# MULTIPOLE EXPANSION
## OF THE RETARDED INTERATOMIC DISPERSION ENERGY
### I. DERIVATION FROM QUANTUM ELECTRODYNAMICS

M. A. J. MICHELS and L. G. SUTTORP

*Instituut voor theoretische fysica, Universiteit van Amsterdam,
Amsterdam, Nederland*

**Synopsis**

The multipole expansion of the retarded dispersion energy of two atoms in non-degenerate ground states is derived. The result shows that multipoles of different order may give rise to dispersion energies varying in the same way for large interatomic separations.

1. *Introduction.* The retarded dispersion energy of two atoms has been evaluated by Casimir and Polder[1]) in the framework of quantum electrodynamics. As a result they found an expression that contains the electrostatic London–van der Waals interaction energy as a special case valid for small interatomic separations $R$; the latter varies as an inverse sixth power of $R$. At large separations, however, the interaction energy turns out to fall off as an inverse seventh power, due to retardation effects. These effects become significant at distances of the order of the wavelength $\lambda$ corresponding to the lowest excited atomic level.

In order to arrive at their results the authors quoted above employed the electric-dipole approximation. Terms of higher order in the multipole expansion lead, in the electrostatic limit, to a dispersion energy that falls off more rapidly with increasing $R$. Due to the occurrence of the parameter $\lambda$, however, retardation effects may change the dependence on $R$ in such a way that terms of different multipole order vary in the same way. Whether this is true may be established when the complete multipole expansion of the retarded dispersion energy has been found. This expansion will be derived in the present paper.

2. *The hamiltonian. Perturbation theory up to fourth order and its diagrammatic representation.* The hamiltonian for a system consisting of two neutral atoms interacting with the electromagnetic field may be split up

into four parts:

$$H = H(a) + H(b) + H_{\text{rad}} + H_{\text{int}}. \tag{1}$$

The first two terms represent the hamiltonians of the free atoms, labelled $a$ and $b$. If these atoms are described non-relativistically and the nuclei are held fixed one has for the hamiltonian of atom $a$:

$$H(a) = \sum_j \frac{p_{aj}^2}{2m} - \sum_j \frac{z_a e^2}{|r_{aj}|} + \frac{1}{2} \sum_{j \neq j'} \frac{e^2}{|r_{aj} - r_{aj'}|}, \tag{2}$$

where the sums are extended over the $z_a$ electrons $j$ with masses $m$, charges $-e$, coordinates $r_{aj}$ (with respect to the nucleus) and momenta $p_{aj}$. The third term of (1) stands for the hamiltonian of the free radiation field. It can be expanded in terms of the annihilation and creation operators, $a(k, \lambda)$ and $a^\dagger(k, \lambda)$, respectively, of photons with wave vector $k$ and polarization vector $e(k, \lambda)$ $(\lambda = 1, 2)$:

$$H_{\text{rad}} = \sum_{k, \lambda} a^\dagger(k, \lambda)\, a(k, \lambda)\, \hbar c k. \tag{3}$$

The radiation field is enclosed in a box (with volume $V$) so that the wave spectrum is discrete. The operators $a(k, \lambda)$ and $a^\dagger(k, \lambda)$ appear in the Fourier decomposition of the vector potential:

$$A(R) = \sum_{k, \lambda} \left( \frac{2\pi \hbar c}{Vk} \right)^{\frac{1}{2}} \{ a(k, \lambda)\, e(k, \lambda)\, \mathrm{e}^{ik \cdot R} + a^\dagger(k, \lambda)\, e^*(k, \lambda)\, \mathrm{e}^{-ik \cdot R} \}. \tag{4}$$

It is chosen to satisfy the Coulomb gauge condition $\nabla \cdot A = 0$, which implies the orthogonality relations

$$k \cdot e(k, \lambda) = 0 \qquad (\lambda = 1, 2). \tag{5}$$

The interaction hamiltonian in the expression (1) is the sum of electrostatic terms and terms which couple the atoms with the radiation field:

$$\begin{aligned}
H_{\text{int}} = {} & \frac{z_a z_b e^2}{|R_a - R_b|} - \sum_j \frac{z_b e^2}{|R_a + r_{aj} - R_b|} - \sum_j \frac{z_a e^2}{|R_b + r_{bj} - R_a|} \\[2mm]
& + \sum_{j, j'} \frac{e^2}{|R_a + r_{aj} - R_b - r_{bj'}|} + \sum_j \frac{e}{mc}\, p_{aj} \cdot A(R_a + r_{aj}) \\[2mm]
& + \sum_j \frac{e}{mc}\, p_{bj} \cdot A(R_b + r_{bj}) + \sum_j \frac{e^2}{2mc^2}\, A^2(R_a + r_{aj}) \\[2mm]
& + \sum_j \frac{e^2}{2mc^2}\, A^2(R_b + r_{bj}),
\end{aligned} \tag{6}$$

where $R_a$ and $R_b$ are the positions of the nuclei of the atoms $a$ and $b$.

To calculate the dispersion energy of the two atoms we shall treat $H_{int}$ as a perturbation on the hamiltonian of the system of free atoms and radiation field and retain only those energy corrections that depend on the interatomic separation $|R_b - R_a|$. This separation is taken sufficiently large for the overlap of the atomic wave functions to be negligible. The unperturbed states will be denoted as $|n\rangle = |\alpha; \beta; k_1, \lambda_1; \ldots; k_m, \lambda_m\rangle$, where $\alpha$, $\beta$ and $k_1, \lambda_1; \ldots; k_m, \lambda_m$ are the quantum numbers that label the states of the atoms $a$ and $b$ and of the photons present in the radiation field; the ground state, which is assumed to be nondegenerate, is written as $|0\rangle \equiv \equiv |\alpha_0; \beta_0\rangle$. If one wants to obtain the energy shifts up to terms proportional to $e^4$, perturbation theory up to fourth order must be applied, as (6) shows. In particular, the ground-state energy shifts in the various orders have the form:

$$E^{(1)} = \langle 0| H_{int} |0\rangle,$$

$$E^{(2)} = -\sum_{n(\neq 0)} \frac{\langle 0| H_{int} |n\rangle\langle n| H_{int} |0\rangle}{\Delta E_n^{(0)}},$$

$$E^{(3)} = \sum_{n, n'(\neq 0)} \frac{\langle 0| H_{int} |n\rangle\langle n| H_{int} |n'\rangle\langle n'| H_{int} |0\rangle}{\Delta E_n^{(0)}\Delta E_{n'}^{(0)}}$$

$$- E^{(1)} \sum_{n(\neq 0)} \frac{\langle 0| H_{int} |n\rangle\langle n| H_{int} |0\rangle}{\Delta E_n^{(0)^2}}, \tag{7}$$

$$E^{(4)} = -\sum_{n, n', n''(\neq 0)} \frac{\langle 0| H_{int} |n\rangle\langle n| H_{int} |n'\rangle\langle n'| H_{int} |n''\rangle\langle n''| H_{int} |0\rangle}{\Delta E_n^{(0)}\Delta E_{n'}^{(0)}\Delta E_{n''}^{(0)}}$$

$$- E^{(2)} \sum_{n(\neq 0)} \frac{\langle 0| H_{int} |n\rangle\langle n| H_{int} |0\rangle}{\Delta E_n^{(0)^2}},$$

where $\Delta E_n^{(0)}$ is the energy difference $E_n^{(0)} - E_0^{(0)}$ of the unperturbed states $|n\rangle$ and $|0\rangle$.

On substituting (6) into (7) several terms vanish as a consequence of the rotation symmetry of the nondegenerate ground states $|\alpha_0\rangle$ and $|\beta_0\rangle$ of the atoms. In fact, the electrostatic interaction in (6) may be written, with a double Taylor expansion, as

$$\sum_{j=1}^{z_a} \sum_{j'=1}^{z_b} (e^{-r_{aj}\cdot \nabla} - 1)(e^{r_{bj'}\cdot \nabla} - 1)\frac{e^2}{R}, \tag{8}$$

with $R \equiv R_b - R_a$; if this operator is written between $\langle \alpha_0|$ and $|\alpha_0\rangle$ (or $\langle \beta_0|$ and $|\beta_0\rangle$) only the invariant part of the atomic operators in the first (or second) factor contributes, with a vanishing result, however, since $\Delta R^{-1} = 0$ if $R \neq 0$. A similar argument shows that the matrix element of

the operator

$$\sum_{j=1}^{z_a} \frac{e}{mc}\, \boldsymbol{p}_{aj} \cdot \boldsymbol{A}(\boldsymbol{R}_a + \boldsymbol{r}_{aj}) \tag{9}$$

between $\langle \alpha_0 |$ and $| \alpha_0 \rangle$ vanishes, as a result of (4) and (5).

The various contributions to the energy corrections (7) may be represented by diagrams[2]). In the present case of the interaction hamiltonian (6) the contributions depending on the interatomic distance are given by a set of connected diagrams that consist of two vertical lines for the atoms and internal lines between them. The latter are of two types: horizontal dotted lines corresponding to electrostatic interactions and wavy lines for photons. A vertex with a dotted line stands for a matrix element containing the electrostatic interaction (8), a vertex with one photon line for a matrix element of one of the operators in (6) that are linear in the vector potential $\boldsymbol{A}$, while a vertex with two photon lines represents a matrix element of one of the operators in (6) that are quadratic with respect to $\boldsymbol{A}$. Retaining only terms up to order $e^4$ and using the properties derived in the preceding section one finds the diagrams drawn in fig. 1, and moreover
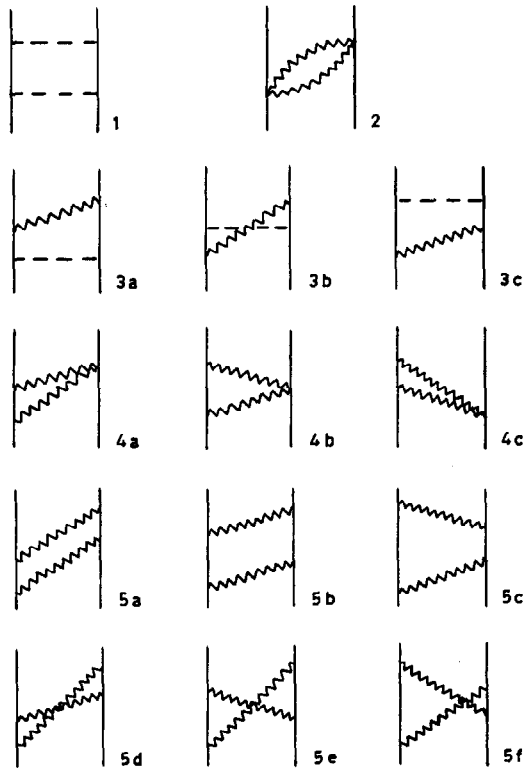


Fig. 1. Connected diagrams for the energy shifts up to order $e^4$.

the diagrams obtained from the asymmetric ones by reflection with respect to a vertical line.

3. *Evaluation of the diagrams.* In fig. 1 five different groups of diagrams occur, which will now be evaluated in succession.

The first, electrostatic diagram leads, upon double Taylor expansion, to a second-order energy correction of the form:

$$V_1(R) = - \sum_{\alpha, \beta(\neq \alpha_0, \beta_0)} \frac{e^4}{\hbar c(k_\alpha + k_\beta)}$$

$$\times \left\{ \langle \alpha_0| \sum_j (e^{-r_{aj}\cdot\boldsymbol{V}} - 1)|\alpha\rangle\langle\beta_0| \sum_j (e^{r_{bj}\cdot\boldsymbol{V}} - 1)|\beta\rangle \frac{1}{R} \right\}$$

$$\times \left\{ \langle\alpha| \sum_j (e^{-r_{aj}\cdot\boldsymbol{V}} - 1)|\alpha_0\rangle\langle\beta| \sum_j (e^{r_{bj}\cdot\boldsymbol{V}} - 1)|\beta_0\rangle \frac{1}{R} \right\}. \qquad (10)$$

The subsidiary condition $(\alpha, \beta) \neq (\alpha_0, \beta_0)$ on the summation may be replaced by the two independent conditions $\alpha \neq \alpha_0$ and $\beta \neq \beta_0$ since all contributions with $\alpha = \alpha_0$ (or $\beta = \beta_0$) vanish as has been shown in the preceding section. Choosing these conditions one may omit the terms $-1$ in the matrix elements. Furthermore two factors $R^{-1}$ occur, both acted upon by functions of the nabla operator $\boldsymbol{V}$. Accordingly, it will be convenient to introduce instead of $R$ two vectors $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ and corresponding nabla operators $\boldsymbol{V}_1$ and $\boldsymbol{V}_2$. After performing all differentiations both $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ should be replaced by $\boldsymbol{R}$. If we introduce moreover the notation $f(\boldsymbol{r}_a, \boldsymbol{p}_a)$ for the sum $\sum_j f(\boldsymbol{r}_{aj}, \boldsymbol{p}_{aj})$ we may write (10) as

$$V_1(R) = - \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{e^4}{\hbar c(k_\alpha + k_\beta)} \langle\alpha_0| e^{-r_a\cdot\boldsymbol{V}_1} |\alpha\rangle\langle\alpha| e^{-r_a\cdot\boldsymbol{V}_2} |\alpha_0\rangle$$

$$\times \langle\beta_0| e^{r_b\cdot\boldsymbol{V}_1} |\beta\rangle\langle\beta| e^{r_b\cdot\boldsymbol{V}_2} |\beta_0\rangle \frac{1}{R_1 R_2}. \qquad (11)$$

In the second type of diagrams a summation over intermediate states with two photons present occurs; it may be written as

$$\tfrac{1}{2} \sum_{\boldsymbol{k}, \lambda; \boldsymbol{k}', \lambda'} |\boldsymbol{k}, \lambda; \boldsymbol{k}', \lambda'\rangle\langle\boldsymbol{k}, \lambda; \boldsymbol{k}', \lambda'|.$$

The energy correction for this group of diagrams reads thus:

$$V_2(R) = - \sum_{\boldsymbol{k}, \lambda; \boldsymbol{k}', \lambda'} \frac{e^4}{8\hbar m^2 c^5} \langle\alpha_0| A^2(\boldsymbol{R}_a + \boldsymbol{r}_a) |\alpha_0; \boldsymbol{k}, \lambda; \boldsymbol{k}', \lambda'\rangle$$

$$\times \langle\beta_0; \boldsymbol{k}, \lambda; \boldsymbol{k}', \lambda'| A^2(\boldsymbol{R}_b + \boldsymbol{r}_b) |\beta_0\rangle \frac{1}{k + k'} + (a, \alpha \leftrightarrow b, \beta), \qquad (12)$$

where the last symbol stands for the preceding term with $(a, \alpha)$ and $(b, \beta)$

interchanged. The summation over the polarization indices $\lambda$ and $\lambda'$ may be performed if one uses the identity

$$\sum_{\lambda=1}^{2} \boldsymbol{e}(\boldsymbol{k}, \lambda)\, \boldsymbol{e}^*(\boldsymbol{k}, \lambda) = \mathsf{U} - \frac{\boldsymbol{k}\boldsymbol{k}}{k^2}. \tag{13}$$

Furthermore, if the volume $V$ of the box enclosing the system tends to infinity, the summations $V^{-1}\sum_{\boldsymbol{k}}$ may be replaced by integrations $(2\pi)^{-3}\int d\boldsymbol{k}$. Then (12) gets the form:

$$V_2(R) = -\frac{e^4\hbar}{2\pi^2 m^2 c^3} \int \frac{d\boldsymbol{k}\, d\boldsymbol{k}'}{(4\pi)^2\, kk'} \langle \alpha_0 | \, e^{i(\boldsymbol{k}+\boldsymbol{k}')\cdot \boldsymbol{r}_a} | \alpha_0 \rangle$$

$$\times \langle \beta_0 | \, e^{-i(\boldsymbol{k}+\boldsymbol{k}')\cdot \boldsymbol{r}_b} | \beta_0 \rangle \left( \mathsf{U} - \frac{\boldsymbol{k}\boldsymbol{k}}{k^2} \right) : \left( \mathsf{U} - \frac{\boldsymbol{k}'\boldsymbol{k}'}{k'^2} \right)$$

$$\times \, e^{-i(\boldsymbol{k}+\boldsymbol{k}')\cdot \boldsymbol{R}} \, \frac{1}{k+k'} + (a, \alpha \leftrightarrow b, \beta). \tag{14}$$

The consequences of Bose–Einstein statistics of the photons for the case $(\boldsymbol{k}, \lambda) = (\boldsymbol{k}', \lambda')$ are disregarded, since that case corresponds to an integration region of vanishing measure. Introducing again $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ by writing $\exp\{-i(\boldsymbol{k}+\boldsymbol{k}')\cdot \boldsymbol{R}\}$ as $\exp(-i\boldsymbol{k}\cdot \boldsymbol{R}_1)\exp(-i\boldsymbol{k}'\cdot \boldsymbol{R}_2)$ we find for (14):

$$V_2(R) = -\frac{e^4\hbar}{2\pi^2 m^2 c^3} \langle \alpha_0 | \, e^{-\boldsymbol{r}_a\cdot(\boldsymbol{\nabla}_1+\boldsymbol{\nabla}_2)} | \alpha_0 \rangle \langle \beta_0 | \, e^{\boldsymbol{r}_b\cdot(\boldsymbol{\nabla}_1+\boldsymbol{\nabla}_2)} | \beta_0 \rangle$$

$$\times (\boldsymbol{\nabla}_1\boldsymbol{\nabla}_1 - \mathsf{U}\Delta_1) : (\boldsymbol{\nabla}_2\boldsymbol{\nabla}_2 - \mathsf{U}\Delta_2) \int \frac{d\boldsymbol{k}\, d\boldsymbol{k}'}{(4\pi)^2\, k^3 k'^3}$$

$$\times (e^{-i\boldsymbol{k}\cdot \boldsymbol{R}_1} - 1)(e^{-i\boldsymbol{k}'\cdot \boldsymbol{R}_2} - 1) \, \frac{1}{k+k'} + (a, \alpha \leftrightarrow b, \beta), \tag{15}$$

where we extracted factors $\boldsymbol{k}$ and $\boldsymbol{k}'$, replacing them by $i\boldsymbol{\nabla}_1$ and $i\boldsymbol{\nabla}_2$, respectively. To assure the convergence of the integrals at the origin we added terms $-1$ to the exponential factors in the integrand; this does not change the expression as a whole. The angular integrations may be carried out by employing the relation

$$\int \frac{d\boldsymbol{k}}{4\pi}\, f(k)(e^{-i\boldsymbol{k}\cdot \boldsymbol{R}} - 1) = \int_{0}^{\infty} dk\, k^2 f(k) \left( \frac{\sin kR}{kR} - 1 \right) \tag{16}$$

for an arbitrary function $f(k)$. Then the integral in (15) becomes

$$\frac{\pi}{2R_1 R_2}\, F_0(R_1, R_2), \tag{17}$$

with the abbreviation:

$$F_0(R_1, R_2) = \frac{2R_1 R_2}{\pi} \int_0^\infty \frac{dk\, dk'}{kk'} \left( \frac{\sin kR_1}{kR_1} - 1 \right)$$

$$\times \left( \frac{\sin k'R_2}{k'R_2} - 1 \right) \frac{1}{k + k'}. \tag{18}$$

This integral is evaluated in appendix A. There it is shown that it differs from the function

$$F(R_1, R_2) = \tfrac{1}{6}(R_1 + R_2)^3 \log(R_1 + R_2) - \tfrac{1}{6}R_1^3 \log R_1 - \tfrac{1}{6}R_2^3 \log R_2 \tag{19}$$

by terms that drop out when inserted into (15). As a result we find for $V_2(R)$:

$$V_2(R) = -\frac{e^4 \hbar}{4\pi m^2 c^3} \langle \alpha_0 | \, e^{-r_a \cdot (\mathbf{V}_1 + \mathbf{V}_2)} \, |\alpha_0\rangle \langle \beta_0 | \, e^{r_b \cdot (\mathbf{V}_1 + \mathbf{V}_2)} \, |\beta_0\rangle$$

$$\times (\mathbf{V}_1 \mathbf{V}_1 - \mathsf{U}\Delta_1) : (\mathbf{V}_2 \mathbf{V}_2 - \mathsf{U}\Delta_2) \, \frac{F(R_1, R_2)}{R_1 R_2} + (a, \alpha \leftrightarrow b, \beta). \tag{20}$$

We now turn to the third group of diagrams, which contain both electrostatic and photon interactions. The electrostatic part is treated as in (10) and (11). In the photon part we carry out the summation over the polarization directions and replace $k$ by $i\mathbf{V}$. Then we get (introducing again $R_1$ and $R_2$) for the first diagram of this group:

$$V_{3a}(R) = \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{e^4}{\pi \hbar m^2 c^3} \langle \alpha_0 | \, e^{-r_a \cdot \mathbf{V}_1} \, |\alpha\rangle$$

$$\times \langle \alpha | \, \boldsymbol{p}_a \, e^{-r_a \cdot \mathbf{V}_2} \, |\alpha_0\rangle \langle \beta_0 | \, e^{r_b \cdot \mathbf{V}_1} \, |\beta\rangle \langle \beta | \, \boldsymbol{p}_b \, e^{r_b \cdot \mathbf{V}_2} \, |\beta_0\rangle$$

$$: (\mathbf{V}_2 \mathbf{V}_2 - \mathsf{U}\Delta_2) \frac{1}{R_1} \int \frac{d\boldsymbol{k}}{4\pi k^3} \, (e^{-i\boldsymbol{k} \cdot \boldsymbol{R}_2} - 1) \, \frac{1}{(k_\alpha + k_\beta)(k_\beta + k)}. \tag{21}$$

Just as in (15) the convergence of the integral at the origin is guaranteed by adding the term $-1$ in the integrand. The expressions that are obtained from the other diagrams have the same form, apart from the occurrence of different energy denominators and a different ordering of the matrix elements. For instance, the product of matrix elements of atom $a$ in the expression corresponding to diagram 3b is:

$$\langle \alpha_0 | \, \boldsymbol{p}_a \, e^{-r_a \cdot \mathbf{V}_2} \, |\alpha\rangle \langle \alpha | \, e^{-r_a \cdot \mathbf{V}_1} \, |\alpha_0\rangle. \tag{22}$$

Since the remaining factors in that expression depend on $\alpha$ only through the energy $\hbar c k_\alpha$, the sum of (22) over all states with the same energy may be performed. This sum then contains the projection operator

$$\sum_{\alpha(k_\alpha \text{ const.})} |\alpha\rangle\langle\alpha|, \tag{23}$$

which is a real operator in the coordinate representation since $H(a)$, given in (2), is real in this representation. For the same reason the eigenfunction of the nondegenerate ground-state level may be chosen to be real. As $r_{aj}$ and $p_{aj}$ are purely real and imaginary, respectively, one finds the relation

$$\sum_{\alpha(k_\alpha \text{ const.})} \langle \alpha_0 | \, p_a \, e^{-r_a \cdot \nabla_2} \, | \alpha \rangle \langle \alpha | \, e^{-r_a \cdot \nabla_1} \, | \alpha_0 \rangle$$

$$= - \sum_{\alpha(k_\alpha \text{ const.})} \langle \alpha_0 | \, e^{-r_a \cdot \nabla_1} \, | \alpha \rangle \langle \alpha | \, e^{-r_a \cdot \nabla_2} \, p_a \, | \alpha_0 \rangle. \tag{24}$$

With the help of this identity (and a similar one for atom $b$) we obtain from the diagrams of the third type:

$$V_3(R) = \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{2e^4}{\pi \hbar m^2 c^3} \, \langle \alpha_0 | \, e^{-r_a \cdot \nabla_1} \, | \alpha \rangle$$

$$\times \, \langle \alpha | \, p_a \, e^{-r_a \cdot \nabla_2} \, | \alpha_0 \rangle \langle \beta_0 | \, e^{r_b \cdot \nabla_1} \, | \beta \rangle \langle \beta | \, p_b \, e^{r_b \cdot \nabla_2} \, | \beta_0 \rangle$$

$$: (\nabla_2 \nabla_2 - \mathsf{U} \Delta_2) \, \frac{1}{R_1} \int \frac{d\mathbf{k}}{4\pi k^3} \, (e^{-i\mathbf{k} \cdot \mathbf{R}_2} - 1)$$

$$\times \left\{ \frac{1}{(k_\alpha + k_\beta)(k_\beta + k)} - \frac{1}{(k_\alpha + k)(k_\beta + k)} + \frac{1}{(k_\alpha + k)(k_\alpha + k_\beta)} \right\}. \tag{25}$$

(The order of the momentum and the exponential operator in the matrix elements is irrelevant due to the contractions with the factor $\nabla_2 \nabla_2 - \mathsf{U} \Delta_2$.) The second term within the curly brackets may be split in the following way:

$$\frac{1}{(k_\alpha + k)(k_\beta + k)} = - \frac{1}{k_\alpha - k_\beta} \left( \frac{1}{k_\alpha + k} - \frac{1}{k_\beta + k} \right). \tag{26}$$

Then the integral in (25) becomes the sum of four parts of similar structure. Carrying out the angular integration with the help of (16) one finds for the integral:

$$\frac{2G_0(k_\alpha R_2)}{k_\alpha(k_\alpha^2 - k_\beta^2) \, R_2} + (\alpha \leftrightarrow \beta), \tag{27}$$

with the abbreviation:

$$G_0(k_\alpha R) = k_\alpha^2 R \int_0^\infty \frac{dk}{k} \left( \frac{\sin kR}{kR} - 1 \right) \frac{1}{k_\alpha + k}. \tag{28}$$

In appendix A we show that in the expression (25) with (27) for $V_3(R)$ the function $G_0$ may be replaced by

$$G(k_\alpha R) = P(k_\alpha R) - k_\alpha R \log k_\alpha R - \tfrac{1}{2}\pi. \tag{29}$$

Here $P$ is the function defined as

$$P(x) = \int_0^\infty dt \frac{\sin t}{x + t} \; ; \tag{30}$$

it is related to the sine and cosine integrals[3]). As a result we have found now for $V_3(R)$:

$$V_3(R) = \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{4e^4}{\pi \hbar m^2 c^3 k_\alpha (k_\alpha^2 - k_\beta^2)} \langle \alpha_0 | e^{-r_a \cdot \nabla_1} | \alpha \rangle$$

$$\times \langle \alpha | \, \boldsymbol{p}_a \, e^{-r_a \cdot \nabla_2} | \alpha_0 \rangle \langle \beta_0 | e^{r_b \cdot \nabla_1} | \beta \rangle \langle \beta | \, \boldsymbol{p}_b \, e^{r_b \cdot \nabla_2} | \beta_0 \rangle$$

$$: (\nabla_2 \nabla_2 - \mathsf{U} \Delta_2) \frac{G(k_\alpha R_2)}{R_1 R_2} + (a, \alpha \leftrightarrow b, \beta). \tag{31}$$

Along similar lines as above one obtains for the contributions of the fourth group of diagrams:

$$V_4(R) = \sum_{\alpha(\neq \alpha_0)} \frac{e^4}{\pi^2 m^3 c^4} \langle \alpha_0 | \, \boldsymbol{p}_a \, e^{-r_a \cdot \nabla_1} | \alpha \rangle \cdot (\nabla_1 \nabla_1 - \mathsf{U} \Delta_1)$$

$$\cdot (\nabla_2 \nabla_2 - \mathsf{U} \Delta_2) \cdot \langle \alpha | \, \boldsymbol{p}_a \, e^{-r_a \cdot \nabla_3} | \alpha_0 \rangle \langle \beta_0 | e^{r_b \cdot (\nabla_1 + \nabla_3)} | \beta_0 \rangle$$

$$\times \int \frac{d\boldsymbol{k} \, d\boldsymbol{k}'}{(4\pi)^2 \, k^3 k'^3} (e^{-i\boldsymbol{k} \cdot \boldsymbol{R}_1} - 1)(e^{-i\boldsymbol{k}' \cdot \boldsymbol{R}_2} - 1) \left\{ \frac{1}{(k_\alpha + k)(k + k')} \right.$$

$$\left. + \frac{1}{(k_\alpha + k)(k_\alpha + k')} + \frac{1}{(k + k')(k_\alpha + k')} \right\} + (a, \alpha \leftrightarrow b, \beta). \tag{32}$$

Using (16) one gets for the integral:

$$\frac{\pi H_0(k_\alpha R_1, k_\alpha R_2)}{k_\alpha^4 R_1 R_2} \, , \tag{33}$$

with the abbreviation:

$$H_0(k_\alpha R_1, k_\alpha R_2)$$

$$= \frac{k_\alpha^4 R_1 R_2}{\pi} \int_0^\infty \frac{dk \, dk'}{kk'} \left( \frac{\sin kR_1}{kR_1} - 1 \right) \left( \frac{\sin k'R_2}{k'R_2} - 1 \right)$$

$$\times \left\{ \frac{1}{(k_\alpha + k)(k + k')} + \frac{1}{(k_\alpha + k)(k_\alpha + k')} + \frac{1}{(k + k')(k_\alpha + k')} \right\}.$$

$$\tag{34}$$

In the first appendix it is proved that instead of $H_0$ one may insert into $V_4$

the function

$$H(k_\alpha R_1, k_\alpha R_2) = G(k_\alpha R_1 + k_\alpha R_2) - G(k_\alpha R_1) - G(k_\alpha R_2)$$
$$+ F(k_\alpha R_1, k_\alpha R_2), \tag{35}$$

so that one arrives at the result:

$$V_4(R) = \sum_{\alpha(\neq \alpha_0)} \frac{e^4}{\pi m^3 c^4 k_\alpha^4} \langle \alpha_0 | \boldsymbol{p}_a \, e^{-\boldsymbol{r}_a \cdot \boldsymbol{\nabla}_1} | \alpha \rangle \cdot (\boldsymbol{\nabla}_1 \boldsymbol{\nabla}_1 - \mathsf{U}\Delta_1)$$

$$\cdot (\boldsymbol{\nabla}_2 \boldsymbol{\nabla}_2 - \mathsf{U}\Delta_2) \cdot \langle \alpha | \boldsymbol{p}_a \, e^{-\boldsymbol{r}_a \cdot \boldsymbol{\nabla}_2} | \alpha_0 \rangle \langle \beta_0 | e^{\boldsymbol{r}_b \cdot (\boldsymbol{\nabla}_1 + \boldsymbol{\nabla}_2)} | \beta_0 \rangle$$

$$\times \frac{H(k_\alpha R_1, k_\alpha R_2)}{R_1 R_2} + (a, \alpha \leftrightarrow b, \beta). \tag{36}$$

Finally, the diagrams of the fifth type yield the expression:

$$V_5(R) = - \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{e^4}{\pi^2 \hbar m^4 c^5} \langle \alpha_0 | \boldsymbol{p}_a \, e^{-\boldsymbol{r}_a \cdot \boldsymbol{\nabla}_1} | \alpha \rangle$$

$$\times \langle \beta_0 | \boldsymbol{p}_b \, e^{\boldsymbol{r}_b \cdot \boldsymbol{\nabla}_1} | \beta \rangle : (\boldsymbol{\nabla}_1 \boldsymbol{\nabla}_1 - \mathsf{U}\Delta_1) \langle \alpha | \boldsymbol{p}_a \, e^{-\boldsymbol{r}_a \cdot \boldsymbol{\nabla}_2} | \alpha_0 \rangle$$

$$\times \langle \beta | \boldsymbol{p}_b \, e^{\boldsymbol{r}_b \cdot \boldsymbol{\nabla}_2} | \beta_0 \rangle : (\boldsymbol{\nabla}_2 \boldsymbol{\nabla}_2 - \mathsf{U}\Delta_2)$$

$$\times \int \frac{d\boldsymbol{k} \, d\boldsymbol{k}'}{(4\pi)^2 \, k^3 k'^3} (e^{-i\boldsymbol{k} \cdot \boldsymbol{R}_1} - 1)(e^{-i\boldsymbol{k}' \cdot \boldsymbol{R}_2} - 1)$$

$$\times \left\{ \frac{1}{(k_\alpha + k)(k + k')(k_\beta + k')} + \frac{1}{(k_\alpha + k)(k_\alpha + k_\beta)(k_\beta + k')} \right.$$

$$+ \frac{1}{(k_\alpha + k)(k_\alpha + k_\beta)(k_\alpha + k')} + \frac{1}{(k_\alpha + k)(k + k')(k_\beta + k)}$$

$$+ \frac{1}{(k_\alpha + k)(k_\alpha + k_\beta + k + k')(k_\beta + k)}$$

$$+ \frac{1}{(k_\alpha + k)(k_\alpha + k_\beta + k + k')(k_\alpha + k')} + (\alpha \leftrightarrow \beta) \right\}. \tag{37}$$

Since the part of the expression in front of the curly brackets is symmetric with respect to an interchange of $(a, \alpha)$ and $(b, \beta)$ we could bring the symbol $(\alpha \leftrightarrow \beta)$ inside these brackets. Furthermore, because $\boldsymbol{\nabla}_1$ and $\boldsymbol{\nabla}_2$ appear in a symmetric way, one may interchange $k$ and $k'$ in each of the terms with energy denominators. The sum of the first three of these (arising from diagrams with non-crossing photon lines) may be rewritten as

$$\frac{k_\alpha + k_\beta + k + k'}{(k_\alpha + k)(k + k')(k_\beta + k')(k_\alpha + k_\beta)} + \frac{1}{(k_\alpha + k)(k_\alpha + k')(k_\alpha + k_\beta)}$$

$$= \frac{1}{k_\alpha + k_\beta} \left\{ \frac{1}{(k_\alpha + k)(k + k')} + \frac{1}{(k_\beta + k')(k + k')} \right. $$
$$\left. + \frac{1}{(k_\alpha + k)(k_\alpha + k')} \right\}. \tag{38}$$

Adding the terms with $\alpha$ and $\beta$ interchanged one may bring this in the form:

$$\frac{1}{k_\alpha + k_\beta} \left\{ \frac{1}{(k_\alpha + k)(k + k')} + \frac{1}{(k_\alpha + k')(k + k')} \right.$$
$$\left. + \frac{1}{(k_\alpha + k)(k_\alpha + k')} \right\} + (\alpha \leftrightarrow \beta). \tag{39}$$

The remaining energy denominator terms in (37) (due to diagrams with crossed photon lines) may be transformed, with the help of (26), into:

$$- \frac{1}{k_\alpha - k_\beta} \left\{ \frac{1}{k + k'} \left( \frac{1}{k_\alpha + k} - \frac{1}{k_\beta + k} \right) \right.$$
$$\left. + \frac{1}{k_\alpha + k'} \left( \frac{1}{k_\alpha + k} - \frac{1}{k_\beta + k} \right) \right\}. \tag{40}$$

Combining this with the expression found by interchanging $\alpha$ and $\beta$, and symmetrizing then with respect to $k$ and $k'$ one gets a result similar to (39):

$$- \frac{1}{k_\alpha - k_\beta} \left\{ \frac{1}{(k_\alpha + k)(k + k')} + \frac{1}{(k_\alpha + k')(k + k')} \right.$$
$$\left. + \frac{1}{(k_\alpha + k)(k_\alpha + k')} \right\} + (\alpha \leftrightarrow \beta). \tag{41}$$

The curly bracket expression in the integral of (37) is given now by the sum of (39) and (41). After integration over the angles with the help of (16) one finds for this integral:

$$- \frac{2\pi k_\beta H_0(k_\alpha R_1, k_\alpha R_2)}{k_\alpha^4(k_\alpha^2 - k_\beta^2) R_1 R_2} + (\alpha \leftrightarrow \beta), \tag{42}$$

where $H_0$ has been given in (34). Just as in $V_4(R)$ one may replace $H_0$ by the function $H$ defined in (35). Then the contribution $V_5(R)$ becomes:

$$V_5(R) = \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{2e^4 k_\beta}{\pi \hbar m^4 c^5 k_\alpha^4 (k_\alpha^2 - k_\beta^2)}$$
$$\times \langle \alpha_0 | \boldsymbol{p}_a \, e^{-\boldsymbol{r}_a \cdot \boldsymbol{\nabla}_1} | \alpha \rangle \langle \beta_0 | \boldsymbol{p}_b \, e^{\boldsymbol{r}_b \cdot \boldsymbol{\nabla}_1} | \beta \rangle : (\boldsymbol{\nabla}_1 \boldsymbol{\nabla}_1 - \mathsf{U}\Delta_1)$$
$$\times \langle \alpha | \boldsymbol{p}_a \, e^{-\boldsymbol{r}_a \cdot \boldsymbol{\nabla}_2} | \alpha_0 \rangle \langle \beta | \boldsymbol{p}_b \, e^{\boldsymbol{r}_b \cdot \boldsymbol{\nabla}_2} | \beta_0 \rangle : (\boldsymbol{\nabla}_2 \boldsymbol{\nabla}_2 - \mathsf{U}\Delta_2)$$
$$\times \frac{H(k_\alpha R_1, k_\alpha R_2)}{R_1 R_2} + (a, \alpha \leftrightarrow b, \beta). \tag{43}$$

Collecting the results we have found now for the retarded interatomic potential energy $V(R)$ of two nondegenerate ground-state atoms at a separation $R$:

$$V(R) = \sum_{s=1}^{5} V_s(R). \tag{44}$$

The various contributions $V_s(R)$ have been written in formulae (11), (20), (31), (36) and (42) with auxiliary functions (19), (29) and (35).

4. *Transformation of the matrix elements. Dispersion energy to all multipole orders.* In the previous section we obtained the interatomic potential energy as a sum of five contributions containing different products of matrix elements. In the electric-dipole approximation[1]) these products may be brought into the same form by transforming the matrix elements. Then it appears that some terms cancel so that a considerable simplification can be achieved. In the following we want to show that a similar situation exists in the general case of arbitrary multipoles.

Let us start by introducing the following notations:

$$\begin{aligned}
\boldsymbol{P}_{\alpha,i} &= \langle\alpha_0| \tfrac{1}{2}\{\boldsymbol{p}_a, e^{-\boldsymbol{r}_a\cdot\boldsymbol{V}_i}\} |\alpha\rangle, \\
\boldsymbol{P}_{\beta,i} &= \langle\beta_0| \tfrac{1}{2}\{\boldsymbol{p}_b, e^{\boldsymbol{r}_b\cdot\boldsymbol{V}_i}\} |\beta\rangle,
\end{aligned} \tag{45}$$

with $i = 1, 2$; the curly brackets indicate an anti-commutator. From a similar reasoning as given in (22)–(25) it follows that the sum

$$\sum_{\alpha(k_\alpha \text{ const.})} \boldsymbol{P}_{\alpha,1}\boldsymbol{P}^*_{\alpha,2}$$

is real.

The fifth contribution, displayed in (43), is already expressed in terms of the matrix elements (45) since the order of the momentum and exponential operators is irrelevant in $V_5(R)$. Thus one has:

$$\begin{aligned}
V_5(R) = &\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)} \left(\frac{e}{mc}\right)^4 \frac{2k_\beta}{\pi\hbar ck_\alpha^4(k_\alpha^2 - k_\beta^2)} \boldsymbol{P}_{\alpha,1}\boldsymbol{P}_{\beta,1} \\
&: (\boldsymbol{V}_1\boldsymbol{V}_1 - \mathsf{U}\Delta_1) \boldsymbol{P}^*_{\alpha,2}\boldsymbol{P}^*_{\beta,2} : (\boldsymbol{V}_2\boldsymbol{V}_2 - \mathsf{U}\Delta_2) \\
&\times \frac{H(k_\alpha R_1, k_\alpha R_2)}{R_1 R_2} + (\alpha \leftrightarrow \beta).
\end{aligned} \tag{46}$$

The remaining contributions contain different matrix elements as well, of the type $\langle\alpha_0| \exp(-\boldsymbol{r}_a\cdot\boldsymbol{V}_i) |\alpha\rangle$ $(i = 1, 2)$ in $V_1$ and $V_3$ and of the type $\langle\alpha_0| \exp\{-\boldsymbol{r}_a\cdot(\boldsymbol{V}_1 + \boldsymbol{V}_2)\} |\alpha_0\rangle$ in $V_2$ and $V_4$.

The matrix element $\langle\alpha_0| \exp(-\boldsymbol{r}_a\cdot\boldsymbol{V}_i) |\alpha\rangle$ may be written, for $\alpha \neq \alpha_0$, as

$$-\frac{1}{\hbar ck_\alpha} \langle\alpha_0| [H(a), e^{-\boldsymbol{r}_a\cdot\boldsymbol{V}_i}] |\alpha\rangle, \tag{47}$$

where the commutator with the hamiltonian given in (2) appears. Inserting this expression we get the relation

$$\langle \alpha_0 | \, e^{-r_a \cdot V_i} \, | \alpha \rangle = \frac{1}{imck_\alpha} \, V_i \cdot P_{\alpha, i}, \tag{48}$$

with $i = 1, 2$. An analogous equality follows when $(a, \alpha)$ is replaced by $(b, \beta)$ and $V_i$ by $-V_i$. Employing these relations we may cast the electrostatic interaction $V_1(R)$ into the form:

$$V_1(R) = - \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \left( \frac{e}{mc} \right)^4 \frac{1}{2\hbar c k_\alpha^2 k_\beta^2 (k_\alpha + k_\beta)} \, P_{\alpha, 1} P_{\beta, 1}$$

$$: (V_1 V_1 - \mathsf{U}\Delta_1) \, P^*_{\alpha, 2} P^*_{\beta, 2} : (V_2 V_2 - \mathsf{U}\Delta_2) \frac{1}{R_1 R_2} + (\alpha \leftrightarrow \beta), \tag{49}$$

where we used the vanishing of $\Delta R^{-1}$ to introduce the same combinations of nabla operators as in (46).

In the mixed contribution $V_3(R)$ the electrostatic part is dealt with as in $V_1(R)$ and the photon part as in $V_5(R)$. If the result is symmetrized in $R_1$ and $R_2$ we get:

$$V_3(R) = \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \left( \frac{e}{mc} \right)^4 \frac{2}{\pi \hbar c k_\alpha^2 k_\beta (k_\alpha^2 - k_\beta^2)} \, P_{\alpha, 1} P_{\beta, 1}$$

$$: (V_1 V_1 - \mathsf{U}\Delta_1) \, P^*_{\alpha, 2} P^*_{\beta, 2} : (V_2 V_2 - \mathsf{U}\Delta_2) \frac{G(k_\alpha R_1) + G(k_\alpha R_2)}{R_1 R_2}$$

$$+ (\alpha \leftrightarrow \beta). \tag{50}$$

The matrix element $\langle \alpha_0 | \exp\{-r_a \cdot (V_1 + V_2)\} | \alpha_0 \rangle$, that occurs in $V_2$ and $V_4$, will be transformed with the use of a sum rule. In fact, we may write:

$$V_1 \sum_j e^{-r_{aj} \cdot (V_1 + V_2)} = \frac{i}{\hbar} \Big[ \sum_j e^{-r_{aj} \cdot V_1}, \sum_{j'} \tfrac{1}{2} \{ p_{aj'}, e^{-r_{aj'} \cdot V_2} \} \Big]. \tag{51}$$

Taking the ground-state expectation value and inserting a sum over intermediate states we get for the right-hand side:

$$\sum_{\alpha(\neq \alpha_0)} \frac{i}{\hbar} \Big[ \langle \alpha_0 | \, e^{-r_a \cdot V_1} | \alpha \rangle \langle \alpha | \, \tfrac{1}{2} \{ p_a, e^{-r_a \cdot V_2} \} | \alpha_0 \rangle$$

$$- \langle \alpha_0 | \, \tfrac{1}{2} \{ p_a, e^{-r_a \cdot V_2} \} | \alpha \rangle \langle \alpha | \, e^{-r_a \cdot V_1} | \alpha_0 \rangle \Big]. \tag{52}$$

With the notation (45) and the relations (24) and (48) we arrive at the sum rule

$$V_1 \langle \alpha_0 | \, e^{-r_a \cdot (V_1 + V_2)} | \alpha_0 \rangle = \sum_{\alpha(\neq \alpha_0)} \frac{2}{\hbar m c k_\alpha} \, V_1 \cdot P_{\alpha, 1} P^*_{\alpha, 2}. \tag{53}$$

Similar relations are obtained if $V_1$ and $V_2$ are interchanged and if $(a, \alpha)$ and $V_i$ are replaced by $(b, \beta)$ and $-V_i$.

The sum rules just obtained will be applied now to $V_2$ and $V_4$ successively. If in (20) the product $(V_1 V_1 - \mathsf{U}\Delta_1) : (V_2 V_2 - \mathsf{U}\Delta_2)$ is written out, $V_2$ becomes the sum of four terms. The first three of these are transformed with the help of the sum rules, while the last term is left unchanged for the present. The result may be written as

$$V_2(R) = -\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)}\left(\frac{e}{mc}\right)^4\frac{1}{\pi\hbar c k_\alpha k_\beta}$$

$$\times\ \{P_{\alpha,1}P_{\beta,1} : (V_1 V_1 - \mathsf{U}\Delta_1)\ P^*_{\alpha,2}P^*_{\beta,2} : (V_2 V_2 - \mathsf{U}\Delta_2)$$

$$-\ P_{\alpha,1}\cdot P_{\beta,1}P^*_{\alpha,2}\cdot P^*_{\beta,2}\Delta_1\Delta_2\}\frac{F(R_1, R_2)}{R_1 R_2}$$

$$-\ \frac{3e^4\hbar}{4\pi m^2 c^3}\ \langle\alpha_0|\,e^{-r_a\cdot(V_1+V_2)}\,|\alpha_0\rangle$$

$$\times\ \langle\beta_0|\,e^{r_b\cdot(V_1+V_2)}\,|\beta_0\rangle\ \Delta_1\Delta_2\ \frac{F(R_1, R_2)}{R_1 R_2} + (a, \alpha \leftrightarrow b, \beta). \tag{54}$$

One of the terms appearing here has the structure of the expressions (46), (49) and (50). The remaining terms both contain explicit factors $\Delta_1$ and $\Delta_2$, due to which only the part of $F(R_1, R_2)$ with double argument $R_1 + R_2$ contributes. If we now transform in $V_2$ the last term as well, with the help of (53), we obtain:

$$V_2(R) = -\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)}\left(\frac{e}{mc}\right)^4\frac{1}{\pi\hbar c k_\alpha k_\beta}\ P_{\alpha,1}P_{\beta,1} : (V_1 V_1 - \mathsf{U}\Delta_1)$$

$$\times\ P^*_{\alpha,2}P^*_{\beta,2} : (V_2 V_2 - \mathsf{U}\Delta_2)\ \frac{F(R_1, R_2)}{R_1 R_2}$$

$$+\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)}\left(\frac{e}{mc}\right)^4\frac{1}{\pi\hbar c k_\alpha k_\beta}\ \{P_{\alpha,1}\cdot P_{\beta,1}P^*_{\alpha,2}\cdot P^*_{\beta,2}\Delta_1\Delta_2$$

$$-\ \tfrac{3}{2}P_{\alpha,1}\cdot V_1 P_{\beta,1}\cdot V_1 P^*_{\alpha,2}\cdot P^*_{\beta,2}\Delta_2 - \tfrac{3}{2}P_{\alpha,1}\cdot P_{\beta,1}\Delta_1 P^*_{\alpha,2}\cdot V_2 P^*_{\beta,2}\cdot V_2\}$$

$$\times\ \frac{(R_1 + R_2)^3 \log(R_1 + R_2)}{6 R_1 R_2} + (\alpha \leftrightarrow \beta). \tag{55}$$

In a similar way the contribution $V_4$, given in (26), may be dealt with. As a result a sum of two terms is found, the first of which has a structure analogous to that of (46), (49) and (50), while the second contains in the numerator again a function of the double argument $R_1 + R_2$ only:

$$V_4(R) = \sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)} \left(\frac{e}{mc}\right)^4 \frac{2}{\pi\hbar ck_\alpha^4 k_\beta} P_{\alpha,1}P_{\beta,1} : (\boldsymbol{\nabla}_1\boldsymbol{\nabla}_1 - \mathsf{U}\Delta_1)$$

$$\times\ P_{\alpha,2}^* P_{\beta,2}^* : (\boldsymbol{\nabla}_2\boldsymbol{\nabla}_2 - \mathsf{U}\Delta_2)\ \frac{H(k_\alpha R_1, k_\alpha R_2)}{R_1 R_2}$$

$$-\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)} \left(\frac{e}{mc}\right)^4 \frac{2}{\pi\hbar ck_\alpha^4 k_\beta} \{P_{\alpha,1}\cdot P_{\beta,1}P_{\alpha,2}^*\cdot P_{\beta,2}^*$$

$$\times\ \Delta_1\Delta_2 - \tfrac{1}{2}P_{\alpha,1}\cdot P_{\alpha,2}^* P_{\beta,1}\cdot\boldsymbol{\nabla}_1 P_{\beta,2}^*\cdot\boldsymbol{\nabla}_1\Delta_2$$

$$-\tfrac{1}{2}P_{\alpha,1}\cdot P_{\alpha,2}^* P_{\beta,1}\cdot\boldsymbol{\nabla}_2 P_{\beta,2}^*\cdot\boldsymbol{\nabla}_2\Delta_1\}$$

$$\times\left\{\frac{G(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2} + \frac{k_\alpha^3(R_1+R_2)^3\log(R_1+R_2)}{6R_1 R_2}\right\} + (\alpha\leftrightarrow\beta).$$

$$(56)$$

Adding the various contributions and using their symmetry with respect to $\alpha$ and $\beta$ one finds indeed that several terms from different diagrams cancel, in such a way that only functions of the double argument $R_1 + R_2$ appear in the numerators. As a result the retarded interatomic potential energy of two nondegenerate ground-state atoms may be brought into the form:

$$V(R) = \sum_{\sigma = \mathrm{I,II,III}} V_\sigma(R), \tag{57}$$

with

$$V_\mathrm{I}(R) = \sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)} \left(\frac{e}{mc}\right)^4 \frac{1}{\pi\hbar ck_\alpha^2 k_\beta(k_\alpha^2 - k_\beta^2)} P_{\alpha,1}P_{\beta,1}$$

$$: (\boldsymbol{\nabla}_1\boldsymbol{\nabla}_1 - \mathsf{U}\Delta_1)\ P_{\alpha,2}^* P_{\beta,2}^* : (\boldsymbol{\nabla}_2\boldsymbol{\nabla}_2 - \mathsf{U}\Delta_2)$$

$$\times\ \frac{P(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2} + (\alpha\leftrightarrow\beta;\ 1\leftrightarrow 2), \tag{58}$$

$$V_\mathrm{II}(R) = -\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)} \left(\frac{e}{mc}\right)^4 \frac{1}{\pi\hbar ck_\alpha^4 k_\beta} \{P_{\alpha,1}\cdot P_{\beta,1}P_{\alpha,2}^*\cdot P_{\beta,2}^*$$

$$\times\ \Delta_1\Delta_2 - P_{\alpha,1}\cdot P_{\alpha,2}^* P_{\beta,1}\cdot\boldsymbol{\nabla}_1 P_{\beta,2}^*\cdot\boldsymbol{\nabla}_1\Delta_2\}$$

$$\times\ \frac{G(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2} + (\alpha\leftrightarrow\beta;\ 1\leftrightarrow 2), \tag{59}$$

$$V_\mathrm{III}(R) = -\sum_{\alpha(\neq\alpha_0),\beta(\neq\beta_0)} \left(\frac{e}{mc}\right)^4 \frac{1}{2\pi\hbar ck_\alpha k_\beta} \{P_{\alpha,1}\cdot P_{\beta,1}$$

$$\times\ P_{\alpha,2}^*\cdot P_{\beta,2}^*\Delta_1\Delta_2 + 3P_{\alpha,1}\cdot\boldsymbol{\nabla}_1 P_{\beta,1}\cdot\boldsymbol{\nabla}_1 P_{\alpha,2}^*\cdot P_{\beta,2}^*\Delta_2$$

$$-2P_{\alpha,1}\cdot P_{\alpha,2}^* P_{\beta,1}\cdot\boldsymbol{\nabla}_1 P_{\beta,2}^*\cdot\boldsymbol{\nabla}_1\Delta_2\}$$

$$\times\ \frac{(R_1+R_2)^3\log(R_1+R_2)}{6R_1 R_2} + (\alpha\leftrightarrow\beta;\ 1\leftrightarrow 2). \tag{60}$$

The symbol $(\alpha \leftrightarrow \beta; 1 \leftrightarrow 2)$ stands for the three terms that arise by interchanging both $\alpha$, $\beta$ and 1, 2 independently in the preceding term.

The expression for $V(R)$ may be written in a form that contains the matrix elements of the electric and magnetic multipole operators [4]

$$\mu_\alpha^{(n)} = -e \left\langle \alpha_0 \left| \frac{1}{n!} \sum_j \boldsymbol{r}_{aj}^n \right| \alpha \right\rangle, \tag{61}$$

$$\nu_\alpha^{(n)} = -\frac{e}{2mc} \left\langle \alpha_0 \left| \frac{n}{(n+1)!} \sum_j \{\boldsymbol{r}_{aj}^{n-1}, \boldsymbol{r}_{aj} \wedge \boldsymbol{p}_{aj}\} \right| \alpha \right\rangle, \tag{62}$$

with $n = 1, 2, \ldots$. In fact from the definition (45) one finds the relation

$$\frac{e}{mc} \boldsymbol{P}_{\alpha, i} = \sum_{n=1}^{\infty} (-\boldsymbol{V}_i)^{n-1} : \{i k_\alpha \mu_\alpha^{(n)} + \nu_\alpha^{(n)} \wedge \boldsymbol{V}_i\}, \tag{63}$$

with $i = 1, 2$.

In the formulae (59) (with (29)) and (60) logarithmic functions occur. However, in (59) the function $\{(R_1 + R_2)/R_1 R_2\} \log(R_1 + R_2)$ is acted upon by at least one Laplace operator. If (60) is rewritten with the help of (53), two of these Laplace operators appear, which are acting on the radial function $\{(R_1 + R_2)^3/R_1 R_2\} \log(R_1 + R_2)$. As a result neither $V_{II}$ nor $V_{III}$ contains any logarithmic function when the differentiations have been performed.

The short-distance behaviour of (58) and (59) may be obtained from the series expansions for the sinc and cosine integrals [3]. From these one gets:

$$P(x) = \tfrac{1}{2}\pi + x \log x + (\gamma - 1) x - \tfrac{1}{4}\pi x^2 + \ldots . \tag{64}$$

Comparison of terms with the same multipole matrix elements in $V_I$, $V_{II}$ and $V_{III}$ shows that $V_I$ becomes dominant for small $R$. Inserting the value $\tfrac{1}{2}\pi$ for $P(k_\alpha R_1 + k_\alpha R_2)$ and using (48) one recovers the electrostatic potential energy (11).

For separations that are large compared to the maximal $k_\alpha^{-1}$ we may employ the expansion of $P(x)$ in powers of $x^{-1}$, which starts with the terms [3]:

$$P(x) = x^{-1} - 2x^{-3} + 24x^{-5} - \ldots . \tag{65}$$

If again contributions with the same multipole matrix elements in $V_I$, $V_{II}$ and $V_{III}$ are compared one finds that the order of magnitude of their leading terms are in the proportion of 1 to $(k_\alpha R)^2$ to $(k_\alpha R)^4$, respectively, so that now $V_{III}$ is dominant. In drawing this conclusion we did not take into account the way of contraction of the nabla operators and the matrix elements, due to which certain multipole contributions vanish. This becomes clear when the electric-dipole approximation is studied.

The electric-dipole approximation is obtained by retaining only the first

term in the Taylor expansion of the exponential operator in $P_{\alpha, i}$ which then becomes $\langle \alpha_0 | \, \boldsymbol{p}_a \, | \alpha \rangle$ or $-imck_\alpha \langle \alpha_0 | \, \boldsymbol{r}_a \, | \alpha \rangle$. Due to the rotational invariance of the nondegenerate ground state $|\alpha_0\rangle$ we may write now:

$$\sum_{\alpha(k_\alpha \text{ const.})} \boldsymbol{P}_{\alpha, i} \boldsymbol{P}^\star_{\alpha, i} = \frac{1}{3} \left( \frac{mc}{e} \right)^2 k_\alpha^2 \mathsf{U} \sum_{\alpha(k_\alpha \text{ const.})} |\boldsymbol{\mu}_\alpha|^2, \tag{66}$$

where $\boldsymbol{\mu}_\alpha$ stands for the dipole matrix element $-e \langle \alpha_0 | \, \boldsymbol{r}_a \, | \alpha \rangle$. On substituting this expression into (57) with (58)–(60) the contributions $V_{\text{II}}$ and $V_{\text{III}}$ drop out due to the vectorial contractions, so that we get:

$$V(R) = \sum_{\alpha(\neq\alpha_0), \beta(\neq\beta_0)} \frac{2k_\alpha k_\beta}{9\pi\hbar c(k_\alpha^2 - k_\beta^2)} |\boldsymbol{\mu}_\alpha|^2 \, |\boldsymbol{\mu}_\beta|^2 \, (\boldsymbol{V}_1 \boldsymbol{V}_1 - \mathsf{U}\Delta_1)$$

$$: (\boldsymbol{V}_2 \boldsymbol{V}_2 - \mathsf{U}\Delta_2) \left\{ \frac{P(k_\alpha R_1 + k_\alpha R_2)}{k_\alpha R_1 R_2} - \frac{P(k_\beta R_1 + k_\beta R_2)}{k_\beta R_1 R_2} \right\}. \tag{67}$$

If we now employ the ancillary relation for an arbitrary function $f$:

$$(\boldsymbol{V}_1 \boldsymbol{V}_1 - \mathsf{U}\Delta_1) : (\boldsymbol{V}_2 \boldsymbol{V}_2 - \mathsf{U}\Delta_2) \frac{f(R_1 + R_2)}{R_1 R_2} \bigg\|_{R_1 = R_2 = R}$$

$$= \frac{2}{R^2} \left\{ f^{(4)}(2R) - \frac{2}{R} f^{(3)}(2R) + \frac{5}{R^2} f^{(2)}(2R) \right.$$

$$\left. - \frac{6}{R^3} f^{(1)}(2R) + \frac{3}{R^4} f(2R) \right\}, \tag{68}$$

(where $f^{(n)}$ denotes the $n$-fold derivative of $f$) and the differentiation formulae

$$P^{(1)}(x) = -Q(x), \qquad P^{(2)}(x) = -P(x) + x^{-1} \tag{69}$$

that follow from the definition (30) for $P(x)$ and the analogous one for $Q(x)$:

$$Q(x) = \int\limits_0^\infty dt \, \frac{\cos t}{x + t}, \tag{70}$$

we get in the dipole approximation:

$$V(R) = \sum_{\alpha(\neq\alpha_0), \beta(\neq\beta_0)} \frac{4k_\alpha k_\beta}{9\pi\hbar c(k_\alpha^2 - k_\beta^2) \, R^5} |\boldsymbol{\mu}_\alpha|^2 \, |\boldsymbol{\mu}_\beta|^2$$

$$\times [\{(k_\alpha R)^3 - 5(k_\alpha R) + 3(k_\alpha R)^{-1}\} \, P(2k_\alpha R)$$

$$+ \{-2(k_\alpha R)^2 + 6\} \, Q(2k_\alpha R) - \tfrac{1}{2}(k_\alpha R)^2 - (\alpha \leftrightarrow \beta)]. \tag{71}$$

An alternative form may be obtained by employing for $P(x)$ in (67) the

integral representation [3])

$$P(x) = \int_0^\infty dt \, \frac{e^{-xt}}{1 + t^2} \, ;$$
(72)

then one finds with (68):

$$V(R) = - \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \frac{4k_\alpha k_\beta}{9\pi\hbar cR^3} |\boldsymbol{\mu}_\alpha|^2 |\boldsymbol{\mu}_\beta|^2$$

$$\times \int_0^\infty dt \, \frac{e^{-2t}(t^4 + 2t^3 + 5t^2 + 6t + 3)}{\{(k_\alpha R)^2 + t^2\}\{(k_\beta R)^2 + t^2\}} \, ,$$
(73)

which is the result of Casimir and Polder [1]).

The long-range expansion (65) for $P(x)$ and the ensuing one for $Q(x) = -dP/dx$ lead to the well-known asymptotic form of (71) containing an inverse seventh power of the interatomic separation $R$.

Closer inspection of the argument that led to the expression (67) shows that $V_{\text{III}}$ vanishes if the matrix elements of at least one of the atoms are considered in the electric-dipole approximation, while $V_{\text{II}}$ disappears if in the matrix elements of both atoms this approximation is used. On the basis of these arguments one may infer that $V_{\text{II}}$ and $V_{\text{III}}$ will fall off, for large separations, as $R^{-6}$ and $R^{-5}$, respectively. However, in the general expressions for $V_{\text{I}}$, $V_{\text{II}}$ and $V_{\text{III}}$ some products of the electric and magnetic multipole matrix elements $\mu_\alpha^{(n)}$ and $\nu_\alpha^{(n)}$, defined in (61) and (62), drop out due to the symmetry properties of the atoms.

Using the rotation invariance of the hamiltonian $H(a)$ given in (2), which implies the invariance of the nondegenerate ground state $|\alpha_0\rangle$, one may prove:

$$\sum_{\alpha(k_\alpha \text{ const.})} \mu_\alpha^{(n_1)} \mu_\alpha^{(n_2)*} = 0 \qquad (n_1 - n_2 \text{ odd}).$$
(74)

Moreover, spatial inversion symmetry of $H(a)$ (and hence of $|\alpha_0\rangle$) results in the relations

$$\sum_{\alpha(k_\alpha \text{ const.})} \nu_\alpha^{(n_1)} \nu_\alpha^{(n_2)*} = 0 \qquad (n_1 - n_2 \text{ odd}),$$
(75)

$$\sum_{\alpha(k_\alpha \text{ const.})} \mu_\alpha^{(n_1)} \nu_\alpha^{(n_2)*} = 0 \qquad (n_1 - n_2 \text{ even}).$$
(76)

Since the hamiltonian $H(a)$ commutes with the total angular-momentum operator $L(a)$ of atom $a$, another consequence of the assumed nondegeneracy of $|\alpha_0\rangle$ is the vanishing of $L(a)|\alpha_0\rangle$. In the approximation of fixed nuclei one may write $L(a)$ as $\sum_j \boldsymbol{r}_{aj} \wedge \boldsymbol{p}_{aj}$. Upon comparing this with (62) one finds:

$$\nu_\alpha^{(1)} = 0,$$
(77)

so that the magnetic-dipole moments do not contribute. (Relations analogous to (74)–(77) hold for atom $b$.)

If the results obtained above are applied to (59) and (60) one is led to the conclusion that not only $V_I$ but also $V_{II}$ and $V_{III}$ will have asymptotic expressions varying as $R^{-7}$. The asymptotic expression of $V_I$ is due to pure dipole–dipole interaction, while in that for $V_{II}$ and $V_{III}$ higher-order multipole moments of at least one of the atoms play a role. Thus multipoles of different order may give rise to dispersion energies varying in the same way for large separations.

<div align="center">APPENDIX A</div>

*The auxiliary functions $F$, $G$ and $H$.* In this appendix we shall evaluate the integrals given in (18), (28) and (34), and show that they may be replaced, in $V(R)$, by the auxiliary functions (19), (29) and (35), respectively.

The integral (18) may be written in the form:

$$
F_0(R_1, R_2) = \frac{R_1 R_2}{\pi} \int_0^\infty \frac{dk\, dk'}{kk'} \left\{ \left( \frac{\sin kR_1}{kR_1} - 1 \right) \left( \frac{\sin k'R_2}{k'R_2} - 1 \right) \right.
$$

$$
\left. + (R_1 \leftrightarrow R_2) \right\} \frac{1}{k + k'}, \tag{A.1}
$$

where the symmetry in $R_1$ and $R_2$ is made manifest. As a consequence a symmetry of the integrand in $k$ and $k'$ is obtained, which allows us to replace the lower limit of the $k'$ integration by $-\infty$. The singularity that arises for $k' = -k$ is avoided by taking the principal value of the integral. Thus the $k'$ integral is of the form:

$$
\fint_{-\infty}^{\infty} \frac{dk'}{k'} \left( \frac{\sin k'R}{k'R} - 1 \right) \frac{1}{k + k'}. \tag{A.2}
$$

Writing the sine function in terms of exponentials and closing the contour in the complex plane one finds for this integral:

$$
\frac{\pi}{k^2 R} (\cos kR - 1). \tag{A.3}
$$

Insertion into (A.1) yields the expression:

$$
F_0(R_1, R_2) = \int_0^\infty \frac{dk}{k^4} \{ \sin k(R_1 + R_2) - \sin kR_1 - \sin kR_2
$$

$$
- kR_1 \cos kR_2 - kR_2 \cos kR_1 + kR_1 + kR_2 \}. \tag{A.4}
$$

If we replace the lower limit by $\varepsilon > 0$, the integral may be split into integrals of the type:

$$I_n(\varepsilon) = \int_\varepsilon^\infty dx \, \frac{\sin x}{x^{n+1}}, \qquad J_n(\varepsilon) = \int_\varepsilon^\infty dx \, \frac{\cos x}{x^{n+1}}. \tag{A.5}$$

For $n = 0, 1, 2$ and $3$ one has (with $\gamma$ the Euler constant):

$$I_0(\varepsilon) = \tfrac{1}{2}\pi, \qquad\qquad J_0(\varepsilon) = -\gamma - \log \varepsilon,$$

$$I_1(\varepsilon) = 1 - \gamma - \log \varepsilon, \qquad\qquad J_1(\varepsilon) = \varepsilon^{-1} - \tfrac{1}{2}\pi,$$

$$I_2(\varepsilon) = \varepsilon^{-1} - \tfrac{1}{4}\pi, \qquad\qquad J_2(\varepsilon) = \tfrac{1}{2}\varepsilon^{-2} - \tfrac{3}{4} + \tfrac{1}{2}\gamma + \tfrac{1}{2}\log \varepsilon,$$

$$I_3(\varepsilon) = \tfrac{1}{2}\varepsilon^{-2} - \tfrac{11}{36} + \tfrac{1}{6}\gamma + \tfrac{1}{6}\log \varepsilon, \tag{A.6}$$

where terms that vanish for $\varepsilon = 0$ have been omitted. Using these formulae one gets (with $\varepsilon \to 0$) for (A.4):

$$F_0(R_1, R_2) = F(R_1, R_2) - \tfrac{1}{8}R_1 R_2^2(3 \log R_2 + 1) - \tfrac{1}{8}R_1^2 R_2(3 \log R_1 + 1), \tag{A.7}$$

where $F(R_1, R_2)$ is the function given in (19). (The arguments of the logarithms, including those in $F(R_1, R_2)$, may be made dimensionless without altering the result by multiplying them with a constant of the dimension of an inverse length.) In (20) the function $F_0(R_1, R_2)$ appears divided by $R_1 R_2$ and acted upon by operators $\nabla_1$ and $\nabla_2$. Therefore the last two terms in (A.7) do not contribute in $V_2(R)$.

The integral (28) may be treated by the method of partial fractions, which yields:

$$G_0(k_\alpha R) = k_\alpha R \int_0^\infty dk \left[ \frac{\sin kR}{R} \left\{ \frac{1}{k^2} - \frac{1}{k_\alpha k} + \frac{1}{k_\alpha(k_\alpha + k)} \right\} \right.$$

$$\left. - \frac{1}{k_\alpha} + \frac{1}{k_\alpha + k} \right]. \tag{A.8}$$

Taking again $\varepsilon$ as lower integration limit and using (A.5)–(A.6) we find for this integral:

$$G_0(k_\alpha R) = G(k_\alpha R) + (1 - \gamma) k_\alpha R, \tag{A.9}$$

with $G(k_\alpha R)$ given in (29). For the same reason as mentioned above in connexion with $F_0$ the last term in (A.9) does not contribute to $V_3(R)$.

Finally we consider the integral $H_0$ written in (34). The second energy denominator term can be split into partial fractions so that the curly

bracket expression becomes:

$$\frac{1}{k_\alpha + k}\left(\frac{1}{k + k'} - \frac{1}{k - k'}\right) + \frac{1}{k_\alpha + k'}\left(\frac{1}{k + k'} + \frac{1}{k - k'}\right). \quad (A.10)$$

Due to the symmetry of this result in $k$ and $k'$ the integral $H_0$ may be cast into the form:

$$H_0(k_\alpha R_1, k_\alpha R_2)$$

$$= \frac{k_\alpha^4 R_1 R_2}{\pi} \int_0^\infty \frac{dk\,dk'}{kk'} \left\{\left(\frac{\sin kR_1}{kR_1} - 1\right)\left(\frac{\sin k'R_2}{k'R_2} - 1\right)\right.$$

$$\left. + (R_1 \leftrightarrow R_2)\right\} \frac{1}{k_\alpha + k}\left(\frac{1}{k + k'} - \frac{1}{k - k'}\right). \quad (A.11)$$

We may omit now the term $1/(k - k')$, extending the $k'$ integration domain to $-\infty$. Then the integral over $k'$ is of the type (A.2), with result (A.3), so that we find for $H_0$:

$$H_0(k_\alpha R_1, k_\alpha R_2) = k_\alpha^4 R_1 R_2 \int_0^\infty \frac{dk}{k^2(k_\alpha + k)} \left\{\frac{\sin k(R_1 + R_2)}{k^2 R_1 R_2}\right.$$

$$\left. - \frac{\sin kR_1}{k^2 R_1 R_2} - \frac{\sin kR_2}{k^2 R_1 R_2} - \frac{\cos kR_1}{kR_1} - \frac{\cos kR_2}{kR_2} + \frac{1}{kR_1} + \frac{1}{kR_2}\right\}.$$

$$(A.12)$$

If again the lower integration limit is replaced by $\varepsilon$ and the method of partial fractions is employed, a sum of integrals appears. Some of these are of the type (A.5); furthermore one encounters the function $P(x)$ and its counterpart $Q(x)$, given in (30) and (70), respectively. Inserting the expressions (A.6) and taking the limit $\varepsilon \to 0$ we get:

$$H_0(k_\alpha R_1, k_\alpha R_2) = H(k_\alpha R_1, k_\alpha R_2) + k_\alpha R_1 Q(k_\alpha R_2) + k_\alpha R_2 Q(k_\alpha R_1)$$

$$- \tfrac{1}{2}k_\alpha^3 R_1^2 R_2 \log k_\alpha R_1 - \tfrac{1}{2}k_\alpha^3 R_1 R_2^2 \log k_\alpha R_2 - \tfrac{1}{6}k_\alpha^3 (R_1^2 R_2 + R_1 R_2^2)$$

$$- \tfrac{1}{2}\pi k_\alpha^2 R_1 R_2 + k_\alpha(R_1 + R_2)\,\gamma, \quad (A.13)$$

where the function $H$ has been defined in (35). Both in $V_4(R)$ and in $V_5(R)$ only $H$ contributes, since the remaining terms of $H_0$ drop out due to the occurrence of the factor $(R_1 R_2)^{-1}$ and the operators $\boldsymbol{V}_1$ and $\boldsymbol{V}_2$.

APPENDIX B

*Evaluation of the dispersion energy with the use of an alternative interaction hamiltonian.* The electromagnetic interaction between neutral atoms results from two different mechanisms, *viz.* electrostatic interaction and photonic exchange. Power and Zienau[2,5]) showed that the electrostatic terms may be eliminated from the interaction hamiltonian by a canonical transformation; moreover, the resulting hamiltonian no longer contains the electromagnetic vector potential $A$, but instead the (gauge-invariant) transversal electric and magnetic fields $E^\perp = -c^{-1}\,\partial A/\partial t$ and $B = V \wedge A$. Their result, which included only the effects of the electric and magnetic dipole moments and electric quadrupole moments, was recently extended by Atkins and Woolley[6,7]) so as to include all multipole moments. The hamiltonian found by these authors has the general form (1), with atomic and field contributions again given by (2) and (3). The interaction term, however, is no longer given by (6) but instead by an expression that, in the case of atoms sufficiently far apart for contact terms to be neglected, may be written as

$$
H_{\text{int}} = - \sum_{n=1}^{\infty} V_a^{n-1} : \{\mu_a^{(n)} \cdot E^\perp(R_a) + v_a^{(n)} \cdot B(R_a)\}
$$

$$
+ \frac{e^2}{2mc^2} \sum_j \left\{ \sum_{n=1}^{\infty} \frac{n}{(n+1)!} \, (r_{aj} \cdot V_a)^{n-1} \, r_{aj} \wedge B(R_a) \right\}^2
$$

$$
+ 2\pi \int \mathrm{d}R \, P_a^{\perp 2} + (a \leftrightarrow b),
\tag{B.1}
$$

Here the electric and magnetic multipole moment operators[4]) (*cf.* (61) and (62) for their matrix elements)

$$
\mu_a^{(n)} = -e \frac{1}{n!} \sum_j r_{aj}^n,
\tag{B.2}
$$

$$
v_a^{(n)} = - \frac{e}{2mc} \frac{n}{(n+1)!} \sum_j \{r_{aj}^{n-1}, r_{aj} \wedge p_{aj}\}
\tag{B.3}
$$

have been introduced. Furthermore $P_a^\perp$ is the transversal part

$$
(U - VV/\Delta) \cdot P_a
$$

of the polarization density

$$
P_a(R) = \sum_{n=1}^{\infty} V_a^{n-1} : \mu_a^{(n)} \delta(R - R_a)
\tag{B.4}
$$

of atom *a*.

The dispersion energy of two neutral atoms in nondegenerate ground states may be calculated by employing again perturbation theory up to fourth order and by considering only terms that depend on the interatomic separation. Since the expectation values of the first two terms of (B.1) for the ground state of atom $a$ vanish (as may be proved from the rotation invariance of that state) one finds that the various contributions to the dispersion energy can be represented by diagrams which have the same structure as those of the type 2, 4 and 5 in fig. 1. In the present case a vertex with one photon line stands for a matrix element containing one of the operators in (B.1) that are linear in the fields, while a vertex with two photon lines represents a matrix element of an operator in (B.1) that is quadratic in the field $B$. The remaining terms from (B.1) do not contribute to the dispersion energy up to fourth-order perturbation theory.

From the diagrams of type 2 one finds, after summation over photon polarizations according to (13), integration over the angles with the help of (16) and introduction of the function $F_0$ given in (18), that may be replaced by $F$ given in (19):

$$V'_1(R) = - \frac{\hbar c}{4\pi} \, \mathbf{M}_{\alpha_0} : \tilde{\mathbf{M}}_{\beta_0} \Delta_1 \Delta_2 \frac{F(R_1, R_2)}{R_1 R_2} + (\alpha \leftrightarrow \beta). \tag{B.5}$$

Here the tensor matrix element $\mathbf{M}_{\alpha_0}$ is defined as

$$\mathbf{M}_{\alpha_0} = \frac{e^2}{mc^2} \langle \alpha_0 | \sum_{n_1, n_2 = 1}^{\infty} \frac{n_1 n_2 (-1)^{n_1 + n_2}}{(n_1 + 1)! \, (n_2 + 1)!} \, (\mathbf{r}_a \cdot \nabla_1)^{n_1 - 1} \, (\mathbf{r}_a \cdot \nabla_2)^{n_2 - 1}$$

$$\times \, (\mathbf{r}_a \mathbf{r}_a \nabla_1 \cdot \nabla_2 - \mathbf{r}_a \nabla_1 \mathbf{r}_a \cdot \nabla_2 - \nabla_2 \mathbf{r}_a \mathbf{r}_a \cdot \nabla_1 + \mathsf{U} \mathbf{r}_a \cdot \nabla_1 \mathbf{r}_a \cdot \nabla_2) | \alpha_0 \rangle \tag{B.6}$$

(the expression for $\mathbf{M}_{\beta_0}$ follows by replacing $(a, \alpha)$ by $(b, \beta)$ and $\nabla_i$ by $-\nabla_i$ $(i = 1, 2)$; $\tilde{\mathbf{M}}_{\beta_0}$ denotes the transposed tensor). As a consequence of the occurrence of the operators $\Delta_1$ and $\Delta_2$ only the first term of $F$ (19), with the double argument $R_1 + R_2$, contributes in (B.5).

In order to evaluate the contributions represented by the diagrams of the fourth type in fig. 1 one must split them into their electric and magnetic multipole parts, since these parts contain different integrals. If one employs the method of appendix A to calculate these integrals and uses the reality of the sums $\sum_{\alpha(k_\alpha \text{ const.})} \mu_\alpha^{(n_1)*} \mu_\alpha^{(n_2)}$, $i \sum_{\alpha(k_\alpha \text{ const.})} \mu_\alpha^{(n_1)*} v_\alpha^{(n_2)}$ and $\sum_{\alpha(k_\alpha \text{ const.})} v_\alpha^{(n_1)*} v_\alpha^{(n_2)}$, containing the multipole matrix elements (61) and (62), one finds:

$$V'_2(R) = \sum_{\alpha(\neq \alpha_0)} \sum_{n_1, n_2 = 1}^{\infty} \frac{(-1)^{n_1 + n_2}}{\pi k_\alpha^2} \left[ (\nabla_1^{n_1 - 1} : \mu_\alpha^{(n_1)*}) \cdot \mathbf{M}_{\beta_0} \right.$$

$$\cdot (\nabla_2^{n_2 - 1} : \mu_\alpha^{(n_2)}) \, \Delta_1 \Delta_2 \frac{G(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2} - \frac{2i}{k_\alpha} \, (\nabla_1^{n_1 - 1} : \mu_\alpha^{(n_1)*})$$

$$\cdot \mathsf{M}_{\beta_0} \cdot (\nabla_2^{n_2-1} : \mathsf{v}_\alpha^{(n_2)} \wedge \nabla_2) \Delta_1 \Delta_2 \frac{G(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2}$$

$$+ \frac{1}{k_\alpha^2} (\nabla_1^{n_1-1} : \mathsf{v}_\alpha^{(n_1)*} \wedge \nabla_1) \cdot \mathsf{M}_{\beta_0} \cdot (\nabla_2^{n_2-1} : \mathsf{v}_\alpha^{(n_2)} \wedge \nabla_2)$$

$$\times \Delta_1 \Delta_2 \frac{1}{R_1 R_2} \{G(k_\alpha R_1 + k_\alpha R_2)$$

$$+ \tfrac{1}{6} k_\alpha^3 (R_1 + R_2)^3 \log(R_1 + R_2)\} \Big] + (\alpha \leftrightarrow \beta), \tag{B.7}$$

with $G$ the function given in (29). Due to the properties $\nabla_1 \cdot \mathsf{M}_{\beta_0} = 0$ and $\mathsf{M}_{\beta_0} \cdot \nabla_2 = 0$ of the matrix element $\mathsf{M}_{\beta_0}$ only the term with two laplaceans in the product $(\nabla_1 \nabla_1 - \mathsf{U}\Delta_1) \cdot \mathsf{M}_{\beta_0} \cdot (\nabla_2 \nabla_2 - \mathsf{U}\Delta_2)$ contributed. As a consequence functions with single arguments $R_1$ or $R_2$ could be suppressed.

Finally the contributions due to the fifth type of diagrams in fig. 1 are to be calculated. Again terms with electric and magnetic multipole moments should be treated separately. Using the reality of the sums of products of matrix elements given in the preceding section one obtains a sum of seven terms, each with a different integral. If these integrals are evaluated one recovers the terms contained in $V_{\mathrm{I}}$ (58), with (63) inserted, together with several extra contributions:

$$V_3'(R) = - \sum_{\alpha(\neq \alpha_0), \beta(\neq \beta_0)} \sum_{n_1, m_1, n_2, m_2 = 1}^{\infty} \frac{2(-1)^{n_1 + n_2}}{\pi \hbar c k_\alpha^2 k_\beta} \Big[ (\nabla_1^{n_1-1} : \mathsf{\mu}_\alpha^{(n_1)})$$

$$\cdot (\nabla_1^{m_1-1} : \mathsf{v}_\beta^{(m_1)} \wedge \nabla_1)(\nabla_2^{n_2-1} : \mathsf{\mu}_\alpha^{(n_2)*}) \cdot (\nabla_2^{m_2-1} : \mathsf{v}_\beta^{(m_2)*} \wedge \nabla_2)$$

$$\times \Delta_1 \Delta_2 \frac{G(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2} - \frac{2i}{k_\alpha} (\nabla_1^{n_1-1} : \mathsf{\mu}_\alpha^{(n_1)}) \cdot (\nabla_1^{m_1-1} : \mathsf{v}_\beta^{(m_1)} \wedge \nabla_1)$$

$$\cdot (\nabla_2^{n_2-1} : \mathsf{v}_\alpha^{(n_2)*} \wedge \nabla_2) \cdot (\nabla_2^{m_2-1} : \mathsf{v}_\beta^{(m_2)*} \wedge \nabla_2) \Delta_1 \Delta_2 \frac{G(k_\alpha R_1 + k_\alpha R_2)}{R_1 R_2}$$

$$+ \frac{1}{k_\alpha^2} (\nabla_1^{n_1-1} : \mathsf{v}_\alpha^{(n_1)} \wedge \nabla_1) \cdot (\nabla_1^{m_1-1} : \mathsf{v}_\beta^{(m_1)} \wedge \nabla_1)(\nabla_2^{n_2-1} : \mathsf{v}_\alpha^{(n_2)*} \wedge \nabla_2)$$

$$\cdot (\nabla_2^{m_2-1} : \mathsf{v}_\beta^{(m_2)*} \wedge \nabla_2) \Delta_1 \Delta_2 \frac{1}{R_1 R_2} \{G(k_\alpha R_1 + k_\alpha R_2)$$

$$+ \tfrac{1}{12} k_\alpha^3 (R_1 + R_2)^3 \log(R_1 + R_2)\} \Big] + (\alpha \leftrightarrow \beta) + V_{\mathrm{I}}(R). \tag{B.8}$$

Again only functions with double arguments are present. The sum of (B.5), (B.7) and (B.8) may be shown to be equal to the expression (57) with (58)–(60), derived in the main text. To that end one has to rewrite the matrix elements $\mathsf{M}_{\alpha_0}$ and $\mathsf{M}_{\beta_0}$. In fact, by inserting intermediate states in a suitable commutator expression, one may prove the sum rule

$$M_{\alpha_0} = \sum_{\alpha(\neq\alpha_0)} \sum_{n_1,n_2=1}^{\infty} \frac{2i(-1)^{n_1+n_2}}{\hbar c} \{(\nabla_1^{n_1-1} : \nu_\alpha^{(n_1)} \wedge \nabla_1)$$

$$\cdot (\nabla_2^{n_2-1} : \mu_\alpha^{(n_2)\star}) + (\nabla_1^{n_1-1} : \mu_\alpha^{(n_1)\star})(\nabla_2^{n_2-1} : \nu_\alpha^{(n_2)} \wedge \nabla_2)$$

$$+ ik_\alpha(\nabla_1^{n_1-1} : \mu_\alpha^{(n_1)})(\nabla_2^{n_2-1} : \mu_\alpha^{(n_2)\star})\}$$

$$+ \frac{e^2}{mc^2} \, U \, \langle\alpha_0| \, e^{-r_a \cdot (\nabla_1 + \nabla_2)} \, |\alpha_0\rangle. \tag{B.9}$$

The last matrix element can be written in terms of multipole matrix elements with the use of (53) and (63).

The outline of the evaluation of the dispersion energy given here shows that the use of the interaction hamiltonian (B.1) for the general case of arbitrary multipoles does not lead to a simplification in the calculations. On the contrary, due to the necessity of splitting the contributions in their electric and magnetic multipole parts the number of integrals that are to be calculated here is larger than that in the main text. The situation is different if one is interested in the lowest-order multipole contributions only. Then, the method of the present appendix permits a short derivation of the dispersion energy [5,8]).

REFERENCES

1) Casimir, H. B. G. and Polder, D., Phys. Rev. **73** (1948) 360.
2) See, *e.g.*, Power, E. A., Introductory Quantum Electrodynamics, Longmans (London, 1964).
3) Abramowitz, M. and Stegun, I. A., Handbook of Mathematical Functions, Dover Publ., Inc. (New York) 1965, Chap. 5.
4) de Groot, S. R. and Suttorp, L. G., Foundations of Electrodynamics, North-Holland Publ. Co. (Amsterdam, 1972).
5) Power, E. A. and Zienau, S., Nuovo Cimento **6** (1957) 7.
6) Atkins, P. W. and Woolley, R. G., Proc. Roy. Soc. **A319** (1970) 549.
7) Woolley, R. G., Proc. Roy. Soc. **A321** (1971) 557.
8) McLone, R. R. and Power, E. A., Proc. Roy. Soc. **A286** (1965) 573.