Physica **61** (1972) 481–505 © *North-Holland Publishing Co.*

MULTIPOLE EXPANSION OF THE RETARDED INTERATOMIC DISPERSION ENERGY

II. EVALUATION IN THE SPHERICAL-TENSOR FORMALISM

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Received 16 February 1972

Synopsis

The multipole expansion of the retarded interatomic dispersion energy is evaluated in the spherical-tensor formalism. The multipole expansion of the electrostatic dispersion energy follows as a special case.

1. *Introduction.* In a preceding paper[1]) we derived an expression for the retarded dispersion energy of two nondegenerate ground-state atoms. It was given as a series expansion containing matrix elements of the cartesian components of all atomic multipole moments. In the following we shall elaborate this expression by employing the spherical-tensor formalism. The result contains the radial dependence of the interaction energy in a more explicit form. For small interatomic separations the spherical multipole expansion of the electrostatic dispersion energy is recovered.

2. *The retarded dispersion energy: summary of previous results.* The expressions (57)–(60) of paper I, giving the interatomic dispersion energy, contain sums over the intermediate states $|\alpha\rangle$ and $|\beta\rangle$ of the atoms labelled a and b; these atomic states could remain unspecified there. From now on we shall choose them as simultaneous eigenstates of the free atomic hamiltonian, the total atomic angular

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momentum and its third component, so that they may be written as

$$|\alpha\rangle = |N_a, L_a, M_a\rangle; \tag{1}$$

the eigenvalues are $\varepsilon_a + \hbar c k_{N_a}$ (with the ground-state energy ε_a), $\hbar^2 L_a(L_a + 1)$ and $\hbar M_a$, respectively. Correspondingly spherical-tensor notation[2]) will be used instead of the cartesian-tensor notation.

In paper I we assumed the ground states to be nondegenerate. The formalism given there does not change, however, if, more generally, one considers the dispersion energy of atoms in degenerate ground states that form irreducible sets under rotations (in other words states characterized by total angular momenta L_a^0 and L_b^0); in that case the formulae represent the dispersion energy averaged over all orientations of both atoms a and b[3]). The complete interaction energy then contains, apart from this dispersion energy, also an induction energy, arising from the terms in the perturbation formulae with ground-level intermediate states for one of the atoms. (In paper I these terms dropped out due to the rotational invariance of the nondegenerate ground states considered there.) This induction energy, which is found to be nonretarded, shall be dealt with in a forthcoming paper.

The general expression for the retarded dispersion energy may be written now as

$$V(R) = \sum_{\sigma = \mathrm{I, II, III}} V_\sigma(R), \tag{2}$$

with

$$V_\sigma(R) = (2L_a^0 + 1)^{-1} (2L_b^0 + 1)^{-1} \sum_{\substack{N_a(\neq 0), L_a, M_a, M_a^0 \\ N_b(\neq 0), L_b, M_b, M_b^0}} \sum_{\substack{\varkappa, \lambda, \mu, \nu \\ k, l, m, n}}$$

$$\times \frac{1}{\pi \hbar c} E_a^\sigma T^\sigma_{\varkappa\lambda\mu\nu klmn} P^\varkappa_{a,1} P^\lambda_{b,1} \nabla_1^k \nabla_1^l P^{*\mu}_{a,2} P^{*\nu}_{b,2} \nabla_2^m \nabla_2^n \frac{f_a^\sigma(R_1 + R_2)}{R_1 R_2}$$

$$+ (a \leftrightarrow b), \tag{3}$$

$\sigma = \mathrm{I, II, III}$. The functions E_a^σ, depending on k_{N_a} and k_{N_b}, are given by:

$$E_a^{\mathrm{I}} = 1/k_{N_a}^2 k_{N_b} (k_{N_a}^2 - k_{N_b}^2), \tag{4}$$

$$E_a^{\mathrm{II}} = 1/k_{N_a}^4 k_{N_b}, \tag{5}$$

$$E_a^{\mathrm{III}} = 1/k_{N_a} k_{N_b}. \tag{6}$$

The vector $P^\varkappa_{a,\iota}$ stands for the matrix element

$$\langle 0, L_a^0, M_a^0 | \sum_j \tfrac{1}{2} \{p^\varkappa_{aj}, \mathrm{e}^{-r_{aj} \cdot \nabla_\iota}\} | N_a, L_a, M_a \rangle, \tag{7}$$

with $i = 1, 2$; it contains a sum over all electrons j of atom a with coordinates $\boldsymbol{r}_{aj}$ (with respect to the fixed nucleus) and momenta $\boldsymbol{p}_{aj}$. The expressions for the other vector matrix elements are obtained if a is replaced by b and $\boldsymbol{\nabla}_i$ by $-\boldsymbol{\nabla}_i$. These vectors are contracted with tensors $T^{\sigma}_{\varkappa\lambda\mu\nu klmn}$, which read in spherical notation:

$$T^{\mathrm{I}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa k}\Delta_{\lambda l}\Delta_{\mu m}\Delta_{\nu n} - 2\Delta_{\varkappa k}\Delta_{\lambda l}\Delta_{\mu\nu}\Delta_{mn}$$
$$+ \Delta_{\varkappa\lambda}\Delta_{kl}\Delta_{\mu\nu}\Delta_{mn} + (\varkappa, \lambda, k, l \leftrightarrow \mu, \nu, m, n), \tag{8}$$

$$T^{\mathrm{II}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa\mu}\Delta_{kl}\Delta_{\lambda m}\Delta_{\nu n} - \Delta_{\varkappa\lambda}\Delta_{kl}\Delta_{\mu\nu}\Delta_{mn} + (\varkappa, \lambda, k, l \leftrightarrow \mu, \nu, m, n), \tag{9}$$

$$T^{\mathrm{III}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa\mu}\Delta_{kl}\Delta_{\lambda m}\Delta_{\nu n} - \tfrac{1}{2}\Delta_{\varkappa\lambda}\Delta_{kl}\Delta_{\mu\nu}\Delta_{mn}$$
$$- \tfrac{3}{2}\Delta_{\varkappa k}\Delta_{\lambda l}\Delta_{\mu\nu}\Delta_{mn} + (\varkappa, \lambda, k, l \leftrightarrow \mu, \nu, m, n), \tag{10}$$

with the abbreviation: $\Delta_{\alpha\beta} = (-1)^{1-\alpha}\delta_{\alpha,-\beta}$; the symbol $(\varkappa, \lambda, k, l \leftrightarrow \mu, \nu, m, n)$ represents the terms obtained from the preceding ones by interchanging $(\varkappa, \lambda, k, l)$ and (μ, ν, m, n). Finally the functions $f^{\sigma}_a(R_1 + R_2)$ in (3) are defined as

$$f^{\mathrm{I}}_a(R_1 + R_2) = P\,(k_{N_a}R_1 + k_{N_a}R_2), \tag{11}$$

$$f^{\mathrm{II}}_a(R_1 + R_2) = G\,(k_{N_a}R_1 + k_{N_a}R_2), \tag{12}$$

$$f^{\mathrm{III}}_a(R_1 + R_2) = \tfrac{1}{6}\,(R_1 + R_2)^3 \log\,(R_1 + R_2), \tag{13}$$

with the auxiliary functions

$$P(x) = \int_0^\infty \mathrm{d}t\,\frac{\sin t}{x + t}; \qquad G(x) = P(x) - x\log x - \tfrac{1}{2}\pi. \tag{14}$$

After the differentiations have been carried out the vectors $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ are to be put equal to the radius vector $\boldsymbol{R} = \boldsymbol{R}_b - \boldsymbol{R}_a$ pointing from the nucleus of atom a to that of b. The expression (3) is symmetric in a and b due to the occurrence of the terms represented by $(a \leftrightarrow b)$.

3. *Separation of the angular and radial parts.* The central quantity in the expression (3) for the partial interaction energy $V_\sigma(R)$ is the tensor

$$P^{\varkappa}_{a,1}P^{\lambda}_{b,1}\nabla^k_1\nabla^l_1P^{*\mu}_{a,2}P^{*\nu}_{b,2}\nabla^m_2\nabla^n_2\,f^{\sigma}_a(R_1 + R_2)/R_1R_2, \tag{15}$$

in which (7) is to be inserted; it contains the atomic matrix elements as well as functions of the interatomic separations R_1 and R_2, acted upon by the corresponding nabla operators $\boldsymbol{\nabla}_1$ and $\boldsymbol{\nabla}_2$. In this section we shall evaluate (15) by separating the parts depending on the angular and radial variables.

In appendix A it is shown how the vectorial differentiations occurring in (15) may be dealt with. From (A18) we obtain the following expansion in spherical harmonics Y_L^M:

$$
\begin{aligned}
&\mathrm{e}^{-r_a\cdot\nabla_1}\,\mathrm{e}^{r_b\cdot\nabla_1}\nabla_1^k\nabla_1^l f(R_1)/R_1 \\
&= \sum_{\substack{L_{a1},L_{b1},L_1\\ M_{a1},M_{b1},M_1}} (-1)^{L_{a1}+M_{a1}+M_{b1}+M_1}(4\pi)^{3/2}\,[(2L_{a1}+1)(2L_{b1}+1)(2L_1+1)]^{\frac{1}{2}} \\
&\times \left\langle \begin{matrix} L_{a1} & L_{b1} & 1 & 1 & L_1 \\ -M_{a1} & -M_{b1} & k & l & -M_1 \end{matrix} \right\rangle \\
&\times \sum_{s_{a1},s_{b1}=0}^{\infty} \frac{r_a^{L_{a1}+2s_{a1}}Y_{L_{a1}}^{M_{a1}}(\omega_a)}{(2s_{a1})!!\,(2L_{a1}+2s_{a1}+1)!!}\,\frac{r_b^{L_{b1}+2s_{b1}}Y_{L_{b1}}^{M_{b1}}(\omega_b)}{(2s_{b1})!!\,(2L_{b1}+2s_{b1}+1)!!} \\
&\times Y_{L_1}^{M_1}(\Omega_1)\,R_1^{L_1}\left(\frac{1}{R_1}\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{L_1}\frac{1}{R_1}\left(\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{N_1-L_1} f(R_1).
\end{aligned} \tag{16}
$$

Here we introduced the symbol

$$
\left\langle \begin{matrix} L_1 & \cdots & L_n \\ M_1 & \cdots & M_n \end{matrix} \right\rangle = \frac{1}{4\pi}\int \mathrm{d}\Omega \prod_{i=1}^{n}\left(\frac{4\pi}{2L_i+1}\right)^{\frac{1}{2}} Y_{L_i}^{M_i}(\Omega); \tag{17}
$$

we shall call it a Gaunt[4]) coefficient. For nonvanishing Gaunt coefficients rotational invariance leads to the conditions $L_j \leqq \sum_{i(\neq j)} L_i$ and $\sum_i M_i = 0$, while the parity of the spherical harmonics implies $\sum_i L_i$ to be even. As a consequence only combinations of quantum numbers with $L_{a1} + L_{b1} + L_1$ even contribute to (16). The (L, M) summations in (16) are extended over the values $\{L = 0, 1, 2, \ldots;\ M = -L, -L+1, \ldots, L\}$. Furthermore the abbreviation $N_1 = L_{a1} + L_{b1} + 2s_{a1} + 2s_{b1} + 2$ has been used. As in paper I we omit, for brevity, the summations over the electrons.

Let us define now the spherical-tensor operator $\Omega_L^M(L_{a1}, s_{a1})$ by:

$$
\begin{aligned}
&\frac{1}{(2s_{a1})!!\,(2L_{a1}+2s_{a1}+1)!!}\left(\frac{4\pi}{2L_{a1}+1}\right)^{\frac{1}{2}}\tfrac{1}{2}\{p_a^{\varkappa}, r_a^{L_{a1}+2s_{a1}}Y_{L_{a1}}^{M_{a1}}(\omega_a)\} \\
&= \sum_{L_{a1}', M_{a1}'} (-1)^{L_{a1}'-M_{a1}'}(2L_{a1}'+1)^{\frac{1}{2}}\begin{pmatrix} L_{a1} & 1 & L_{a1}' \\ M_{a1} & \varkappa & -M_{a1}' \end{pmatrix}\Omega_{L_{a1}'}^{M_{a1}'}(L_{a1}, s_{a1}),
\end{aligned} \tag{18}
$$

where a $3j$-symbol occurs. With the help of the orthogonality relation

$$
\begin{aligned}
&\sum_{M_1,M_2}(-1)^{L_1-M_1+L_2-M_2}\begin{pmatrix} L_1 & L_2 & L_3 \\ M_1 & M_2 & M_3 \end{pmatrix}\begin{pmatrix} L_1 & L_2 & L_3' \\ -M_1 & -M_2 & -M_3' \end{pmatrix} \\
&= \frac{(-1)^{L_3-M_3}}{2L_3+1}\,\delta_{L_3,L_3'}\delta_{M_3,M_3'}\{L_1, L_2, L_3\}
\end{aligned} \tag{19}
$$

(with $\{L_1, L_2, L_3\}$ equal to unity if L_1, L_2, L_3 satisfy the triangular condition, and zero otherwise) one finds the inverse of (18) as

$$\Omega_{L_{a1}'}^{M_{a1}'}(L_{a1}, s_{a1}) = \sum_{\varkappa, M_{a1}} (-1)^{1-\varkappa+L_{a1}-M_{a1}} (2L_{a1}' + 1)^{\frac{1}{2}} \begin{pmatrix} L_{a1} & 1 & L_{a1}' \\ -M_{a1} & -\varkappa & M_{a1}' \end{pmatrix} \times \frac{1}{(2s_{a1})!!\,(2L_{a1} + 2s_{a1} + 1)!!} \left(\frac{4\pi}{2L_{a1} + 1}\right)^{\frac{1}{2}} \times \tfrac{1}{2} \{p_a^{\varkappa}, r_a^{L_{a1}+2s_{a1}} Y_{L_{a1}}^{M_{a1}}(\omega_a)\}. \quad (20)$$

The matrix elements of the operator $\Omega_{L_{a1}'}^{M_{a1}'}(L_{a1}, s_{a1})$ may be factorized with the help of the Wigner–Eckart theorem:

$$\langle 0, L_a^0, M_a^0 |\, \Omega_{L_{a1}'}^{M_{a1}'}(L_{a1}, s_{a1})\, | N_a, L_a, M_a \rangle = (-1)^{L_a^0 - M_a^0} \begin{pmatrix} L_a^0 & L_{a1}' & L_a \\ -M_a^0 & M_{a1}' & M_a \end{pmatrix} \langle 0, L_a^0 \| \,\Omega_{L_{a1}'}(L_{a1}, s_{a1})\, \| N_a, L_a \rangle. \quad (21)$$

Instead of the reduced matrix elements we will employ in the following the symbols

$$\Omega_{N_a, L_a}(L_{a1}', L_{a1}, s_{a1}) = (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 \| \,\Omega_{L_{a1}'}(L_{a1}, s_{a1})\, \| N_a, L_a \rangle. \quad (22)$$

Using (21) and (22) one gets for the matrix element of the operator at the left-hand side of (18):

$$\frac{1}{(2s_{a1})!!\,(2L_{a1} + 2s_{a1} + 1)!!} \left(\frac{4\pi}{2L_{a1} + 1}\right)^{\frac{1}{2}} \times \langle 0, L_a^0, M_a^0 |\, \tfrac{1}{2} \{p_a^{\varkappa}, r_a^{L_{a1}+2s_{a1}} Y_{L_{a1}}^{M_{a1}}(\omega_a)\}\, | N_a, L_a, M_a \rangle$$
$$= \sum_{L_{a1}', M_{a1}'} (-1)^{L_a^0 - M_a^0 + L_{a1}' - M_{a1}'} [(2L_a^0 + 1)(2L_{a1}' + 1)]^{\frac{1}{2}} \times \begin{pmatrix} L_{a1} & 1 & L_{a1}' \\ M_{a1} & \varkappa & -M_{a1}' \end{pmatrix} \begin{pmatrix} L_a^0 & L_{a1}' & L_a \\ -M_a^0 & M_{a1}' & M_a \end{pmatrix} \Omega_{N_a, L_a}(L_{a1}', L_{a1}, s_{a1}). \quad (23)$$

From (20), (21) and (22) the inverse of this relation is obtained as

$$\begin{pmatrix} L_a^0 & L_{a1}' & L_a \\ -M_a^0 & M_{a1}' & M_a \end{pmatrix} \Omega_{N_a, L_a}(L_{a1}', L_{a1}, s_{a1}) = \sum_{M_{a1}, \varkappa} (-1)^{L_a^0 - M_a^0 + L_{a1} - M_{a1} + 1 - \varkappa} \left(\frac{2L_{a1}' + 1}{2L_a^0 + 1}\right)^{\frac{1}{2}} \times \begin{pmatrix} L_{a1} & 1 & L_{a1}' \\ -M_{a1} & -\varkappa & M_{a1}' \end{pmatrix} \frac{1}{(2s_{a1})!!\,(2L_{a1} + 2s_{a1} + 1)!!} \left(\frac{4\pi}{2L_{a1} + 1}\right)^{\frac{1}{2}} \times \langle 0, L_a^0, M_a^0 |\, \tfrac{1}{2} \{p_a^{\varkappa}, r_a^{L_{a1}+2s_{a1}} Y_{L_{a1}}^{M_{a1}}(\omega_a)\}\, | N_a, L_a, M_a \rangle. \quad (24)$$

Formulae analogous to (18) and (20)–(24) may be given for atom b. Then from (16) with (7) and (23) (together with their counterparts for atom b) one finds:

$$P^{\varkappa}_{a,1} P^{\lambda}_{b,1} \nabla^k_1 \nabla^l_1 \frac{f(R_1)}{R_1}$$

$$= \sum_{\substack{L_{a1}, L_{b1}, L_{a1}', L_{b1}', L_1 \\ M_{a1}, M_{b1}, M_{a1}', M_{b1}', M_1}} (-1)^{L_{a1}+L_a{}^0-M_a{}^0+L_b{}^0-M_b{}^0+\Sigma(L-M)} (4\pi)^{\frac{1}{2}} (2L_{a1}+1)$$

$$\times (2L_{b1}+1) [(2L_a^0+1)(2L_b^0+1)(2L_{a1}'+1)(2L_{b1}'+1)(2L_1+1)]^{\frac{1}{2}}$$

$$\times \left\langle \begin{matrix} L_{a1} & L_{b1} & 1 & 1 & L_1 \\ -M_{a1} & -M_{b1} & k & l & -M_1 \end{matrix} \right\rangle \begin{pmatrix} L_{a1} & 1 & L_{a1}' \\ M_{a1} & \varkappa & -M_{a1}' \end{pmatrix} \begin{pmatrix} L_a^0 & L_{a1}' & L_a \\ -M_a^0 & M_{a1}' & M_a \end{pmatrix}$$

$$\times \begin{pmatrix} L_{b1} & 1 & L_{b1}' \\ M_{b1} & \lambda & -M_{b1}' \end{pmatrix} \begin{pmatrix} L_b^0 & L_{b1}' & L_b \\ -M_b^0 & M_{b1}' & M_b \end{pmatrix} \Omega_{N_a, L_a}(L_{a1}', L_{a1}, s_{a1})$$

$$\times \Omega_{N_b, L_b}(L_{b1}', L_{b1}, s_{b1}) \, Y_{L_1}^{M_1}(\Omega_1) \, R_1^{L_1} \left(\frac{1}{R_1}\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{L_1} \frac{1}{R_1} \left(\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{N_1-L_1} f(R_1). \tag{25}$$

The symbol $\sum(L-M)$ appearing in the exponent of the phase factor is defined here such as to contain a term $L-M$ for each summation over a magnetic quantum number M. An expression for $P^{*\mu}_{a,2} P^{*\nu}_{b,2} \nabla^m_2 \nabla^n_2 f(R_2)/R_2$ is found by taking the complex conjugate of the right-hand side of (25), replacing 1 by 2 and $(\varkappa, \lambda, k, l)$ by $(-\mu, -\nu, -m, -n)$, and multiplying by the phase factor $(-1)^{\mu+\nu+m+n}$ (this prescription follows from the relation $X^{\mu *} = (-1)^{\mu}(X^*)^{-\mu}$ for an arbitrary spherical vector X^{μ}). Combining that expression with (25) one may obtain for (15) an expansion in spherical-tensor notation in which the dependence on the directions of $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ is given by a product of spherical harmonics

$$Y_{L_1}^{M_1}(\Omega_1) \, Y_{L_2}^{M_2 *}(\Omega_2) = (-1)^{M_2} \, Y_{L_1}^{M_1}(\Omega_1) \, Y_{L_2}^{-M_2}(\Omega_2).$$

Both Ω_1 and Ω_2 may now be put equal to the solid angle Ω that characterizes the direction of $\boldsymbol{R}$. Then the coupling relation

$$Y_{L_1}^{M_1}(\Omega) \, Y_{L_2}^{-M_2}(\Omega) = \sum_{L', M'} (-1)^{M'} \left[\frac{(2L_1+1)(2L_2+1)(2L'+1)}{4\pi}\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} L_1 & L_2 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L' \\ M_1 & -M_2 & -M' \end{pmatrix} Y_{L'}^{M'}(\Omega) \tag{26}$$

may be employed. As a consequence of rotational invariance the interatomic potential (averaged over the ground states) depends only on the length of the radius vector $\boldsymbol{R} = \boldsymbol{R}_b - \boldsymbol{R}_a$, so that only the term with $L' = 0$ from (26) will contribute. For that reason we will replace the left-hand side of (26) by

$$(1/4\pi)(-1)^{M_1}\,\delta_{L_1,L_2}\delta_{M_1,M_2}. \tag{27}$$

(A formal justification of this step will be given at the end of section 4.)

For the expression (15), summed over all intermediate states with the same energy and total angular momentum, and averaged over the ground states, we have found now the expansion:

$$\begin{aligned}
&(2L_a^0+1)^{-1}(2L_b^0+1)^{-1}\\
&\quad\times\sum_{M_a^0,M_b^0,M_a,M_b} P_{a,1}^{\varkappa}P_{b,1}^{\lambda}\nabla_1^k\nabla_1^l P_{a,2}^{*\mu}P_{b,2}^{*\nu}\nabla_2^m\nabla_2^n f_a^\sigma(R_1+R_2)/R_1R_2\\
&=\sum_{\substack{L_{a1},L_{a2},L_{a1}',L_{a2}',L\\ L_{b1},L_{b2},L_{b1}',L_{b2}'}}\ \sum_{\substack{s_{a1},s_{a2}\\ s_{b1},s_{b2}=0}}^{\infty}(2L_{a1}+1)(2L_{b1}+1)(2L_{a2}+1)\\
&\quad\times(2L_{b2}+1)(2L+1)\,[(2L_{a1}'+1)(2L_{b1}'+1)(2L_{a2}'+1)(2L_{b2}'+1)]^{\frac{1}{2}}\\
&\quad\times\Omega_{N_a,L_a}(L_{a1}',L_{a1},s_{a1})\,\Omega_{N_b,L_b}(L_{b1}',L_{b1},s_{b1})\\
&\quad\times\Omega_{N_a,L_a}^{*}(L_{a2}',L_{a2},s_{a2})\,\Omega_{N_b,L_b}^{*}(L_{b2}',L_{b2},s_{b2})\\
&\quad\times\hat{K}_a^{\varkappa\lambda\mu\nu klmn}R_1^L\left(\frac{1}{R_1}\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^L\frac{1}{R_1}\left(\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{N_1-L}\\
&\quad\times R_2^L\left(\frac{1}{R_2}\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^L\frac{1}{R_2}\left(\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^{N_2-L} f_a^\sigma(R_1+R_2);
\end{aligned}\tag{28}$$

here the "angular" tensor $\hat{K}_a^{\varkappa\lambda\mu\nu klmn}$ is defined as

$$\begin{aligned}
\hat{K}_a^{\varkappa\lambda\mu\nu klmn} &= \sum_{\substack{M_{a1},M_{a2},M_{a1}',M_{a2}',M_a^0,M_a,M\\ M_{b1},M_{b2},M_{b1}',M_{b2}',M_b^0,M_b}}(-1)^{\Sigma(L-M)}\\
&\quad\times\left\langle\begin{matrix}L_{a1} & L_{b1} & 1 & 1 & L\\ -M_{a1} & -M_{b1} & k & l & -M\end{matrix}\right\rangle\left\langle\begin{matrix}L_{a2} & L_{b2} & 1 & 1 & L\\ M_{a2} & M_{b2} & m & n & M\end{matrix}\right\rangle\\
&\quad\times\begin{pmatrix}L_{a1} & 1 & L_{a1}'\\ M_{a1} & \varkappa & -M_{a1}'\end{pmatrix}\begin{pmatrix}L_a^0 & L_{a1}' & L_a\\ -M_a^0 & M_{a1}' & M_a\end{pmatrix}\begin{pmatrix}L_{b1} & 1 & L_{b1}'\\ M_{b1} & \lambda & -M_{b1}'\end{pmatrix}\\
&\quad\times\begin{pmatrix}L_b^0 & L_{b1}' & L_b\\ -M_b^0 & M_{b1}' & M_b\end{pmatrix}\begin{pmatrix}L_{a2} & 1 & L_{a2}'\\ -M_{a2} & \mu & M_{a2}'\end{pmatrix}\begin{pmatrix}L_a^0 & L_{a2}' & L_a\\ M_a^0 & -M_{a2}' & -M_a\end{pmatrix}\\
&\quad\times\begin{pmatrix}L_{b2} & 1 & L_{b2}'\\ -M_{b2} & \nu & M_{b2}'\end{pmatrix}\begin{pmatrix}L_b^0 & L_{b2}' & L_b\\ M_b^0 & -M_{b2}' & -M_b\end{pmatrix}.
\end{aligned}\tag{29}$$

Its counterpart $\hat{K}_b$ follows by interchanging a and b or, equivalently, $(\varkappa, \mu)$ and (λ, ν). In deriving the phase factor in $\hat{K}_a$ we employed, apart from the properties of the 3j-symbols and Gaunt coefficients, the space-inversion invariance of the free atomic hamiltonian; in fact, only products of matrix elements with quantum numbers satisfying

$$L_{a1} + L_{a2} = \text{even}, \qquad L_{b1} + L_{b2} = \text{even}, \tag{30}$$

contribute to (28).

In this section we obtained expression (28) for the tensor that occurs, contracted with T^σ, in each of the partial dispersion energies $V_\sigma(R)$, (3). The main feature of this result consists in the fact that the angular and radial parts of this tensor have been separated in such a way that its indices $\varkappa, \lambda, \mu, \nu, k, l, m, n$ appear only in $\hat{K}_a$, given by (29). Consequently, in carrying out the contractions, we may confine ourselves to a consideration of T^σ and $\hat{K}_a$. This will be the subject of the next section.

4. *The angular coefficients.* To carry out the contractions of the tensors T^σ, (8)–(10), and $\hat{K}_a$, (29), it is convenient to employ a graphical notation[5,6]) for the 3j-symbols, the Gaunt coefficients and sums of products of these. A summary of this notation and the associated calculus is given in appendix B. In particular, the coefficient $\hat{K}_a$ may be represented by the graph in fig. 1. Here a simple vertex

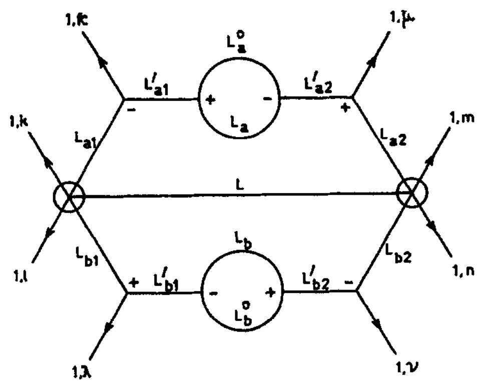


Fig. 1. Graphical representation of the angular tensor $\hat{K}_a^{\varkappa\lambda\mu\nu klmn}$.

corresponds to a 3j-symbol (the sign at a vertex indicating the order of the columns in the 3j-symbol), an encircled vertex to a Gaunt coefficient. For each internal line L the summation over the corresponding azimuthal quantum number M is carried out, after multiplication with a phase factor $(-1)^{L-M}$.

A simplification of the diagram is achieved by eliminating the double bonds with the help of the transformation (B7). In fact we may write:

$$\hat{K}_a^{\varkappa\lambda\mu\nu klmn} = \delta_{L_{a1}', L_{a2}'}\delta_{L_{b1}', L_{b2}'} (2L_{a1}' + 1)^{-1} (2L_{b1}' + 1)^{-1} \times \{L_a^0, L_{a1}', L_a\} \{L_b^0, L_{b1}', L_b\} K_a^{\varkappa\lambda\mu\nu klmn}, \tag{31}$$

where the tensor K_a is represented by the diagram in fig. 2. From now on $L_{a1}' = L_{a2}'$ will be replaced by L_a' and $L_{b1}' = L_{b2}'$ by L_b'. The triangular delta's occurring in (31) may be omitted after substitution of $\hat{\mathsf{K}}_a$ into (28), since they are already present implicitly in the definition (21), with (22), of the reduced matrix elements.

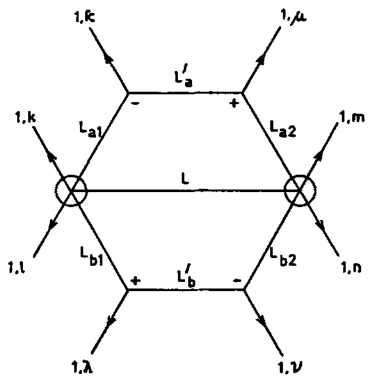


Fig. 2. The angular tensor $K_a^{\varkappa\lambda\mu\nu klmn}$.

The tensors T^σ, (8)–(10), are linear combinations of the tensors

$$T^{\mathrm{A}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa k}\Delta_{\lambda l}\Delta_{\mu m}\Delta_{\nu n}, \tag{32}$$

$$T^{\mathrm{B}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa\lambda}\Delta_{kl}\Delta_{\mu\nu}\Delta_{mn}, \tag{33}$$

$$T^{\mathrm{C(1)}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa k}\Delta_{\lambda l}\Delta_{\mu\nu}\Delta_{mn}, \tag{34}$$

$$T^{\mathrm{D(1)}}_{\varkappa\lambda\mu\nu klmn} = \Delta_{\varkappa\mu}\Delta_{kl}\Delta_{\lambda m}\Delta_{\nu n}, \tag{35}$$

together with $\mathsf{T}^{\mathrm{C(2)}}$ and $\mathsf{T}^{\mathrm{D(2)}}$, which follow from $\mathsf{T}^{\mathrm{C(1)}}$ and $\mathsf{T}^{\mathrm{D(1)}}$ by the interchange of $(\varkappa, \lambda, k, l)$ and (μ, ν, m, n). In terms of these six tensors the expressions (8)–(10) may now be written as

$$\mathsf{T}^{\mathrm{I}} = 2\mathsf{T}^{\mathrm{A}} + 2\mathsf{T}^{\mathrm{B}} - 2\mathsf{T}^{\mathrm{C(1)}} - 2\mathsf{T}^{\mathrm{C(2)}}, \tag{36}$$

$$\mathsf{T}^{\mathrm{II}} = -2\mathsf{T}^{\mathrm{B}} + \mathsf{T}^{\mathrm{D(1)}} + \mathsf{T}^{\mathrm{D(2)}}, \tag{37}$$

$$\mathsf{T}^{\mathrm{III}} = -\mathsf{T}^{\mathrm{B}} - \tfrac{3}{2}\mathsf{T}^{\mathrm{C(1)}} - \tfrac{3}{2}\mathsf{T}^{\mathrm{C(2)}} + \mathsf{T}^{\mathrm{D(1)}} + \mathsf{T}^{\mathrm{D(2)}}. \tag{38}$$

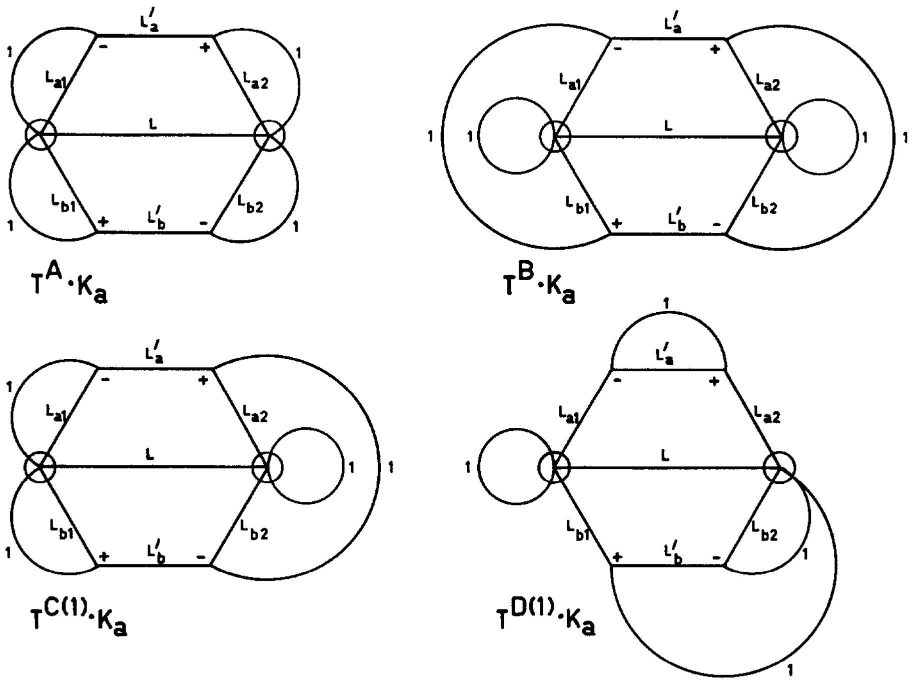


Fig. 3. Contraction of K_a with T^{A}, T^{B}, $\mathsf{T}^{\mathrm{C}(1)}$ and $\mathsf{T}^{\mathrm{D}(1)}$.

Contraction of the tensor K_a with the six tensors $\mathsf{T}^{\mathrm{A}}, \mathsf{T}^{\mathrm{B}}, \ldots, \mathsf{T}^{\mathrm{D}(2)}$ is graphically represented (see appendix B) by a corresponding pairwise linkage of the external lines in fig. 2. In this way one gets for the angular coefficients $\mathsf{T}^{\mathrm{A}} \cdot \mathsf{K}_a$, $\mathsf{T}^{\mathrm{B}} \cdot \mathsf{K}_a$, $\mathsf{T}^{\mathrm{C}(1)} \cdot \mathsf{K}_a$ and $\mathsf{T}^{\mathrm{D}(1)} \cdot \mathsf{K}_a$ the diagrams drawn in fig. 3. The loops and the double bonds ending at the (encircled) Gaunt coefficient vertices may be removed with the help of the transformations (B18) and (B20). Then the set of diagrams given in fig. 4 is obtained. The basic graphs of (B9) and (B15), with (B14), may be recognized now. In fact $\mathsf{T}^{\mathrm{A}} \cdot \mathsf{K}_a$ and $\mathsf{T}^{\mathrm{C}(1)} \cdot \mathsf{K}_a$ are already expressed completely in terms of these graphs. The same may be achieved for $\mathsf{T}^{\mathrm{B}} \cdot \mathsf{K}_a$ by cutting the lines L_a', L, L_b' with the help of the transformation rule (B5), while $\mathsf{T}^{\mathrm{D}(1)} \cdot \mathsf{K}_a$ gets a final form when in its leading diagram (B7) is used, see fig. 5. If the diagrams of figs. 4 and 5 are translated into algebraic form and the parity selection rules (30) are used the angular coefficients become:

$$\mathsf{T}^{\mathrm{A}} \cdot \mathsf{K}_a = \begin{pmatrix} L_a' & 1 & L_{a1} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b' & 1 & L_{b1} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_a' & 1 & L_{a2} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b' & 1 & L_{b2} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_a' & L_b' & L \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{39}$$

$$\mathsf{T}^{\mathrm{B}} \cdot \mathsf{K}_a = \begin{pmatrix} L_{a1} & L_{b1} & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L_a' & L_b' & L \\ L_{b1} & L_{a1} & 1 \end{Bmatrix} \begin{pmatrix} L_{a2} & L_{b2} & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L_a' & L_b' & L \\ L_{b2} & L_{a2} & 1 \end{Bmatrix}, \tag{40}$$

$$\mathsf{T}^{C(1)} \cdot \mathsf{K}_a = (-1)^{L+1} \begin{pmatrix} L'_a & 1 & L_{a1} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L'_b & 1 & L_{b1} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_{a2} & L_{b2} & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L'_a & L'_b & L \\ 0 & 0 & 0 \end{pmatrix} \times \begin{Bmatrix} L'_a & L'_b & L \\ L_{b2} & L_{a2} & 1 \end{Bmatrix}, \tag{41}$$

$$\mathsf{T}^{D(1)} \cdot \mathsf{K}_a = \delta_{L_{a1}, L_{a2}} (2L_{a1} + 1)^{-1} \times \{L'_a, 1, L_{a1}\} \begin{pmatrix} L_{a1} & L_{b1} & L \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} L'_b & 1 & L_{b1} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L'_b & 1 & L_{b2} \\ 0 & 0 & 0 \end{pmatrix}. \tag{42}$$

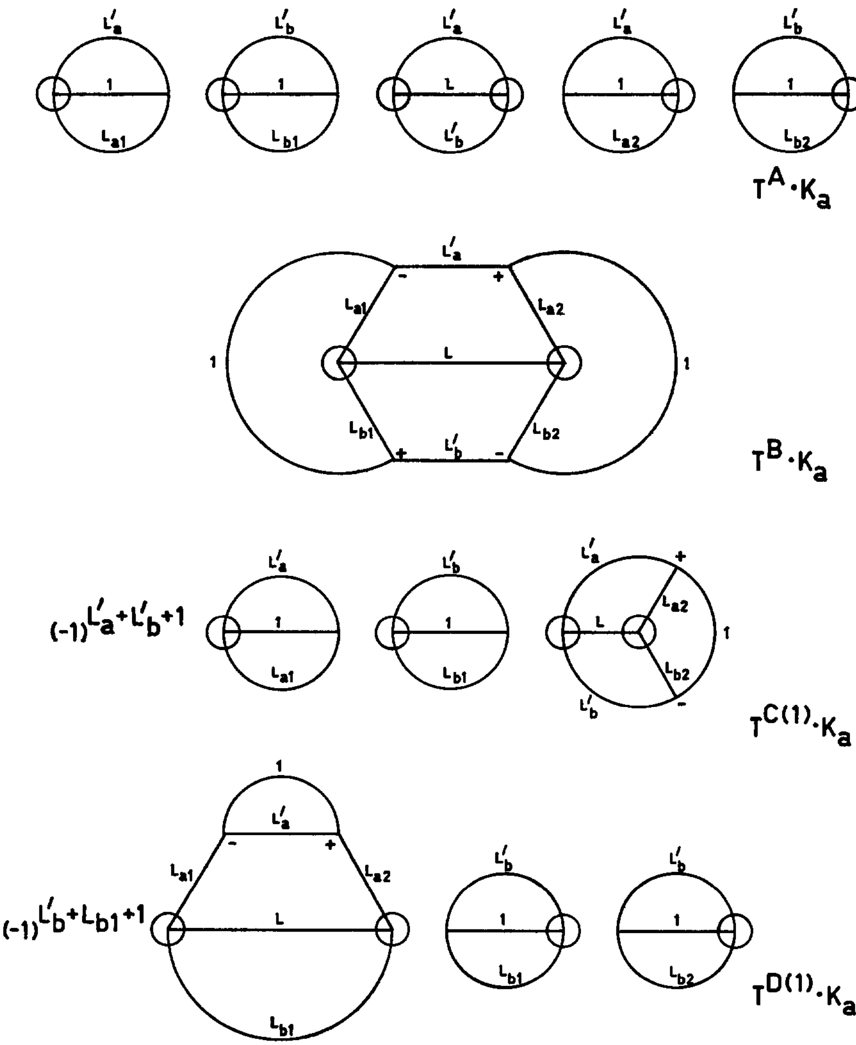


FIG. 4. Simplified diagrams of the angular coefficients $\mathsf{T}^A \cdot \mathsf{K}_a$, $\mathsf{T}^B \cdot \mathsf{K}_a$, $\mathsf{T}^{C(1)} \cdot \mathsf{K}_a$ and $\mathsf{T}^{D(1)} \cdot \mathsf{K}_a$.

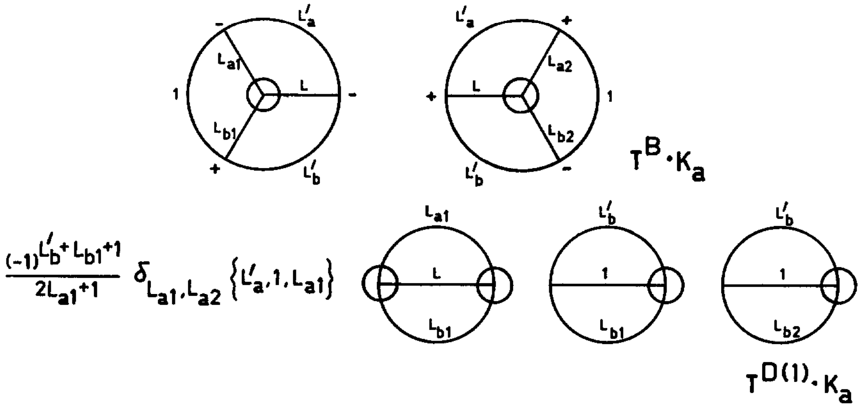
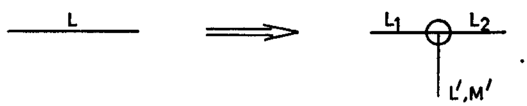


Fig. 5. Final forms for the diagrams of $\mathsf{T}^{\mathrm{B}} \cdot \mathsf{K}_a$ and $\mathsf{T}^{\mathrm{D}(1)} \cdot \mathsf{K}_a$.

The expressions for $\mathsf{T}^{\mathrm{C}(2)} \cdot \mathsf{K}_a$ and $\mathsf{T}^{\mathrm{D}(2)} \cdot \mathsf{K}_a$ follow from (41) and (42) by an interchange of the indices 1 and 2.

With the help of the graphical analysis employed above a formal justification may now be given for putting $L' = 0$ in the right-hand side of (26). If instead the complete expression had been used we would have found diagrams which follow from those of fig. 3 by replacing the internal line L in the following way:



(43)

Application of (B3) would have led then again to $L' = 0$.

5. *The retarded interatomic dispersion energy in spherical-tensor notation.* The results of the preceding sections may be used now to bring the three contributions $V_\sigma(R)$, (3), to the retarded interatomic dispersion energy $V(R)$ in a form that contains the dependence on the interatomic separation R more explicitly. In fact, upon substituting (28) with (31) into (3), we get:

$$
\begin{aligned}
V_\sigma(R) = &\sum_{\substack{N_a(\neq 0),\, L_a,\, L_a',\, L_{a1},\, L_{a2},\, L \\ N_b(\neq 0),\, L_b,\, L_b',\, L_{b1},\, L_{b2}}} \;\sum_{\substack{s_{a1},\, s_{a2},\\ s_{b1},\, s_{b2}=0}}^{\infty} \left(\frac{e}{mc}\right)^4 \frac{1}{\pi\hbar c} \\
&\times E_a^\sigma (2L_{a1}+1)(2L_{b1}+1)(2L_{a2}+1)(2L_{b2}+1)(2L+1) \\
&\times \Omega_{N_a, L_a}(L_a', L_{a1}, s_{a1})\, \Omega_{N_b, L_b}(L_b', L_{b1}, s_{b1}) \\
&\times \Omega^*_{N_a, L_a}(L_a', L_{a2}, s_{a2})\, \Omega^*_{N_b, L_b}(L_b', L_{b2}, s_{b2})\, \mathsf{T}^\sigma \cdot \mathsf{K}_a \\
&\times R_1^L \left(\frac{1}{R_1}\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^L \frac{1}{R_1}\left(\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{N_1-L} R_2^L \left(\frac{1}{R_2}\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^L \frac{1}{R_2}\left(\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^{N_2-L} \\
&\times f_a^\sigma(R_1+R_2) + (a \leftrightarrow b),
\end{aligned} \tag{44}
$$

with σ = I, II, III. The coefficients $\mathsf{T}^{\sigma} \cdot \mathsf{K}_a$ follow from (36)–(42) and the reduced matrix elements Ω_{N_a,L_a} and Ω_{N_b,L_b} from (24). The expressions for E_a^{σ} and f_a^{σ} have been given in (4)–(6) and (11)–(13), respectively. Furthermore N_i stands for the sum $L_{ai} + L_{bi} + 2s_{ai} + 2s_{bi} + 2$ $(i = 1, 2)$.

The radial part of (44) may be written in an alternative form with the help of the identity (A29), which leads to the relation

$$R_1^L\left(\frac{1}{R_1}\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^L\frac{1}{R_1}\left(\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^{N_1-L} R_2^L\left(\frac{1}{R_2}\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^L\frac{1}{R_2}\left(\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^{N_2-L} f_a^{\sigma}(R_1+R_2)$$

$$= \sum_{k_1,k_2=0}^{L} (-\tfrac{1}{2})^{k_1+k_2}\,(L+\tfrac{1}{2},k_1)\,(L+\tfrac{1}{2},k_2)$$

$$\times \frac{1}{R^{k_1+k_2+2}}\left\{\frac{\mathrm{d}}{\mathrm{d}\,(2R)}\right\}^{N_1+N_2-k_1-k_2} f_a^{\sigma}(2R), \tag{45}$$

where at the right-hand side both R_1 and R_2 could be put equal to the interatomic separation R; the Hankel symbol $(L + \frac{1}{2}, k)$ stands for $(L + k)!/k!\,(L - k)!$. If one uses the formulae [see (I.69), (I.70)]

$$\frac{\mathrm{d}P}{\mathrm{d}x} = -Q(x); \qquad \frac{\mathrm{d}^2P}{\mathrm{d}x^2} = -P(x) + x^{-1}, \tag{46}$$

the differentiations of the functions f_a^{σ} may be evaluated explicitly.

The expression (2) with (44) gives the complete multipole expansion of the retarded dispersion energy for atoms in their lowest energy states. If these ground states are degenerate in such a way as to form irreducible sets under rotations, it represents the dispersion energy averaged over all atomic orientations.

The general formula (44) simplifies considerably in the electrostatic limit. This will be demonstrated in the following section.

6. *The electrostatic limit.* As has been shown in section 4 of paper I the expression for the electrostatic dispersion energy is obtained by considering the dominant term at short distances in $V(R)$. That term is contained in $V_{\mathrm{I}}(R)$ and may be found by replacing f_a^{I} by its limiting value $\frac{1}{2}\pi$ [see (I.64)].

The form of the radial part of (44) shows that only terms with $N_1 = N_2 = L$ do contribute in that case, so that we have:

$$R_1^L\left(\frac{1}{R_1}\frac{\mathrm{d}}{\mathrm{d}R_1}\right)^L\frac{1}{R_1}\, R_2^L\left(\frac{1}{R_2}\frac{\mathrm{d}}{\mathrm{d}R_2}\right)^L\frac{1}{R_2}\,\frac{\pi}{2} = \frac{\{(2L-1)!!\}^2}{R^{2L+2}}\,\frac{\pi}{2}, \tag{47}$$

where R_1 and R_2 have been put equal to R.

The angular coefficient $\mathsf{T}^{\mathrm{I}} \cdot \mathsf{K}_a$ is different from zero only if the inequalities $L \leqq L_{ai} + L_{bi} + 2$ $(i = 1, 2)$ are satisfied, as follows from (36) and (39)–(41).

Since $N_i = L_{ai} + L_{bi} + 2s_{ai} + 2s_{bi} + 2$ equals L, the variables s_{ai} and s_{bi} are zero and the equalities $L = L_{ai} + L_{bi} + 2$ hold. Then one has $L_{ai} + 1 = L'_a$, $L_{bi} + 1 = L'_b$ and $L'_a + L'_b = L$, so that the angular coefficient becomes:

$$\mathsf{T}^{\mathrm{I}} \cdot \mathsf{K}_a = 2 \begin{pmatrix} L'_a & 1 & L'_a - 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} L'_b & 1 & L'_b - 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} L'_a & L'_b & L'_a + L'_b \\ 0 & 0 & 0 \end{pmatrix}^2 . \quad (48)$$

The reduced matrix elements in (44) contain in the present case tensor operators with components of the type Ω_L^M $(L - 1, 0)$, which follow from (20). From (A21), with (A19) and (A22), an expression for

$$(\mathrm{i}m/\hbar)\, [H(a), r_a^L Y_L^M (\omega_a)] = \tfrac{1}{2} \{\boldsymbol{p}_a \cdot \nabla_{r_a}, r_a^L Y_L^M (\omega_a)\}$$

may be derived. Comparing this expression with that for Ω_L^M $(L - 1, 0)$ we find, in terms of reduced matrix elements [see (22)]:

$$\Omega_{N_a, L_a} (L, L - 1, 0)$$
$$= -\mathrm{i}mck_{N_a} \frac{(-1)^L (4\pi)^{\frac{1}{2}}}{(2L + 1)!!\,(2L - 1)} \begin{pmatrix} L & 1 & L - 1 \\ 0 & 0 & 0 \end{pmatrix}^{-1} (r^L Y_L)_{N_a, L_a}, \quad (49)$$

where we used the notation

$$(r^L Y_L)_{N_a, L_a} \equiv (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 \| \, r^L Y_L (\omega_a) \, \| N_a, L_a \rangle .$$

Inserting in (48) the 3*j*-symbol

$$\begin{pmatrix} L'_a & L'_b & L'_a + L'_b \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{L_a' + L_b'} \left[\frac{(2L'_a)!\,(2L'_b)!}{(2L'_a + 2L'_b + 1)!} \right]^{\frac{1}{2}} \frac{(L'_a + L'_b)!}{L'_a!\, L'_b!}, \quad (50)$$

we arrive at the following formula for the electrostatic dispersion energy:

$$V_{\mathrm{es}}(R) = - \sum_{\substack{N_a(\neq 0), L_a, L_a' \\ N_b(\neq 0), L_b, L_b'}} \frac{16\pi^2 e^4 (2L'_a + 2L'_b)!}{\hbar c (k_{N_a} + k_{N_b}) (2L'_a + 1)(2L'_b + 1)(2L'_a + 1)!\,(2L'_b + 1)!}$$
$$\times \, |(r^{L_a'} Y_{L_a'})_{N_a, L_a}|^2 \, |(r^{L_b'} Y_{L_b'})_{N_b, L_b}|^2 \, 1/R^{2L_a' + 2L_b' + 2} . \quad (51)$$

Of course, a shorter derivation of this result may be obtained by starting from (I.11) and inserting the two-centre expansion[7,8]) of the function $f(R) = R^{-1}$ (see appendix A). Along such lines the electrostatic dispersion energy has been studied earlier[9,10]).

In a following paper the short- and long-range behaviour of the general expression (44) will be studied. Furthermore, the contributions of the lowest-order multipoles will be discussed separately.

APPENDIX A

Expansions in spherical harmonics. In this appendix an expansion in spherical harmonics will be derived for the q-fold spatial derivative of a function F depending on the sum $\boldsymbol{R} + \boldsymbol{r}_1 + \cdots + \boldsymbol{r}_p$ of the $p + 1$ vectors $\boldsymbol{R}, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_p$. Employing a formal Taylor expansion we may write this derivative as

$$(\prod_{\alpha=1}^{p} \mathrm{e}^{\boldsymbol{r}_\alpha \cdot \nabla}) \nabla^{m_1} \cdots \nabla^{m_q} F(\boldsymbol{R}), \tag{A1}$$

where $m_1, \ldots, m_q$, with values 0, ± 1, label the components of the nabla operators. Upon expanding the function $F(\boldsymbol{R})$ in spherical harmonics $Y_L^M(\Omega)$ it turns out that we can confine ourselves to a consideration of the expression

$$(\prod_{\alpha=1}^{p} \mathrm{e}^{\boldsymbol{r}_\alpha \cdot \nabla}) \nabla^{m_1} \cdots \nabla^{m_q} f(R)\, Y_L^M(\Omega). \tag{A2}$$

Let us introduce the ancillary variables $\boldsymbol{r}_{p+1}, \ldots, \boldsymbol{r}_{p+q}$ and write the identity

$$(\prod_{\alpha=1}^{p+q} \mathrm{e}^{\boldsymbol{r}_\alpha \cdot \nabla})\, \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}} = (\prod_{\alpha=1}^{p+q} \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_\alpha})\, \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}}. \tag{A3}$$

When we substitute on both sides the expansion of $\exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r})$ in spherical waves:

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}} = 4\pi \sum_{L', M'} (-1)^{M'} \mathrm{i}^{L'} j_{L'}(kr)\, Y_{L'}^{-M'}(\Omega_k)\, Y_{L'}^{M'}(\Omega_r), \tag{A4}$$

we obtain, after multiplication with $Y_L^M(\Omega_k)$ and integration over the solid angle Ω_k,

$$\begin{aligned}
&(\prod_{\alpha=1}^{p+q} \mathrm{e}^{\boldsymbol{r}_\alpha \cdot \nabla})\, \mathrm{i}^L j_L(kR)\, Y_L^M(\Omega) \\
&\quad = \sum_{\substack{L_1, \ldots, L_{p+q}, L' \\ M_1, \ldots, M_{p+q}, M'}} (-1)^{M'} [(2L+1)(2L'+1)]^{\frac{1}{2}} \begin{pmatrix} L_1 & \cdots & L_{p+q} & L & L' \\ M_1 & \cdots & M_{p+q} & -M & M' \end{pmatrix} \\
&\quad \times \{\prod_{\alpha=1}^{p+q} (-1)^{M_\alpha} [4\pi(2L_\alpha+1)]^{\frac{1}{2}}\, \mathrm{i}^{L_\alpha} \\
&\quad \times j_{L_\alpha}(kr_\alpha)\, Y_{L_\alpha}^{M_\alpha}(\omega_\alpha)\}\, \mathrm{i}^{L'} j_{L'}(kR)\, Y_{L'}^{M'}(\Omega),
\end{aligned} \tag{A5}$$

with the Gaunt[4]) coefficient

$$\left\langle \begin{matrix} L_1 & \cdots & L_n \\ M_1 & \cdots & M_n \end{matrix} \right\rangle = \frac{1}{4\pi} \int \mathrm{d}\Omega \prod_{i=1}^{n} \left(\frac{4\pi}{2L_i + 1} \right)^{\frac{1}{2}} Y_{L_i}^{M_i}(\Omega). \tag{A6}$$

As may be inferred from the properties of the spherical harmonics, the Gaunt coefficient differs from zero only if $\sum_i L_i$ is even and if the relations $\sum_i M_i = 0$,

$L_j \leqq \sum_{l(\neq j)} L_l$ are satisfied. The (L, M) summations in (A4) and (A5) are extended over the values $\{L = 0, 1, 2, \ldots; M = -L, -L+1, \ldots, L\}$. Equating the terms linear in $\boldsymbol{r}_{p+1}, \ldots, \boldsymbol{r}_{p+q}$ on both sides of (A5) and using the power series expression for the spherical Bessel function[11]):

$$j_L(z) = \sum_{s=0}^{\infty} \frac{(-1)^s z^{L+2s}}{(2s)!!\,(2L+2s+1)!!}, \tag{A7}$$

we get

$$\begin{aligned}
&\left(\prod_{\alpha=1}^{p} \mathrm{e}^{\boldsymbol{r}\cdot\nabla_\alpha}\right)\left(\prod_{\alpha=p+1}^{p+q} \boldsymbol{r}_\alpha\cdot\nabla\right) \mathrm{i}^L j_L(kR)\, Y_L^M(\Omega) \\
&= \sum_{\substack{L_1,\ldots,L_p,L' \\ M_1,\ldots,M_p,M_{p+1},\ldots,M_{p+q},M'}} (-1)^{M'}\left[(2L+1)(2L'+1)\right]^{\frac{1}{2}} \\
&\times \begin{pmatrix} L_1 & \cdots & L_p & 1 & \cdots & 1 & L & L' \\ M_1 & \cdots & M_p & M_{p+1} & \cdots & M_{p+q} & -M & M' \end{pmatrix} \\
&\times \Big\{\prod_{\alpha=1}^{p} (-1)^{M_\alpha}\left[4\pi(2L_\alpha+1)\right]^{\frac{1}{2}} \mathrm{i}^{L_\alpha} j_{L_\alpha}(kr_\alpha)\, Y_{L_\alpha}^{M_\alpha}(\omega_\alpha)\Big\} \\
&\times \left\{\prod_{\alpha=p+1}^{p+q} (-1)^{M_\alpha}\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \mathrm{i}kr_\alpha Y_1^{M_\alpha}(\omega_\alpha)\right\} \mathrm{i}^{L'} j_{L'}(kR)\, Y_{L'}^{M'}(\Omega).
\end{aligned} \tag{A8}$$

The scalar products in the second factor at the left-hand side read in spherical notation:

$$\boldsymbol{r}_\alpha\cdot\nabla = \sum_{M_\alpha} (-1)^{M_\alpha}\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} r_\alpha Y_1^{M_\alpha}(\omega_\alpha)\, \nabla^{-M_\alpha}, \tag{A9}$$

so that we obtain from (A8):

$$\begin{aligned}
&\left(\prod_{\alpha=1}^{p} \mathrm{e}^{\boldsymbol{r}_\alpha\cdot\nabla}\right) \nabla^{m_1}\cdots\nabla^{m_q}\, \mathrm{i}^L j_L(kR)\, Y_L^M(\Omega) \\
&= \sum_{\substack{L_1,\ldots,L_p,L' \\ M_1,\ldots,M_p,M'}} (-1)^{M'}\left[(2L+1)(2L'+1)\right]^{\frac{1}{2}} \\
&\times \begin{pmatrix} L_1 & \cdots & L_p & 1 & \cdots & 1 & L & L' \\ M_1 & \cdots & M_p & -m_1 & \cdots & -m_q & -M & M' \end{pmatrix} \\
&\times \Big\{\prod_{\alpha=1}^{p} (-1)^{M_\alpha}\left[4\pi(2L_\alpha+1)\right]^{\frac{1}{2}} \mathrm{i}^{L_\alpha} j_{L_\alpha}(kr_\alpha)\, Y_{L_\alpha}^{M_\alpha}(\omega_\alpha)\Big\} \\
&\times (\mathrm{i}k)^q\, \mathrm{i}^{L'} j_{L'}(kR)\, Y_{L'}^{M'}(\Omega).
\end{aligned} \tag{A10}$$

With the help of (A7) the curly-bracket expression gets the form:

$$\sum_{s_1, \ldots, s_p=0}^{\infty} \left\{ \prod_{\alpha=1}^{p} (-1)^{M_\alpha} \frac{[4\pi(2L_\alpha + 1)]^{\frac{1}{2}}}{(2s_\alpha)!!\,(2L_\alpha + 2s_\alpha + 1)!!} r_\alpha^{L_\alpha + 2s_\alpha} Y_{L_\alpha}^{M_\alpha}(\omega_\alpha) \right\} (\mathrm{i}k)^{N-q}, \tag{A11}$$

with $N = q + \sum_{\alpha=1}^{p} (L_\alpha + 2s_\alpha)$. The factor $(\mathrm{i}k)^N j_{L'}(kR)$ at the right-hand side of (A10), with (A11) inserted, may be written as $j_L(kR)$, acted upon by a differential operator, if the recurrence relations[11])

$$\left(\frac{1}{z}\frac{\mathrm{d}}{\mathrm{d}z}\right)^m z^{n+1} j_n(z) = z^{n-m+1} j_{n-m}(z),$$
$$\left(\frac{1}{z}\frac{\mathrm{d}}{\mathrm{d}z}\right)^m z^{-n} j_n(z) = (-1)^m z^{-n-m} j_{n+m}(z) \tag{A12}$$

are employed. In fact, for $L \geqq L'$ we use the first relation, choosing the values $n = L$ and $n - m = L'$, and employ subsequently $\frac{1}{2}(N - L + L')$ times the differential equation

$$j_L(z) = -\left\{\frac{1}{z}\frac{\mathrm{d}^2}{\mathrm{d}z^2} z - \frac{L(L+1)}{z^2}\right\} j_L(z) = -z^{L-1}\frac{\mathrm{d}}{\mathrm{d}z}\frac{1}{z^{2L}}\frac{\mathrm{d}}{\mathrm{d}z} z^{L+1} j_L(z). \tag{A13}$$

[$N - L + L'$ is even as follows from the Gaunt coefficient occurring in (A10).] Then we find:

$$(\mathrm{i}k)^N \mathrm{i}^{L'} j_{L'}(kR) = D(L', L, N)\, \mathrm{i}^L j_L(kR), \tag{A14}$$

where the differential operator $D(L', L, N)$ is defined as

$$D(L', L, N) = \frac{1}{R^{L'+1}}\left(\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}R}\right)^{L-L'}\left(R^{2L}\frac{\mathrm{d}}{\mathrm{d}R}\frac{1}{R^{2L}}\frac{\mathrm{d}}{\mathrm{d}R}\right)^{\frac{1}{2}(N-L+L')} R^{L+1} \qquad (L \geqq L'). \tag{A15}$$

For $L \leqq L'$ we employ the second relation of (A12), with $n = L$ and $n + m = L'$, and then $\frac{1}{2}(N + L - L')$ times (A13). In this way an identity of the form (A14) is obtained in which now the differential operator

$$D(L', L, N) = R^{L'}\left(\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}R}\right)^{L'-L}\frac{1}{R^{2L+1}}\left(R^{2L}\frac{\mathrm{d}}{\mathrm{d}R}\frac{1}{R^{2L}}\frac{\mathrm{d}}{\mathrm{d}R}\right)^{\frac{1}{2}(N+L-L')} R^{L+1} \qquad (L \leqq L') \tag{A16}$$

appears. Upon substituting (A14) into (A10) with (A11), multiplying the result by an arbitrary function of k and integrating over k, we finally arrive at the formula

$$\left(\prod_{\alpha=1}^{p} e^{r_\alpha\cdot\nabla}\right)\nabla^{m_1}\cdots\nabla^{m_q} f(R)\, Y_L^M(\Omega) = \sum_{\substack{L_1,\ldots,L_p,L'\\ M_1,\ldots,M_p,M'}} (-1)^{M'}\,[(2L+1)(2L'+1)]^{\frac{1}{2}}$$
$$\times \begin{pmatrix} L_1 & \cdots & L_p & 1 & \cdots & 1 & L & L' \\ M_1 & \cdots & M_p & -m_1 & \cdots & -m_q & -M & M' \end{pmatrix}$$
$$\times \sum_{s_1,\ldots,s_p=0}^{\infty} \left\{ \prod_{\alpha=1}^{p} (-1)^{M_\alpha} \frac{[4\pi(2L_\alpha+1)]^{\frac{1}{2}}}{(2s_\alpha)!!\,(2L_\alpha+2s_\alpha+1)!!}\, r_\alpha^{L_\alpha+2s_\alpha} Y_{L_\alpha}^{M_\alpha}(\omega_\alpha) \right\}$$
$$\times\, Y_{L'}^{M'}(\Omega)\, D(L',L,N) f(R), \tag{A17}$$

which gives the expansion of the expression (A2) in spherical harmonics. A special case of the general formula is found by considering a spherically symmetric function, *i.e.* by putting $L = 0$. In that case (A17) reduces to:

$$\left(\prod_{\alpha=1}^{p} e^{r_\alpha\cdot\nabla}\right)\nabla^{m_1}\cdots\nabla^{m_q} f(R) = \sum_{\substack{L_1,\ldots,L_p,L\\ M_1,\ldots,M_p,M}} (-1)^{M}\,[4\pi(2L+1)]^{\frac{1}{2}}$$
$$\times \begin{pmatrix} L_1 & \cdots & L_p & 1 & \cdots & 1 & L \\ M_1 & \cdots & M_p & -m_1 & \cdots & -m_q & M \end{pmatrix}$$
$$\times \sum_{s_1,\ldots,s_p=0}^{\infty} \left\{ \prod_{\alpha=1}^{p} (-1)^{M_\alpha} \frac{[4\pi(2L_\alpha+1)]^{\frac{1}{2}}}{(2s_\alpha)!!\,(2L_\alpha+2s_\alpha+1)!!}\, r_\alpha^{L_\alpha+2s_\alpha} Y_{L_\alpha}^{M_\alpha}(\omega_\alpha) \right\}$$
$$\times\, Y_L^M(\Omega)\, R^L \left(\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}R}\right)^{L} \frac{1}{R}\left(\frac{\mathrm{d}}{\mathrm{d}R}\right)^{N-L} R f(R), \tag{A18}$$

with $N = q + \sum_{\alpha=1}^{p}(L_\alpha + 2s_\alpha)$. Expansions of the types obtained above have been studied earlier, with the help of different methods. In fact, (A17) for $p = 1, q = 0$, and (A18) for $p = 2$, $q = 0$ have been written down by Sack[12]). For $p = 2$, $q = 2$ the result is employed in the main text of this paper.

Formula (A17) simplifies considerably when it is applied to solid harmonics, *i.e.* when for $f(R)$ the functions R^L and R^{-L-1} are chosen. For the regular solid harmonics only (A15), with $N = L - L'$, plays a role, while for the irregular ones only (A16) with $N = L' - L$ contributes. Then one has:

$$D(L',L,L-L')\,R^L = [(2L+1)!!/(2L'+1)!!]\,R^{L'} \qquad (L \geqq L'), \tag{A19}$$

$$D(L',L,L'-L)\,R^{-L-1} = (-1)^{L'-L}\,[(2L'-1)!!/(2L-1)!!]\,R^{-L'-1} \qquad (L \leqq L'). \tag{A20}$$

The form of the Gaunt coefficient in (A17) now implies that in both cases only terms with $s_1 = \cdots = s_p = 0$ occur. Substitution of (A19) or (A20) yields, for the values $p = 1, 2$, $q = 0$, the results found already by Chiu[13]).

Finally, for $p = 0$ the general formula (A17) reduces to:

$$\nabla^{m_1} \cdots \nabla^{m_q} f(R)\, Y_L^M(\Omega) = \sum_{L', M'} (-1)^{M'} [(2L+1)(2L'+1)]^{\frac{1}{2}}$$
$$\times \left\langle \begin{matrix} 1 & \cdots & 1 & L & L' \\ -m_1 & \cdots & -m_q & -M & M' \end{matrix} \right\rangle Y_{L'}^{M'}(\Omega)\, D(L', L, q) f(R). \tag{A21}$$

Putting moreover $q = 1$ one recovers the well-known gradient formula[2]), as can be seen by expressing the Gaunt coefficient in terms of $3j$-symbols:

$$\left\langle \begin{matrix} 1 & L & L' \\ -m & -M & M' \end{matrix} \right\rangle = \begin{pmatrix} 1 & L & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & L & L' \\ -m & -M & M' \end{pmatrix}. \tag{A22}$$

The radial part in (A18), *viz.*

$$D(L, 0, N) f(R) = R^L \left(\frac{1}{R} \frac{\mathrm{d}}{\mathrm{d}R} \right)^L \frac{1}{R} \left(\frac{\mathrm{d}}{\mathrm{d}R} \right)^{N-L} R f(R), \tag{A23}$$

may be brought in a more convenient form by writing:

$$f(R) = \int_0^\infty \mathrm{d}k j_0(kR)\, \phi(k), \tag{A24}$$

and applying (A14), with the result:

$$D(L, 0, N) f(R) = \int_0^\infty \mathrm{d}k\, (\mathrm{i}k)^N\, \mathrm{i}^L j_L(kR)\, \phi(k). \tag{A25}$$

The spherical Bessel function $j_L(z)$ may be given as[11])

$$j_L(z) = [(-\mathrm{i})^{L+1}/2z]\, \mathscr{R}(L + \tfrac{1}{2}, -\mathrm{i}z)\, \mathrm{e}^{\mathrm{i}z} + \text{c.c.}, \tag{A26}$$

where the polynomial

$$\mathscr{R}(L + \tfrac{1}{2}, z) = \sum_{k=0}^{L} (L + \tfrac{1}{2}, k)(2z)^{-k} \tag{A27}$$

containing the Hankel symbol $(L + \frac{1}{2}, k) = (L+k)!/k!\,(L-k)!$ occurs; it is related to Lommel's polynomials. Inserting (A26) and (A27) into (A25) we get:

$$D(L, 0, N) f(R)$$
$$= \sum_{k=0}^{L} (-\tfrac{1}{2})^k (L + \tfrac{1}{2}, k) \frac{1}{R^{k+1}} \left(\frac{\mathrm{d}}{\mathrm{d}R} \right)^{N-k} \int_0^\infty \mathrm{d}k \frac{\mathrm{e}^{\mathrm{i}kR}}{2\mathrm{i}k} \phi(k) + \text{c.c.}; \tag{A28}$$

here we have replaced the factors ik by $\mathrm{d}/\mathrm{d}R$ acting on the exponential. Since $j_0(z) = \sin z/z$ we find with the help of (A23) and (A24):

$$R^L \left(\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}R}\right)^L \frac{1}{R}\left(\frac{\mathrm{d}}{\mathrm{d}R}\right)^{N-L} Rf(R)$$

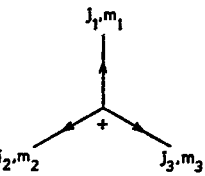
$$= \sum_{k=0}^{L} (-\tfrac{1}{2})^k (L+\tfrac{1}{2}, k)\, \frac{1}{R^{k+1}} \left(\frac{\mathrm{d}}{\mathrm{d}R}\right)^{N-k} Rf(R), \tag{A29}$$

so that the radial part of (A18) has been expanded now into a sum of derivatives of the function $Rf(R)$.

APPENDIX B

Graphical methods for the evaluation of the angular coefficients. In this appendix a summary is given of the graphical methods[5,6]) employed in the main text for representing $3j$-symbols, Gaunt coefficients and the angular coefficients constructed from these. In particular the transformation rules used in evaluating the latter are written down.

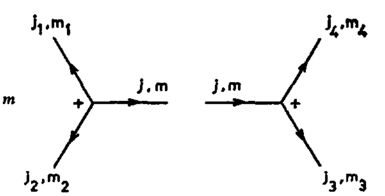
For the $3j$-symbol the graphical representation is defined by:

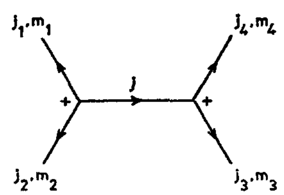
$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} =$$ 

. (B1)

Each of the directed lines in the diagram corresponds to a pair of quantum numbers (j_i, m_i); an outward (inward) arrow indicates a positive (negative) sign in front of m_i. For a vertex with a positive (negative) sign the order of the columns in the $3j$-symbols is determined by a counterclockwise (clockwise) orientation of the lines. Changing the order of the lines in the diagram induces either a change in the vertex sign as well, or the addition of a phase factor $(-1)^{j_1+j_2+j_3}$, as follows from the properties of the $3j$-symbols.

Summation of the product of two $3j$-symbols over a magnetic quantum number m, after multiplication with the appropriate phase factor, is graphically represented by a linkage of the corresponding (j, m) lines. In fact we have:

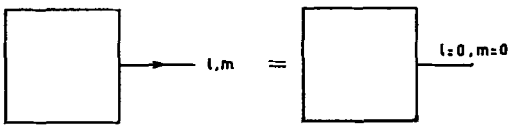
$$\sum_m (-1)^{j-m}$$ 

= 

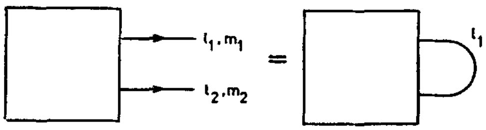
. (B2)

When j is an integer, as is always the case in the main text of this paper, the direction of the internal line in (B2) is irrelevant. From now on we shall confine ourselves to these integer values and write accordingly l instead of j.

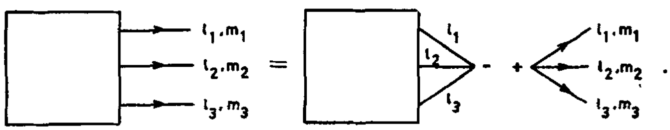
In the way illustrated above any product of $3j$-symbols, summed over magnetic quantum numbers, may be represented graphically. In several cases the diagrams thus obtained can be reduced to simpler ones by employing certain transformation rules. In particular, rules for factorizing diagrams with one, two or three external lines may be proved. They read in graphical notation:



$\delta_{l,0}\delta_{m,0}$, (B3)



$\dfrac{(-1)^{l_1-m_1}}{2l_1+1}\,\delta_{l_1,l_2}\delta_{m_1,-m_2}$, (B4)



(B5)

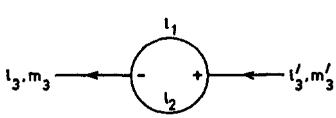
Here the structure of part of the diagrams needed not be specified in detail. This part is denoted by a block, which is supposed to have no external lines apart from those drawn explicitly. In order to apply the rules (B3)–(B5) it is often necessary to isolate blocks by cutting internal lines in the diagrams with the help of (B2).

The $3j$-symbols satisfy the orthogonality relation

$$\sum_{m_1,m_2}(-1)^{l_1-m_1+l_2-m_2}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l'_3 \\ -m_1 & -m_2 & -m'_3 \end{pmatrix}$$

$$= [(-1)^{l_3-m_3}/(2l_3+1)]\,\delta_{l_3,l'_3}\delta_{m_3,m'_3}\{l_1, l_2, l_3\} \tag{B6}$$

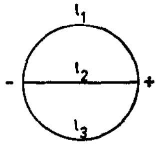
(with the triangular delta $\{l_1, l_2, l_3\}$ equal to unity if l_1, l_2, l_3 satisfy the triangular condition and zero otherwise). It may be written now as



$= [(-1)^{l_3-m_3}/(2l_3+1)]\,\delta_{l_3,l'_3}\delta_{m_3,m'_3}\{l_1, l_2, l_3\}$.

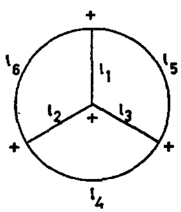
(B7)

Comparing this with (B4) one finds for the closed diagram constructed from two $3j$-symbols:



$$= \{l_1, l_2, l_3\}. \tag{B8}$$

Similarly the closed diagram made up of four $3j$-symbols is written as



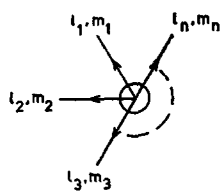
$$= \begin{Bmatrix} l_1 & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix}. \tag{B9}$$

The coefficient defined in this way is the so-called $6j$-symbol.

For the Gaunt coefficient, given by:

$$\left\langle \begin{matrix} l_1 & l_2 & l_3 & \cdots & l_n \\ m_1 & m_2 & m_3 & \cdots & m_n \end{matrix} \right\rangle = \frac{1}{4\pi} \int \mathrm{d}\Omega \prod_{i=1}^{n} \left(\frac{4\pi}{2l_i + 1} \right)^{\frac{1}{2}} Y_{l_i}^{m_i}(\Omega), \tag{B10}$$

we introduce the graphical notation:



$$. \tag{B11}$$

The definition (B10) shows that the order of the lines around the vertex is irrelevant here; furthermore a line having quantum numbers $l = 0$, $m = 0$ may be omitted from the diagram.

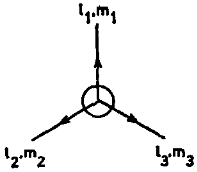
From the definition (B10) the Gaunt coefficients with one and two columns follow immediately as[2])

$$\left\langle \begin{matrix} l_1 \\ m_1 \end{matrix} \right\rangle = \delta_{l_1,0}\delta_{m_1,0}; \qquad \left\langle \begin{matrix} l_1 & l_2 \\ m_1 & m_2 \end{matrix} \right\rangle = \frac{(-1)^{m_1}}{2l_1 + 1} \delta_{l_1,l_2}\delta_{m_1,-m_2}. \tag{B12}$$

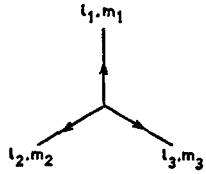
The first nontrivial Gaunt coefficient may be written as a product of two $3j$-symbols:

$$\left\langle \begin{matrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{matrix} \right\rangle = \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \tag{B13}$$

This relation may be given graphically by:

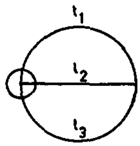


$$= \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}$$



. (B14)

In particular we have then, with (B8):

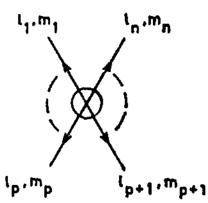


$$= \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}. \tag{B15}$$

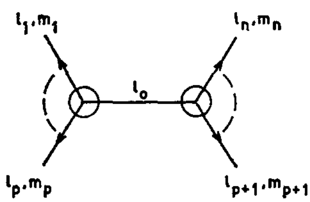
Replacing at the right-hand side of (B10) the integration $\int \mathrm{d}\Omega$ by $\int \mathrm{d}\Omega \int \mathrm{d}\Omega' \times \delta(\Omega - \Omega')$ and substituting the closure relation for spherical harmonics:

$$\sum_{l,m} (-1)^m \, Y_l^m(\Omega) \, Y_l^{-m}(\Omega') = \delta(\Omega - \Omega'), \tag{B16}$$

we get:



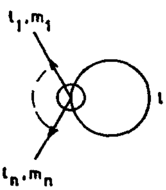
$$= \sum_{l_0} (-1)^{l_0} (2l_0 + 1)$$



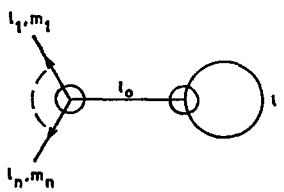
. (B17)

Gaunt coefficients having more than three external lines may be expressed now as sums of products of Gaunt coefficients with three external lines, which may subsequently be rewritten by means of (B14). Diagrams with Gaunt vertices may thus be transformed into sums of diagrams with 3*j*-vertices only. As a consequence the theorems (B3)–(B5) remain valid for blocks containing Gaunt vertices as well.

Some special consequences of (B17) are used in the main text of this paper. In particular, a loop connected to a Gaunt vertex may be eliminated with the transformation rule



$$= \sum_{l_0} (-1)^{l_0} (2l_0 + 1)$$



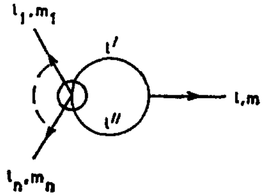
$$= (-1)^l$$

, (B18)

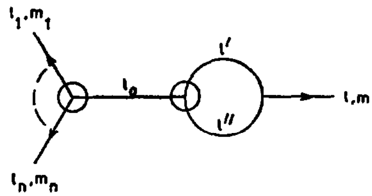
where we used (B3) and the formula

$$\begin{pmatrix} l & l & 0 \\ m & -m & 0 \end{pmatrix} = \frac{(-1)^{l-m}}{(2l+1)^{\frac{1}{2}}}. \tag{B19}$$

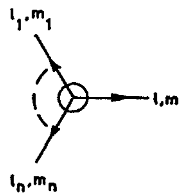
Furthermore, a double bond ending at a Gaunt vertex may be removed with the help of the transformation rule



$$= \sum_{l_0} (-1)^{l_0} (2l_0 + 1)$$



$$= (-1)^{l} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix}$$



, (B20)

that follows from (B4) and (B15).

Acknowledgements. The authors are indebted to Messrs. J. M. Baas and N. W. Blom for drawing the figures. One of the authors (M.A.J.M.) acknowledges a travel grant by the "Lorentz-Fonds", Leiden, the other (L.G.S.) the financial support of the "Netherlands Organization for the Advancement of Pure Research (Z.W.O.)". Furthermore the authors wish to thank Professor A. Salam and Professor P. Budini for the hospitality at the International Centre for Theoretical Physics, Trieste.

The work by M.A.J.M. is part of the research progamme of the "Stiching F.O.M.".

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