L}{2l}^{1/2}[\boldsymbol{R}_l(\boldsymbol{r}_{\mathrm{a}})\otimes\boldsymbol{R}_L(\boldsymbol{r}_{\mathrm{b}})]_{l+L}\cdot\boldsymbol{I}_{l+L}(\boldsymbol{R}). \tag{21}$$

If we insert (21) into (17) we get the spherical tensor form of the multipole expansion (2).

We see that Stone's CS transformation formalism has allowed us to derive the spherical tensor form of the multipole expansion in a very natural way, i.e. directly, starting from the Taylor series (1). This means that the ingenious CS transformation formalism can be treated as a powerful group-theoretical method which preserves the conceptual simplicity of Taylor expansion methods. Our derivation of (2) is very compact and shows the direct connection between the cartesian and spherical tensor forms of the multipole expansion; these forms are the most popular. The convergence criterion for expansion (2), i.e. $|\boldsymbol{r}_{\mathrm{b}}-\boldsymbol{r}_{\mathrm{a}}|<R$, cannot be determined easily from some previous derivations of the spherical tensor form of the multipole series. However, in our method the convergence criterion for expansion (2) is fulfilled automatically because it is valid for series (1). Finally, we note that the general formula (13) and its special case (16) can be useful in other physical applications of the spherical tensor algebra.

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