

MULTIPOLE EXPANSION OF THE RETARDED INTERATOMIC DISPERSION ENERGY

III. THE LONG AND SHORT RANGE BEHAVIOUR

M. A. J. MICHELS

*Instituut voor Theoretische Fysica, Universiteit van Amsterdam,
Amsterdam, Nederland*

and

L. G. SUTTROP*

*International Centre for Theoretical Physics,
Trieste, Italy*

Received 16 February 1972

Synopsis

The long-range asymptotic expression for the multipole expansion of the retarded interatomic dispersion energy is shown to consist of contributions from electric dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, all varying as the inverse seventh power of the interatomic separation. The general expressions for these interactions lead to short-range series expansions which extend results obtained earlier with the help of the Breit hamiltonian.

1. *Introduction.* In the first two papers of this series¹⁾ the interatomic dispersion energy $V(R)$ of two ground-state atoms at a distance R has been found as a sum of three terms $V_\sigma(R)$ ($\sigma = \text{I, II, III}$), written in spherical-tensor notation in formula (44) of paper II. The radial dependence is represented there by functions f_a^σ [defined in (II.11)–(II.13)], acted upon by a number of differential operators. Furthermore coefficients $\mathbf{T}^\sigma \cdot \mathbf{K}_a$ appear which have been given in terms of $3j$ - and $6j$ -symbols by (II.36)–(II.42). The properties of the atoms enter in the form of squared matrix elements of operators that have been defined in (II.20). Expression (II.44) is valid for nondegenerate ground-state atoms and, as an averaged energy, for atoms in ground states that form irreducible sets under rotations; then the squared matrix elements are to be understood as averages over these ground states.

The results described above will now be studied in the limiting cases of large and small interatomic separations. First, the long-range asymptotic form of the

* On leave of absence from the Instituut voor Theoretische Fysica, Universiteit van Amsterdam.

dispersion energy will be derived. Then, on the basis of the complete expressions for the contributions of lowest multipole order, short-range expansions will be given.

2. *The interatomic dispersion energy for large separations.* In paper I it has been shown that the terms with the largest range in the interatomic dispersion energy fall off as the inverse seventh power of the separation R between the atoms. Since, as R tends to infinity, the functions f_a^σ in the general expression (II.44) are proportional to R^{-1} , R and R^3 for $\sigma = \text{I, II, III}$, respectively, the leading terms of V_{I} , V_{II} and V_{III} are found by choosing the summation variables L_{ai} , L_{bi} , s_{ai} , s_{bi} ($i = 1, 2$) such that

$$\sum_{i=1}^2 N_i = \sum_{i=1}^2 (L_{ai} + L_{bi} + 2s_{ai} + 2s_{bi} + 2)$$

is equal to 4, 6 and 8, respectively. We shall now consider the contributions of V_{I} , V_{II} and V_{III} successively.

With regard to $V_{\text{I}}(R)$, the definitions of N_1 and N_2 imply that we may confine ourselves to the term with all parameters L_{ai} , L_{bi} , s_{ai} , s_{bi} ($i = 1, 2$) equal to zero. As can be inferred from (II.20) the operator $\Omega_{L_{ai}}^{M_{ai}'}$ then reduces to $\delta_{L_{ai}'-1} P_a^{M_{ai}'}$, so that the electric-dipole approximation of $V_{\text{I}}(R)$ is recovered, which is equal to that of $V(R)$, since $V_{\text{II}}(R)$ and $V_{\text{III}}(R)$ do not contribute in this approximation. The result has been given already in (I.71). With the use of (I.65) and (I.69) we obtain from it the leading term in the long-range expansion of $V_{\text{I}}(R)$:

$$V_{\text{I}}^{\text{I}}(R) = - \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{23e^4}{9\pi\hbar ck_N k_{N_b} R^7} |r_{N_a, L_a}|^2 |r_{N_b, L_b}|^2, \quad (1)$$

which is the well-known result of Casimir and Polder²). Here we employed as a basis of atomic states the set of eigenstates $|N_a, L_a, M_a\rangle$ of the atomic hamiltonian, the angular momentum and its third component; the atomic ground states are accordingly written as $|0, L_a^0, M_a^0\rangle$. The difference between the atomic energy level characterized by N_a and the ground level is $\hbar ck_{N_a}$. Furthermore the Wigner-Eckart theorem enabled us to rewrite the squared electric-dipole matrix element in the following way:

$$(2L_a^0 + 1)^{-1} \sum_{M_a^0, M_a} |\mu_{N_a, L_a, M_a}|^2 = e^2 |r_{N_a, L_a}|^2, \quad (2)$$

with the abbreviation

$$r_{N_a, L_a} = (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 || r_a || N_a, L_a \rangle.$$

Let us consider now the leading term in the long-range expression for $V_{II}(R)$. In this case only terms with parameters satisfying the equality

$$L_{a1} + L_{b1} + L_{a2} + L_{b2} + 2s_{a1} + 2s_{b1} + 2s_{a2} + 2s_{b2} = 2$$

contribute. If, moreover, the parity conditions (II.30) are used, three types of parameter combinations are found to be relevant: those with $L_{ai} = 1$, $L_{bi} = s_{ai} = s_{bi} = 0$ ($i = 1, 2$), and ($a \leftrightarrow b$); those with $L_{a1} = 2, L_{a2} = 0, L_{bi} = s_{ai} = s_{bi} = 0$ ($i = 1, 2$), and ($a \leftrightarrow b; 1 \leftrightarrow 2$); finally those with $s_{a1} = 1, s_{a2} = 0, L_{ai} = L_{bi} = s_{bi} = 0$ ($i = 1, 2$), and ($a \leftrightarrow b; 1 \leftrightarrow 2$). For these combinations of parameters only certain values of L'_a, L'_b and L lead to a nonvanishing coefficient $T^{II} \cdot K_a$ (see table I; the $3j$ - and $6j$ -symbols have been taken from ref. 3). Since this coefficient is symmetric with respect to an interchange of 1 and 2, parameter combinations following from those given in the table by such an interchange have

TABLE I

The coefficient $T^{II} \cdot K_a$							
L'_a	L_{a1}	L_{a2}	L'_b	L_{b1}	L_{b2}	L	$T^{II} \cdot K_a$
1	0	0	0	1	1	1	4/27
1	0	0	1	1	1	1	-2/27
1	0	0	2	1	1	1	2/135
1	0	0	1	2	0	0	$-10^{\frac{1}{2}}/15$
1	0	0	1	2	0	2	$-10^{\frac{1}{2}}/75$

been omitted. However, $T^{II} \cdot K_a$ is not symmetric in a and b : it turns out to vanish for parameter combinations obtained by interchanging these labels. The third combination mentioned above, with $L_{ai} = L_{bi} = 0$ ($i = 1, 2$), does not occur in the table, since $T^{II} \cdot K_a$ is equal to zero in that case (in fact the coefficient is then identical to that of the electric dipole-dipole contribution to V_{II}).

The reduced matrix elements $\Omega_{N_a, L_a}(L'_a, L_{ai}, s_{ai})$ in $V_{II}(R)$ will be transformed now in such a way that the electric and magnetic multipole moments appear explicitly. We have to consider for the parameter combinations (L'_a, L_{ai}, s_{ai}) the values (1, 0, 0), (0, 1, 0), (1, 1, 0), (2, 1, 0) and (1, 2, 0).

From the definitions (II.20) and (II.22) we find for the first matrix element:

$$\Omega_{N_a, L_a}(1, 0, 0) = (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 \| p_a \| N_a, L_a \rangle, \quad (3)$$

and hence, with the commutation relation

$$p_a^\lambda = (im/\hbar) [H(a), r_a^\lambda], \quad (4)$$

the expression

$$\Omega_{N_a, L_a}(1, 0, 0) = -imck_{N_a} r_{N_a, L_a}, \tag{5}$$

where again the notation $r_{N_a, L_a} = (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 \| r_a \| N_a, L_a \rangle$ for the reduced electric-dipole matrix element has been used.

For the second matrix element we get from (II.20) and (II.22), with the 3j-symbol³⁾

$$\begin{pmatrix} 1 & 1 & 0 \\ M & -M & 0 \end{pmatrix} = \frac{(-1)^{1-M}}{\sqrt{3}} \tag{6}$$

and the commutation rule (4), the expression

$$\Omega_{N_a, L_a}(0, 1, 0) = (i\sqrt{3/18}) mck_{N_a} (r^2)_{N_a, L_a}. \tag{7}$$

Here we employed the abbreviation

$$(r^2)_{N_a, L_a} = (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 \| r_a^2 \| N_a, L_a \rangle$$

for the matrix element of the trace of the electric-quadrupole moment.

With the help of (II.20), (II.22) and the 3j-symbol³⁾

$$\begin{pmatrix} 1 & 1 & 1 \\ M & -M & 0 \end{pmatrix} = \frac{M(-1)^{1-M}}{\sqrt{6}}, \tag{8}$$

the third matrix element gets the form:

$$\Omega_{N_a, L_a}(1, 1, 0) = (-i\sqrt{2/6}) (\mathbf{r} \wedge \mathbf{p})_{N_a, L_a}, \tag{9}$$

where at the right-hand side the matrix element

$$(\mathbf{r} \wedge \mathbf{p})_{N_a, L_a} = (2L_a^0 + 1)^{-\frac{1}{2}} \langle 0, L_a^0 \| \mathbf{r}_a \wedge \mathbf{p}_a \| N_a, L_a \rangle$$

of the magnetic-dipole moment (multiplied by $2mc$) occurs. However, $\mathbf{r}_a \wedge \mathbf{p}_a$ is the angular-momentum operator, which commutes with the free atomic hamiltonian. Therefore the matrix element $(\mathbf{r} \wedge \mathbf{p})_{N_a, L_a}$ vanishes unless $N_a = 0$. This parameter value is excluded from the summations occurring in the expression (II.44) for the dispersion energy $V_\sigma(R)$, so that terms with magnetic-dipole matrix elements do not contribute. In a similar way we may derive the expression:

$$\Omega_{N_a, L_a}(2, 1, 0) = \frac{-imc}{3\sqrt{6}} k_{N_a} q_{N_a, L_a}, \tag{10}$$

with the abbreviation

$$q_{N_a, L_a} = (2L_a^0 + 1)^{-\frac{1}{2}} (4\pi/5)^{\frac{1}{2}} \langle 0, L_a^0 \| r_a^2 Y_2(\omega_a) \| N_a, L_a \rangle$$

for the matrix element of the traceless part of the quadrupole moment in spherical notation.

In the terms of $V_{II}(R)$ written out explicitly in (II.44) the matrix elements (7) and (10) occur only in the combination

$$\sum_{N_b(\neq 0), L_b} k_{N_b}^{-1} \Omega_{N_b, L_b}(L'_b, 1, 0) \Omega_{N_b, L_b}^*(L'_b, 1, 0), \quad (11)$$

with $L'_b = 0$ and 2, respectively (see table I). In the appendix it has been shown that the following sum rule holds:

$$\sum_{N_b(\neq 0), L_b} k_{N_b}^{-1} |\Omega_{N_b, L_b}(2, 1, 0)|^2 = 5 \sum_{N_b(\neq 0), L_b} k_{N_b}^{-1} |\Omega_{N_b, L_b}(0, 1, 0)|^2. \quad (12)$$

Therefore we may eliminate in $V_{II}(R)$ either the matrix element (7) or (10); the latter will be retained in the following.

A similar sum rule may be applied for matrix elements Ω_{N_b, L_b} with parameter values (1, 0, 0) and (1, 2, 0). In fact one may prove the sum rule

$$\sum_{N_b(\neq 0), L_b} k_{N_b}^{-1} \Omega_{N_b, L_b}(1, 0, 0) \Omega_{N_b, L_b}^*(1, 2, 0) = 0, \quad (13)$$

which permits the matrix element $\Omega_{N_b, L_b}(1, 2, 0)$ to be eliminated from $V_{II}(R)$.

The radial differential operator in (II.44) may be evaluated with the help of (II.45); for $N_1 = N_2 = 3$ and $L = 1$ we find:

$$\frac{1}{R^2} \frac{d^6}{d(2R)^6} - \frac{2}{R^3} \frac{d^5}{d(2R)^5} + \frac{1}{R^4} \frac{d^4}{d(2R)^4}. \quad (14)$$

The dominant term of $f_a^{II}(2R)$ (II.12) for large separations is $-2k_{N_a}R \log(2k_{N_a}R)$, as follows from (I.65). Carrying out the differentiations and using (5), (7), (12), (13) and table I we arrive at the asymptotic form of $V_{II}(R)$:

$$V_{II}^I(R) = - \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{7e^4}{180\pi\hbar ck_{N_a}k_{N_b}R^7} \times (k_{N_a}^2 |q_{N_a, L_a}|^2 |r_{N_b, L_b}|^2 + k_{N_b}^2 |r_{N_a, L_a}|^2 |q_{N_b, L_b}|^2); \quad (15)$$

it represents an electric dipole-quadrupole dispersion energy.

For the third term $V_{III}(R)$ of the interatomic dispersion energy the asymptotic expression may be found in a similar way. The coefficient $T^{III} \cdot K_a$ has to be

calculated for all possible parameter values compatible with

$$L_{a1} + L_{b1} + L_{a2} + L_{b2} + 2s_{a1} + 2s_{b1} + 2s_{a2} + 2s_{b2} = 4.$$

Since the coefficient is multiplied, in (II.44), by an expression which is symmetric in a and b we have to consider only the symmetric coefficient $T^{III} \cdot (K_a + K_b)$. The latter turns out to vanish when both L_{a1} and L_{a2} or L_{b1} and L_{b2} are zero (a coefficient with these parameter values occurs in the contributions to V_{III} containing electric dipoles; indeed, such contributions vanish). In table II we have collected³⁾ all nonvanishing coefficients $T^{III} \cdot (K_a + K_b)$ with the exclusion of those that will give no contribution to V_{III} as a consequence of the sum rule (13).

TABLE II

The coefficient $T^{III} \cdot (K_a + K_b)$							
L'_a	L_{a1}	L_{a2}	L'_b	L_{b1}	L_{b2}	L	$T^{III} \cdot (K_a + K_b)$
0	1	1	0	1	1	0	-20/27
0	1	1	0	1	1	2	8/135
0	1	1	2	1	1	0	14/135
0	1	1	2	1	1	2	-4/135
2	1	1	2	1	1	0	-26/675
2	1	1	2	1	1	2	23/3375

(For brevity parameter combinations with a and b interchanged have been omitted from the table.) The radial operators acting on $f_a^{III}(2R)$ (II.13) are found from (II.45) by putting $N_1 = N_2 = 4$ and $L = 0$ or 2 ; we get for these two cases:

$$\frac{1}{R^2} \frac{d^8}{d(2R)^8}, \tag{16}$$

$$\frac{1}{R^2} \frac{d^8}{d(2R)^8} - \frac{6}{R^3} \frac{d^7}{d(2R)^7} + \frac{15}{R^4} \frac{d^6}{d(2R)^6} - \frac{18}{R^5} \frac{d^5}{d(2R)^5} + \frac{9}{R^6} \frac{d^4}{d(2R)^4}. \tag{17}$$

When the differentiations are performed and (10), (12) and (13) are used, we find for the long-range behaviour of $V_{III}(R)$ the expression:

$$V_{III}^L(R) = - \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{23e^4 k_{N_a} k_{N_b}}{3600\pi \hbar c R^7} |q_{N_a, L_a}|^2 |q_{N_b, L_b}|^2, \tag{18}$$

which represents an electric quadrupole-quadrupole dispersion energy.

The complete expression for the long-range retarded dispersion energy (averaged over atomic orientations) is given by the sum of (1), (15) and (18). It falls off as the inverse seventh power of the separation between the atoms and contains contributions with electric-dipole and quadrupole matrix elements. Hence the use of the electric-dipole approximation is not sufficient to determine the long-range behaviour of the interatomic dispersion energy. The relative magnitude of the various terms may be estimated by comparing the quantities $|r_{N_a, L_a}|^2$ and $k_{N_a}^2 |q_{N_a, L_a}|^2$.

3. *The dispersion energy up to terms with electric-quadrupole moments; the asymptotic form for small separations.* In the preceding section the long-range asymptotic form of the dispersion energy has been obtained. It turned out to contain electric dipole-dipole, dipole-quadrupole and -quadrupole-quadrupole interaction energies. The complete expression for the dispersion energy up to electric-quadrupole terms will be given in the following. On the basis of this expression the asymptotic form for small interatomic separations will be found.

The electric dipole-dipole dispersion energy follows from (I.71), with (2), as

$$V_{d-d}(R) = \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{4e^4 k_{N_a} k_{N_b}}{9\pi \hbar c R^3} |r_{N_a, L_a}|^2 |r_{N_b, L_b}|^2 (\varrho_a^2 - \varrho_b^2)^{-1} \\ \times [(\varrho_a^3 - 5\varrho_a + 3\varrho_a^{-1}) P(2\varrho_a) + (-2\varrho_a^2 + 6) Q(2\varrho_a) - \frac{1}{2}\varrho_a^2 - (a \leftrightarrow b)], \quad (19)$$

where the abbreviation $\varrho_a = k_{N_a} R$ has been introduced. The symbol $(a \leftrightarrow b)$ represents the terms arising from the preceding ones by interchanging a and b . The functions $P(x)$ and $Q(x)$ have been defined in (I.30) and (I.70).

The short-range expansion⁴⁾ of (19) follows by employing the series expansions of $P(x)$ and $Q(x)$. In fact the latter read⁵⁾:

$$P(x) = \frac{1}{2}\pi + x \log x + (\gamma - 1)x - \frac{1}{4}\pi x^2 - \frac{1}{8}x^3 \log x - \frac{1}{36}(6\gamma - 11)x^3 + \dots, \quad (20)$$

$$Q(x) = -\log x - \gamma + \frac{1}{2}\pi x + \frac{1}{2}x^2 \log x + \frac{1}{4}(2\gamma - 3)x^2 + \dots, \quad (21)$$

so that we find immediately for the electric dipole-dipole interaction at small separations R :

$$V_{d-d}^s(R) = - \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{2e^4 |r_{N_a, L_a}|^2 |r_{N_b, L_b}|^2}{3\hbar c (k_{N_a} + k_{N_b}) R^6} \\ \times \left[1 - \frac{1}{3}k_{N_a} k_{N_b} R^2 + \frac{7}{9\pi} k_{N_a} k_{N_b} (k_{N_a} + k_{N_b}) R^3 + \dots \right]. \quad (22)$$

The first term is the well-known electrostatic London–Van der Waals dispersion interaction; the second has been derived on the basis of the Breit hamiltonian as well^{6,7}).

The mixed electric dipole–quadrupole interaction is the sum of two terms, originating from V_I and V_{II} , respectively:

$$\begin{aligned}
 V_{d-q}(R) = & \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{e^4 k_{N_a} k_{N_b}}{45\pi\hbar c R^5} |r_{N_a, L_a}|^2 |q_{N_b, L_b}|^2 \\
 & \times \{(\varrho_a^2 - \varrho_b^2)^{-1} [(-\varrho_a^5 + 27\varrho_a^3 - 162\varrho_a + 90\varrho_a^{-1}) P(2\varrho_a) \\
 & + (6\varrho_a^4 - 84\varrho_a^2 + 180) Q(2\varrho_a) + \frac{1}{2}\varrho_a^4 - \frac{61}{4}\varrho_a^2 - (a \leftrightarrow b)] \\
 & + (-\varrho_a^3 + \varrho_a) P(2\varrho_a) + 2\varrho_a^2 Q(2\varrho_a) + \frac{1}{2}\varrho_a^2 - \frac{5}{4}\} + (a \leftrightarrow b). \quad (23)
 \end{aligned}$$

The short-range behaviour of this expression may be obtained with the help of the expansions (20)–(21); the result is:

$$\begin{aligned}
 V_{d-q}^S(R) = & - \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{e^4}{\hbar c (k_{N_a} + k_{N_b}) R^8} \\
 & \times (|r_{N_a, L_a}|^2 |q_{N_b, L_b}|^2 + |q_{N_a, L_a}|^2 |r_{N_b, L_b}|^2) \\
 & \times [1 - \frac{1}{3} k_{N_a} k_{N_b} R^2 + (5/18\pi) k_{N_a} k_{N_b} (k_{N_a} + k_{N_b}) R^3 + \dots]. \quad (24)
 \end{aligned}$$

The first term forms part of the electrostatic dispersion energy given in (II.51); the second has been derived earlier from the Breit hamiltonian^{6,7}.

The electric quadrupole–quadrupole interaction contains contributions from V_I , V_{II} and V_{III} . It reads:

$$\begin{aligned}
 V_{q-q}(R) = & \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{e^4 k_{N_a} k_{N_b}}{900\pi\hbar c R^7} |q_{N_a, L_a}|^2 |q_{N_b, L_b}|^2 \\
 & \times \{(\varrho_a^2 - \varrho_b^2)^{-1} [(\varrho_a^7 - 89\varrho_a^5 + 1983\varrho_a^3 - 9360\varrho_a + 5040\varrho_a^{-1}) P(2\varrho_a) \\
 & + (-10\varrho_a^6 + 510\varrho_a^4 - 5280\varrho_a^2 + 10080) Q(2\varrho_a) \\
 & - \frac{1}{2}\varrho_a^6 + \frac{189}{4}\varrho_a^4 - \frac{4583}{4}\varrho_a^2 - (a \leftrightarrow b)] \\
 & + [(\varrho_a^5 - 15\varrho_a^3 + 9\varrho_a) P(2\varrho_a) + (-6\varrho_a^4 + 18\varrho_a^2) Q(2\varrho_a) \\
 & - \frac{1}{2}\varrho_a^4 + \frac{37}{4}\varrho_a^2 - \frac{63}{4} + (a \leftrightarrow b)] - \frac{23}{4}\}. \quad (25)
 \end{aligned}$$

From (25) the short-range behaviour may be found as

$$V_{q^{-q}}^S = - \sum_{\substack{N_a(\neq 0), L_a \\ N_b(\neq 0), L_b}} \frac{14e^4}{5\hbar c (k_{N_a} + k_{N_b}) R^{10}} |q_{N_a, L_a}|^2 |q_{N_b, L_b}|^2 \\ \times [1 - \frac{1}{7} k_{N_a} k_{N_b} R^2 + (383/2520\pi) k_{N_a} k_{N_b} (k_{N_a} + k_{N_b}) R^3 + \dots]. \quad (26)$$

Again the leading term is the electrostatic contribution contained in (II.51).

In this paper we have evaluated the contributions of the electric dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions to the dispersion energy of two atoms in their ground states; the results have been written in (19), (23) and (25). For small separations R the contributions, specified in (22), (24) and (26), vary as R^{-6} and R^{-8} and R^{-10} , respectively, with first-order corrections proportional to R^{-4} , R^{-6} and R^{-8} . The asymptotic expressions for large R have been given in (1), (15) and (18), respectively; together they form the complete long-range dominant term, varying as the inverse seventh power of the interatomic separation.

APPENDIX

Sum rules in spherical-tensor notation. In this appendix we want to derive sum rules for the reduced matrix elements $\Omega_{N_a, L_a}(L'_a, L_{a1}, s_{a1})$ ($i = 1, 2$), defined in (II.22) with (II.20). Let us consider to that end the expression

$$\sum_{N_a(\neq 0), L_a} k_{N_a}^{-1} \Omega_{N_a, L_a}(L'_a, L_{a1}, s_{a1}) \Omega_{N_a, L_a}^*(L'_a, L_{a2}, s_{a2}), \quad (A1)$$

which may be written, with the help of (II.19) and (II.24), as

$$\sum_{N_a(\neq 0), L_a} \sum_{\kappa, \lambda, M_{a1}, M_{a2}, M_a^0, M_a, M_a'} k_{N_a}^- \\ \times \frac{(-1)^{M_a'} 4\pi (2L'_a + 1)}{(2L_a^0 + 1) (2s_{a1})!! (2s_{a2})!! (2L_{a1} + 2s_{a1} + 1)!! (2L_{a2} + 2s_{a2} + 1)!!} \\ \times \frac{1}{[(2L_{a1} + 1) (2L_{a2} + 1)]^{\frac{1}{2}}} \begin{pmatrix} L_{a1} & 1 & L'_a \\ -M_{a1} & -\kappa & M_a' \end{pmatrix} \begin{pmatrix} L_{a2} & 1 & L'_a \\ -M_{a2} & -\lambda & M_a' \end{pmatrix} \\ \times \langle 0, L_a^0, M_a^0 | \frac{1}{2} \{ p_a^\kappa, r_a^{L_{a1} + 2s_{a1}} Y_{L_{a1}}^{M_{a1}}(\omega_a) \} | N_a, L_a, M_a \rangle \\ \times \langle N_a, L_a, M_a | \frac{1}{2} \{ p_a^{-\lambda}, r_a^{L_{a2} + 2s_{a2}} Y_{L_{a2}}^{-M_{a2}}(\omega_a) \} | 0, L_a^0, M_a^0 \rangle. \quad (A2)$$

The projectors on states with the same energy are real in the coordinate representation, since the atomic hamiltonian is real in this representation. If, moreover, the parity selection rules (II.30) are used it may be shown that (A2) is real.

The sum over intermediate states may be eliminated if it is possible to extract from one of the matrix elements a factor k_{N_a} . To achieve this the operator in one of the matrix elements in (A2) has to be written as a commutator with the atomic hamiltonian $H(a)$. From the gradient formula [see (II.A21)] the following commutator relation may be derived:

$$\begin{aligned} (im/\hbar) [H(a), r_a^p Y_L^M(\omega_a)] &= (-1)^M (p-L) [(2L+1)(2L+3)]^{\frac{1}{2}} \\ &\times \sum_{\kappa, M'} \begin{pmatrix} L & 1 & L+1 \\ M & -\kappa & -M' \end{pmatrix} \begin{pmatrix} L & 1 & L+1 \\ 0 & 0 & 0 \end{pmatrix} \frac{1}{2} \{p_a^\kappa, r_a^{p-1} Y_{L+1}^{M'}(\omega_a)\} \\ &+ (-1)^M (p+L+1) [(2L+1)(2L-1)]^{\frac{1}{2}} \\ &\times \sum_{\kappa, M'} \begin{pmatrix} L & 1 & L-1 \\ M & -\kappa & -M' \end{pmatrix} \begin{pmatrix} L & 1 & L-1 \\ 0 & 0 & 0 \end{pmatrix} \frac{1}{2} \{p_a^\kappa, r_a^{p-1} Y_{L-1}^{M'}(\omega_a)\}. \end{aligned} \quad (\text{A3})$$

The right-hand side contains operators and $3j$ -symbols of the type occurring in (A2). For the special case $L=0$ the second term drops out, while for $L=p$ the first vanishes. Thus, a factor k_{N_a} may be extracted from the i th matrix element in (A2) if $L_{ai}=1$, $L'_a=0$, or if $L_{ai}=L'_a-1$, $s_{ai}=0$ ($i=1, 2$). In the former case (choosing $i=1$) we find, by taking half the sum of (A2), with (A3) inserted, and its complex conjugate, the expression

$$\begin{aligned} \delta_{L_{a2}, 1} \sum_{\lambda, M_a^0} \frac{2\sqrt{3} \pi i m c (-1)^{\lambda+1} (2s_{a2}+2)}{9 (2L_a^0+1) (2s_{a1}+3)! (2s_{a2}+3)!} \\ \times \langle 0, L_a^0, M_a^0 | [r_a^{2s_{a1}+2} Y_0^0(\omega_a), \frac{1}{2} \{p_a^{-\lambda}, r_a^{2s_{a2}+1} Y_1^\lambda(\omega_a)\}] | 0, L_a^0, M_a^0 \rangle. \end{aligned} \quad (\text{A4})$$

With the commutation rule (6) we find then the sum rule

$$\begin{aligned} \sum_{N_a(\neq 0), L_a} k_{N_a}^{-1} \Omega_{N_a, L_a}(0, 1, s_{a1}) \Omega_{N_a, L_a}^*(0, L_{a2}, s_{a2}) \\ = \delta_{L_{a2}, 1} \sum_{M_a^0} \frac{\hbar m c (2s_{a1}+2)(2s_{a2}+2)}{6 (2L_a^0+1) (2s_{a1}+3)! (2s_{a2}+3)!} \\ \times \langle 0, L_a^0, M_a^0 | r_a^{2s_{a1}+2s_{a2}+2} | 0, L_a^0, M_a^0 \rangle. \end{aligned} \quad (\text{A5})$$

In the second case, with $L_{a1}=L'_a-1$, $s_{a1}=0$, we get for (A2), with (A3):

$$\begin{aligned} - \sum_{\lambda, M_{a2}, M_a^0, M_a'} \frac{2\pi i m c}{(2L_a^0+1) (2s_{a2})!! (2L_{a2}+2s_{a2}+1)!! (2L'_a-1)!! (2L'_a-1)} \\ \times \frac{1}{[(2L'_a+1)(2L_{a2}+1)]^{\frac{1}{2}}} \begin{pmatrix} L_{a2} & 1 & L'_a \\ -M_{a2} & -\lambda & M_a' \end{pmatrix} \begin{pmatrix} 1 & L'_a-1 & L'_a \\ 0 & 0 & 0 \end{pmatrix}^{-1} \\ \times \langle 0, L_a^0, M_a^0 | [r_a^{L'_a} Y_{L'_a}^{M_a'}(\omega_a), \frac{1}{2} \{p_a^{-\lambda}, r_a^{L_{a2}+2s_{a2}} Y_{L_{a2}}^{-M_{a2}}(\omega_a)\}] | 0, L_a^0, M_a^0 \rangle. \end{aligned} \quad (\text{A6})$$

Using the commutation rule (6), the gradient formula and the orthogonality relation (II.19) we may write this as

$$\delta_{L_{a2}, L'_a - 1} \sum_{M_{a2}, M_a^0} \frac{2\pi\hbar mc (-1)^{M_{a2}} (2L'_a + 1)}{(2L_a^0 + 1) (2s_{a2})!! (2L'_a + 2s_{a2} - 1)!! (2L'_a - 1)!! (2L'_a - 1)^2} \times \langle 0, L_a^0, M_a^0 | r_a^{2L'_a + 2s_{a2} - 2} Y_{L_a^0 - 1}^{M_{a2}}(\omega_a) Y_{L'_a - 1}^{-M_{a2}}(\omega_a) | 0, L_a^0, M_a^0 \rangle. \quad (\text{A7})$$

Employing the relation

$$\sum_M (-1)^M Y_L^M(\omega_a) Y_L^{-M}(\omega_a) = \frac{2L + 1}{4\pi} \quad (\text{A8})$$

we arrive then at the sum rule

$$\sum_{N_a(\neq 0), L_a} k_{N_a}^{-1} \Omega_{N_a, L_a}(L'_a, L'_a - 1, 0) \Omega_{N_a, L_a}^*(L'_a, L_{a2}, s_{a2}) = \delta_{L_{a2}, L'_a - 1} \sum_{M_a^0} \times \frac{\hbar mc (2L'_a + 1)}{2(2L_a^0 + 1) (2s_{a2})!! (2L'_a + 2s_{a2} - 1)!! (2L'_a - 1)!! (2L'_a - 1)} \times \langle 0, L_a^0, M_a^0 | r_a^{2L'_a + 2s_{a2} - 2} | 0, L_a^0, M_a^0 \rangle. \quad (\text{A9})$$

Both sum rules (A5) and (A9) have been used in the main text. In fact (12) follows by combining (A5) (with $L_{a2} = 1, s_{a1} = s_{a2} = 0$) and (A9) (with $L'_a = 2, L_{a2} = 1, s_{a2} = 0$). Furthermore (13) is obtained by putting $L'_a = 1, L_{a2} = 2, s_{a2} = 0$ in (A9).

Acknowledgements. 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 programme of the "Stichting F.O.M."

REFERENCES

- 1) Michels, M.A.J. and Suttorp, L.G., *Physica* **59** (1972) 609; **61** (1972) 481.
- 2) Casimir, H.B.G. and Polder, D., *Phys. Rev.* **73** (1948) 360.
- 3) Rotenberg, M., Bivins, R., Metropolis, N. and Wooten, J.K., *The 3j- and 6j-symbols*, Technology Press, M.I.T. (Cambridge, 1959).
- 4) Meath, W.J. and Hirschfelder, J.O., *J. chem. Phys.* **44** (1966) 3210.
- 5) Abramowitz, M. and Stegun, I.A., *Handbook of Mathematical Functions*, Dover Publ., Inc. (New York, 1965) ch. 5.
- 6) Meath, W.J. and Hirschfelder, J.O., *J. chem. Phys.* **44** (1966) 3197.
- 7) Meath, W.J., University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-75 (1965).