Form-factor representation and multipole expansion of the retarded interatomic dispersion energy

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Dispersion-relation methods are used to derive a form-factor representation for the retarded dispersion energy of two hydrogen atoms that are described by relativistic electron theory. By expressing the electromagnetic form factors in terms of atomic transition matrix elements the complete multipole expansion of the interatomic dispersion energy is obtained. The long-range asymptotic limit of the successive multipole interactions is given explicitly.

1. INTRODUCTION

The retarded dispersion energy of a pair of atoms is due to the exchange of two virtual photons. The evaluation of the associated Feynman diagrams may be carried out either by straightforward integration over the photon momenta or by making use of the analytic behaviour of the atomic two-photon vertex functions. In the latter approach the atomic properties enter through the so-called electric and magnetic form factors, the introduction of which has the advantage that in the course of the calculations the explicit symmetry between electric and magnetic phenomena can be maintained [1–7]. The form-factor representation for the dispersion energy obtained in this way remains rather formal, however, as long as the form factors are left unspecified. The purpose of the present paper is to show how this formal representation may be written in a more transparent way by making a complete expansion in terms of atomic multipole matrix elements. The function giving the dependence of each multipole contribution on the interatomic separation will be cast into the form of an integral that may be recognized as a generalization of the well-known Casimir–Polder integral [8]; crucial for this step is the derivation of a differential operator that generates squares of modified Bessel functions. Finally, the long-range asymptotic limit of the successive multipole interactions will be discussed.

2. FORM-FACTOR REPRESENTATION OF THE DISPERSION ENERGY

In the following we will study the interaction of two hydrogen atoms of which the nuclei are held fixed while the electrons are described by the relativistic Dirac theory. Furthermore, at the interatomic separations considered, the overlap of the electronic wave functions is assumed to be negligible.

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The dispersion energy of two atoms may be obtained from the scattering matrix S_{fi} for a transition between initial and final states i and f of the system. In fact, the scattering matrix will have the general form

$$S_{fi} = \delta_{fi} - 2\pi i \delta(E_f - E_i) V_{fi}, \tag{1}$$

with a delta function showing energy conservation. The dispersion energy is found by diagonalizing the part of the matrix V_{fi} that is due to the exchange of two photons between the atoms [7, 9] ; in particular, by taking the trace one gets the average of the interaction energy over the atomic ground states.

The two-photon-exchange process may be represented by two Feynman diagrams, with non-crossing and crossing photon lines respectively. The rules for evaluating these diagrams lead to an interaction energy V that depends on the difference $\mathbf{R} = \mathbf{R}_b - \mathbf{R}_a$ of the position vectors for the nuclei of the atoms a and b. Its Fourier transform, defined by

$$V(\mathbf{R}) = \frac{1}{(2\pi)^3} \int d\mathbf{Q} \exp(i\mathbf{Q} \cdot \mathbf{R}) F(\mathbf{Q}), \tag{2}$$

is the dispersive two-photon-exchange amplitude. As a function of the total photon-momentum transfer $\mathbf{Q}$ this amplitude reads

$$F(\mathbf{Q}) = \frac{i}{2(2\pi)^4} \int d^4k \, d^4k' \, \Gamma_a^{\mu\nu}(k, k') \Gamma_{b,\,\mu\nu}(-k, -k')$$
$$\times \frac{\delta(k^0 + k'^0)\delta(\mathbf{k} + \mathbf{k'} - \mathbf{Q})}{(k^2 + i0)(k'^2 + i0)}. \tag{3}$$

When the eigenstates of the atomic hamiltonian and the corresponding eigenvalues are denoted by α and E_α, with α_0 labelling the states of the g-fold degenerate ground level, the two-photon vertex function occurring here may be written as

$$\Gamma_a^{\mu\nu}(k, k') = \frac{1}{g} \sum_{\alpha_0} \sum_{\alpha}' \left[\frac{\Gamma_{\alpha_0\alpha}^{\mu}(k)\Gamma_{\alpha\alpha_0}^{\nu}(k')}{k_\alpha(1 - i0) - k^0} + \frac{\Gamma_{\alpha_0\alpha}^{\nu}(k')\Gamma_{\alpha\alpha_0}^{\mu}(k)}{k_\alpha(1 - i0) - k'^0} \right]. \tag{4}$$

The prime at the summation sign indicates that from the intermediate states α ground-level atomic states are to be excluded; furthermore k_α is the energy difference $E_\alpha - E_{\alpha_0}$. The symbol $\Gamma^\mu(k)$ in the numerators of (4) stands for the one-photon vertex function

$$\Gamma_{\alpha_0\alpha}^{\mu}(k) = -e\langle\alpha_0|\gamma^0\gamma^\mu \exp(-i\mathbf{k} \cdot \mathbf{r}) - g^{0\mu}|\alpha\rangle, \tag{5}$$

with $\mathbf{r}$ the position of the electron relative to its nucleus and $g^{\mu\nu}$ the metric tensor, which is chosen as diag $(1, -1, -1, -1)$.

Since in (3) with (4) the average is taken over the ground states of both atoms the amplitude $F(\mathbf{Q})$ depends only on the square $\mathbf{Q}^2 \equiv -t$ of the momentum transfer (and hence the interaction energy $V(\mathbf{R})$ only on the internuclear separation $R = |\mathbf{R}|$). The behaviour of F for complex values of t has been studied in previous papers [6, 7] ; there it has been shown that the function F is analytic in the complex t plane apart from a cut along the positive axis, a branch point being present at $t = 0$. Consequently complex contour integration may be employed to express the interaction energy (2) in terms of the discontinuity

across the cut in the following way :

$$V(R) = -\frac{\mathrm{i}}{8\pi^2 R} \int\limits_0^\infty \mathrm{d}t \, \exp\left(-R\sqrt{t}\right)[F(t+\mathrm{i}0) - F(t-\mathrm{i}0)]. \tag{6}$$

In accordance with Cutkosky's rules [10] this discontinuity for $t > 0$ has been found as

$$F(t+\mathrm{i}0) - F(t-\mathrm{i}0) = -\sum_{\kappa,\,\lambda=\pm} \frac{\mathrm{i}}{8\pi} \int\limits_0^{\frac{1}{2}\sqrt{t}} \mathrm{d}k_\perp k_\perp$$

$$\times \frac{\epsilon_\kappa \cdot \tilde{\Gamma}_{\mathrm{a}}(k,\,k') \cdot \epsilon_\lambda' \epsilon_\kappa \cdot \tilde{\Gamma}_{\mathrm{b}}(-k,\,-k') \cdot \epsilon_\lambda'}{[t(\frac{1}{4}t - k_\perp{}^2)]^{1/2}}, \tag{7}$$

where $\tilde{\Gamma}_{\mathrm{a}}(k,\,k')$ is equal to the two-photon vertex function (4) for photon momenta satisfying $k^0 = -k'^0$, $k^{02} = \boldsymbol{k}^2 = \boldsymbol{k}'^2$, which corresponds to mass-shell photons. The vertex functions are contracted with complete sets of transverse polarization vectors $\epsilon_\kappa{}^\mu = (0,\,\boldsymbol{\epsilon}_\kappa)$ and $\epsilon_\lambda'{}^\mu = (0,\,\boldsymbol{\epsilon}_\lambda')$. Upon writing $\boldsymbol{k} = \frac{1}{2}\boldsymbol{Q} + \boldsymbol{k}_\perp$, $\boldsymbol{k}' = \frac{1}{2}\boldsymbol{Q} - \boldsymbol{k}_\perp$, with $\boldsymbol{Q} \cdot \boldsymbol{k}_\perp = 0$, the product of contracted vertex functions summed over the polarizations becomes a function of $\boldsymbol{Q}^2 = -t$ and $\boldsymbol{k}_\perp{}^2$ only. In the integrand of (7) the analytical continuation of this function towards positive t, with fixed $\boldsymbol{k}_\perp{}^2$, is to be substituted†.

Rotation-invariance arguments permit one to write the contracted vertex function for an atom interacting with two mass-shell photons in the general form

$$\boldsymbol{\epsilon} \cdot \tilde{\Gamma}(k,\,k') \cdot \boldsymbol{\epsilon}' = \boldsymbol{k}^2 \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}' F_{\mathrm{E}}(k,\,t) - (\boldsymbol{\epsilon} \wedge \boldsymbol{k}) \cdot (\boldsymbol{\epsilon}' \wedge \boldsymbol{k}') F_{\mathrm{M}}(k,\,t). \tag{8}$$

The functions $F_i(k,\,t)$ introduced in this way are the electric and magnetic form factors of the atom ; in the following their series expansions in powers of t, viz

$$F_i(k,\,t) = \sum_{m=0}^\infty F_{i,\,m}(k) t^m, \quad i = \mathrm{E,\,M}, \tag{9}$$

will be employed.

When (7) with (8) is substituted into (6) and the new integration variables $z \equiv \frac{1}{2}t^{1/2}$, $x \equiv (1 - 4\boldsymbol{k}_\perp{}^2/t)^{1/2}$ are introduced, the dispersion energy becomes

$$V(R) = -\frac{1}{8\pi^3 R} \int\limits_0^\infty \mathrm{d}z \, z^5 \exp\left(-2zR\right) \int\limits_0^1 \mathrm{d}x \sum_{i,\,j=\mathrm{E,\,M}} \phi_{ij}(x)$$

$$\times F_i{}^{\mathrm{a}}(\mathrm{i}zx,\,4z^2) F_j{}^{\mathrm{b}}(\mathrm{i}zx,\,4z^2) ; \tag{10}$$

the polynomials ϕ_{ij} occurring here are defined by

$$\phi_{\mathrm{EE}}(x) = \phi_{\mathrm{MM}}(x) = x^4 - 2x^2 + 2, \tag{11}$$

$$\phi_{\mathrm{EM}}(x) = \phi_{\mathrm{ME}}(x) = x^4 - 2x^2. \tag{12}$$

Inserting the series expansion (9) one may rewrite (10) as

$$V(R) = -\frac{1}{8\pi^3 R} \sum_{m_{\mathrm{a}},\,m_{\mathrm{b}}=0}^\infty 4^{m_{\mathrm{a}}+m_{\mathrm{b}}} \int\limits_0^\infty \mathrm{d}z \, z^{2(m_{\mathrm{a}}+m_{\mathrm{b}})+5} \exp\left(-2zR\right)$$

$$\times \int\limits_0^1 \mathrm{d}x \sum_{i,\,j=\mathrm{E,\,M}} \phi_{ij}(x) F_{i,\,m_{\mathrm{a}}}{}^{\mathrm{a}}(\mathrm{i}zx) F_{j,\,m_{\mathrm{b}}}{}^{\mathrm{b}}(\mathrm{i}zx). \tag{13}$$

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† In reference [7] the formula (59) for the discontinuity across the cut is incorrect, the denominator being absent there.

When factors $(-2z)$ in the integrand are replaced by operators (d/dR) acting on the exponential, and subsequently the integration over x is performed with the help of the auxiliary formula (A 4), the form-factor representation of the dispersion energy is found to be

$$V(R) = -\frac{1}{16\pi^3 R} \sum_{m_a, m_b = 0}^{\infty} \left(\frac{d}{dR}\right)^{2(m_a + m_b)} \frac{1}{R^5} \int_0^\infty dz \exp\left(-2zR\right)$$
$$\times \sum_{i, j = E, M} P_{ij}(zR) F_{i,\,m_a}{}^a(iz) F_{j,\,m_b}{}^b(iz), \quad (14)$$

where the polynomials P_{ij} are

$$P_{EE}(y) = P_{MM}(y) = y^4 + 2y^3 + 5y^2 + 6y + 3, \quad (15)$$

$$P_{EM}(y) = P_{ME}(y) = -y^4 - 2y^3 - y^2. \quad (16)$$

It should be remarked that the formula (14) has been obtained previously in reference [5]. However in the presentation given there additional dispersion relations were used for the form factors without further justification, whereas in the above derivation such form-factor dispersion relations are dispensed with.

In the representation (14) of the interatomic dispersion energy $V(R)$ the atomic properties enter through the form-factor coefficients $F_{i,\,m}$ in an as yet unspecified way. A more transparent expression for $V(R)$ may be deduced if these coefficients are evaluated in terms of the atomic matrix elements characteristic for electron–photon interactions.

3. Multipole expansion of the dispersion energy

In order to relate the electromagnetic form factors, which occur in the final formulae of the preceding section, to atomic matrix elements the definitions (8) with (4) and (5) may be employed. If these matrix elements are written in terms of atomic electric and magnetic multipole moments, the resulting expressions for the form factors enable one to obtain the multipole expansion of the dispersion energy, as will be shown in this section.

In the following it will be convenient to use the spherical tensor formalism [11]. The operator occurring in the space part of the one-photon vertex function (5) may be expressed then, with the help of Rayleigh's expansion, in terms of vector spherical harmonics :

$$\sum_{M', M''} (-1)^{L-M}(2L+1)^{1/2} \begin{pmatrix} L' & 1 & L \\ -M' & -M'' & M \end{pmatrix} Y_{L'}{}^{M'}(\hat{r})\gamma^0\gamma^{M''}$$
$$= Y_{L,\,L}{}^M(\hat{r}) \cdot \gamma^0\gamma. \quad (17)$$

In particular the transversal space part of (5), i.e. the part perpendicular to the wave vector k, can be expanded into matrix elements of the so-called transversal electric and magnetic multipole operators [7, 9]

$$\kappa_L{}^M(s) = -e\frac{[4\pi(L+1)]^{1/2}}{(2s)!!(2L+2s-1)!!}\left(\frac{L}{L+1}\right)^{1/2} r^{L+2s-1}Y_{L,\,L-1}{}^M(\hat{r}) \cdot \gamma^0\gamma$$

$$-e\frac{[4\pi L]^{1/2}}{(2s-2)!!(2L+2s+1)!!}\left(\frac{L}{L+1}\right)^{1/2} r^{L+2s-1}Y_{L,\,L+1}{}^M(\hat{r}) \cdot \gamma^0\gamma, \quad (18)$$

$$v_L{}^M(s) = ie\,\frac{[4\pi(2L+1)]^{1/2}}{(2s)!!(2L+2s+1)!!}\left(\frac{L}{L+1}\right)^{1/2} r^{L+2s}\mathbf{Y}_{L,\,L}{}^M(\mathbf{r})\cdot\gamma^0\boldsymbol{\gamma}, \qquad (19)$$

of which the parity eigenvalues are $(-1)^L$ and $(-1)^{L+1}$ respectively. Likewise the time component and the longitudinal space part of the operator in (5) may be related to the longitudinal electric multipoles

$$\mu_L{}^M(s) = -e\,\frac{[4\pi(2L+1)]^{1/2}}{(2s)!!(2L+2s+1)!!} r^{L+2s}\mathbf{Y}_L{}^M(\hat{\mathbf{r}}). \qquad (20)$$

For $s=0$ the latter reduce to the familiar electrostatic multipoles; in this case the two electric multipoles (18) and (20) are connected by the commutator relation

$$\kappa_L{}^M(0) = i[H_{\mathrm{at}},\,\mu_L{}^M(0)], \qquad (21)$$

where H_{at} is the atomic Dirac hamiltonian. (In references [7, 9] the multipole operators κ and v were defined as linear combinations of spherical tensor operators $\Omega_L{}^M(L',s)$; indeed, the latter are proportional to the inner product of $r^{L'+2s}\mathbf{Y}_{L,\,L'}{}^M(\hat{\mathbf{r}})$ and $\gamma^0\boldsymbol{\gamma}$).

When the electromagnetic form factors $F_i(k,t)$ are written as double power series in k and t the properties of the atoms enter only through matrix elements of the transverse electromagnetic multipole moments (18) and (19); in fact, in references [6, 7] it is shown that the coefficients $F_{i,\,m}(k)$ as defined in (9), have the form

$$F_{i,\,m}(k) = \sum_N{}'\,\sum_{L,\,S}\frac{k_N}{k_N{}^2-k^2-i0}\frac{(-k^2)^{L+S-m-1}}{4^m L(L+1)}$$

$$\times [\![a_i{}^L k^{-2}\mathcal{K}_N(L,S) + b_i{}^L\mathcal{N}_N(L,S)]\!]_m, \quad (i=\mathrm{E},\,\mathrm{M}). \qquad (22)$$

Here the atomic states have been chosen as simultaneous eigenstates of the atomic hamiltonian H_{at} and the angular-momentum operators J^2, J_z; the label α has accordingly been replaced by N, M, with M the magnetic quantum number corresponding to J_z. In (22) the reduced matrix elements $\kappa_N(L,s)$ of the operators (18) occur in the combination

$$\mathcal{K}_N(L,S) = \frac{L+1}{L(2L+1)}\sum_s\kappa_N(L,s)\kappa_N{}^*(L,S-s); \qquad (23)$$

the reduced matrix elements $v_N(L,s)$ show up in an analogous sum $\mathcal{N}_N(L,S)$. Furthermore, in (22) the brackets $[\![\;]\!]_m$, defined by

$$f(\cos\theta) = \sum_m[\![f]\!]_m(\tfrac{1}{2}+\tfrac{1}{2}\cos\theta)^m, \qquad (24)$$

act on the following linear combinations of differentiated Legendre polynomials:

$$a_{\mathrm{E}}{}^L = b_{\mathrm{M}}{}^L = P_{L+1}'' - P_L' + P_{L-1}'', \qquad (25)$$

$$a_{\mathrm{M}}{}^L = b_{\mathrm{E}}{}^L = 2P_L''. \qquad (26)$$

From the commutator identity (21) one may prove the relation

$$\mathcal{K}_N(L,0) = k_N{}^2\mathcal{M}_N(L,0), \qquad (27)$$

where $\mathcal{M}_N(L,S)$, on a par with (23), stands for a sum over products of reduced

matrix elements $\mu_N(L, s)$. These matrix elements may be shown to satisfy the sum rule [7, 9]

$$\sideset{}{'}\sum_N k_N \mu_N(L, s_1)\mu_N{}^*(L, s_2) = 0, \tag{28}$$

which is in fact a generalization of the Thomas–Reiche–Kuhn sum rule. With the help of (27) and (28) the coefficients (22) may be cast into the form

$$F_{i,\,m}(k) = \sideset{}{'}\sum_N \; \sum_{L,\,S} \frac{k_N}{k_N{}^2 - k^2 - \mathrm{i}0} \frac{(-k^2)^{L+S-m-1}}{4^m L(L+1)}$$

$$\times [a_i{}^L[\mathcal{M}_N(L, S)\delta_{S,\,0} - \mathcal{K}_N(L, S+1)] + b_i{}^L \mathcal{N}_N(L, S)]_m, \quad (i = \mathrm{E, M}). \tag{29}$$

This expression is the desired multipole expansion of the atomic electromagnetic form factors. It may be used now to expand the dispersion energy into electric and magnetic multipoles.

Upon substituting (29) into (13) the summations over m_{a}, m_{b} can be reduced to a summation over one single parameter m ; subsequently we may use then the identity

$$\sum_{m=0}^{p_{\mathrm{a}}+p_{\mathrm{b}}} x^{2(p_{\mathrm{a}}+p_{\mathrm{b}}-m)} \sum_{i,\,j=\mathrm{E,\,M}} \phi_{ij}(x)[f_i{}^{\mathrm{a}}f_j{}^{\mathrm{b}}]_m = \sum_{m=0}^{p_{\mathrm{a}}+p_{\mathrm{b}}+2} x^{2(p_{\mathrm{a}}+p_{\mathrm{b}}-m+2)}$$

$$\times \sum_{\lambda=\pm 1} [(f_{\mathrm{E}}{}^{\mathrm{a}} + \lambda f_{\mathrm{M}}{}^{\mathrm{a}})(f_{\mathrm{E}}{}^{\mathrm{b}} + \lambda f_{\mathrm{M}}{}^{\mathrm{b}})\tfrac{1}{4}(1 - \lambda \cos \theta)^2]_m, \tag{30}$$

which is valid for arbitrary polynomials $f_i{}^{\mathrm{a}}(\cos \theta)$, $f_j{}^{\mathrm{b}}(\cos \theta)$ of degree p_{a}, p_{b}. In the resulting formula for $V(R)$ one recognizes products of the rotation matrix elements [11]

$$d_{1,\,-\lambda}{}^L(\theta) = [L(L+1)]^{-1}\tfrac{1}{2}(1 - \lambda \cos \theta)(a_{\mathrm{E}}{}^L + \lambda a_{\mathrm{M}}{}^L) ; \tag{31}$$

when these products are evaluated with the help of the Clebsch–Gordan series and the summation over λ is carried out the interaction energy is found to be

$$V(R) = \sideset{}{'}\sum_{N_{\mathrm{a}},\,N_{\mathrm{b}}} \; \sum_{L_{\mathrm{a}},\,L_{\mathrm{b}},\,S_{\mathrm{a}},\,S_{\mathrm{b}},\,L} \frac{k_{N_{\mathrm{a}}}k_{N_{\mathrm{b}}}}{8\pi^3} (2L+1) \begin{pmatrix} L_{\mathrm{a}} & L_{\mathrm{b}} & L \\ 1 & -1 & 0 \end{pmatrix}^2$$

$$\times (\delta_{L_{\mathrm{a}}+L_{\mathrm{b}}+L,\text{ even}}[\mathcal{M}_{N_{\mathrm{a}}}(L_{\mathrm{a}}, S_{\mathrm{a}})\delta_{S_{\mathrm{a}},\,0} - \mathcal{K}_{N_{\mathrm{a}}}(L_{\mathrm{a}}, S_{\mathrm{a}}+1)]$$

$$\times [\mathcal{M}_{N_{\mathrm{b}}}(L_{\mathrm{b}}, S_{\mathrm{b}})\delta_{S_{\mathrm{b}},\,0} - \mathcal{K}_{N_{\mathrm{b}}}(L_{\mathrm{b}}, S_{\mathrm{b}}+1)] - \delta_{L_{\mathrm{a}}+L_{\mathrm{b}}+L,\text{ odd}}$$

$$\times \{[\mathcal{M}_{N_{\mathrm{a}}}(L_{\mathrm{a}}, S_{\mathrm{a}})\delta_{S_{\mathrm{a}},\,0} - \mathcal{K}_{N_{\mathrm{a}}}(L_{\mathrm{a}}, S_{\mathrm{a}}+1)]\mathcal{N}_{N_{\mathrm{b}}}(L_{\mathrm{b}}, S_{\mathrm{b}}) + (\mathrm{a}\leftrightarrow \mathrm{b})\}$$

$$+ \delta_{L_{\mathrm{a}}+L_{\mathrm{b}}+L,\text{ even}}\mathcal{N}_{N_{\mathrm{a}}}(L_{\mathrm{a}}, S_{\mathrm{a}})\mathcal{N}_{N_{\mathrm{b}}}(L_{\mathrm{b}}, S_{\mathrm{b}}))F_{\mathrm{ab}}{}^{NL}(2R). \tag{32}$$

The radial function $F_{\mathrm{ab}}{}^{NL}(2R)$ is defined by

$$F_{\mathrm{ab}}{}^{NL}(2R) = -\frac{2}{R}\sum_m [P_L]_m \int_0^\infty \mathrm{d}z\, z^{2m+1} \exp(-2zR)$$

$$\times \int_0^1 \mathrm{d}x\, \frac{(zx)^{N-2m}}{(k_{N_{\mathrm{a}}}{}^2 + z^2 x^2)(k_{N_{\mathrm{b}}}{}^2 + z^2 x^2)}, \tag{33}$$

for $N \equiv 2(L_{\mathrm{a}} + L_{\mathrm{b}} + S_{\mathrm{a}} + S_{\mathrm{b}}) \geq 2L$. The integration over x occurring here can be performed with the help of (A 4) ; if first a factor $z^{2m} \exp\{-2zR\}$ is replaced by $[\mathrm{d}/\mathrm{d}(2R)]^{2m} \exp(-2zR)$ one finds in this way

$$F_{\mathrm{ab}}{}^{NL}(2R) = D(N, L)f_{\mathrm{ab}}(2R), \tag{34}$$

with the differential operator

$$D(N, L) = \sum_{m=0}^{L} [\![P_L]\!]_m \frac{1}{R} \left[\frac{d}{d(2R)} \right]^{2m} \frac{1}{R} \left[\frac{d}{d(2R)} \right]^{N-2m} \tag{35}$$

acting on the function

$$f_{ab}(2R) = - \int_{0}^{\infty} dz \frac{\exp(-2zR)}{(k_{N_a}^2 + z^2)(k_{N_b}^2 + z^2)}. \tag{36}$$

For the right-hand side of (34) an integral representation can be derived in which all radial differentiations have been performed. To show this let us first consider the action of the operator (35) on the exponential $\exp(-2zR)$ in the integrand of (36). In fact, from the definition (24) of the bracket symbol one gets

$$D(N, L) \exp(-2zR) = \frac{2z^{N+1}}{\pi R} P_L \left\{ 2 \left[\frac{d}{d(2zR)} \right]^2 - 1 \right\} [K_{1/2}(zR)]^2, \tag{37}$$

where the modified Bessel function of the third kind [12]

$$K_{L+1/2}(u) = \left(\frac{\pi}{2u} \right)^{1/2} \exp(-u) \sum_{k=0}^{L} \frac{(L+k)!}{(2k)!!(L-k)!} u^{-k} \tag{38}$$

has been introduced. In Appendix B it is shown that the differential operator $P_L(2d^2/dz^2 - 1)$ is the generator of the squares of modified Bessel functions, so that the right-hand side of (37) is proportional to $[K_{L+1/2}(zR)]^2$. One may write therefore instead of (34) with (35), (36):

$$F_{ab}^{NL}(2R) = - \frac{2}{\pi R^{N-1}} \int_{0}^{\infty} du \frac{u^{N+1}[K_{L+1/2}(u)]^2}{(k_{N_a}^2 R^2 + u^2)(k_{N_b}^2 R^2 + u^2)}. \tag{39}$$

If this form for the radial function is inserted into (32) the generalization to higher multipoles is obtained for the integral representation of the electric-dipole dispersion energy as given originally by Casimir and Polder [8].

4. Asymptotic behaviour of the dispersion energy

In this section we want to study the long-range asymptotic behaviour of the dispersion energy for multipoles with fixed parameters L_a, L_b. As is clear from (32) with (39), we then only need to consider the operators $\mu_L^M(0)$ and $\nu_L^M(0)$, which are simply the static electric and magnetic multipole operators. For convenience we shall introduce now instead of $\mu_L^M(0)$ the regular solid harmonics

$$\mathscr{Y}_L^M(\boldsymbol{r}) = r^L Y_L^M(\hat{\boldsymbol{r}}), \tag{40}$$

while $\nu_L^M(0)$ will be replaced by

$$\mathscr{Z}_L^M(\boldsymbol{r}) = \left(\frac{L}{L+1} \right)^{1/2} r^L \boldsymbol{Y}_{L,\,L}^M(\hat{\boldsymbol{r}}) \cdot \gamma^0 \boldsymbol{\gamma} ; \tag{41}$$

in fact this choice is tantamount to extracting a common factor from both $\mu_L^M(0)$ and $\nu_L^M(0)$.

At large interatomic separations R the terms u^2 in the denominator at the

right-hand side of (39) can be neglected, whereupon the integral becomes [13]

$$\int_0^\infty du\, u^{N+1}[K_{L+1/2}(u)]^2 = \tfrac{1}{4}\pi \frac{[(\tfrac{1}{2}N)!]^2}{(N+1)!}(N+2L+1)!!(N-2L-1)!!. \quad (42)$$

The desired long-range asymptotic form of the dispersion energy for fixed L_a, L_b is then found to be

$$V_{L_aL_b}{}^\infty(R) = -\sum_{N_a,N_b}' \frac{e^4}{\pi k_{N_a}k_{N_b}R^{2L_a+2L_b+3}}$$

$$\times \{C_{even}{}^\infty(L_a, L_b)[|\mathscr{Y}_{N_a}(L_a)|^2\,|\mathscr{Y}_{N_b}(L_b)|^2+(\mathscr{Y}\leftrightarrow\mathscr{Z})]$$

$$-C_{odd}{}^\infty(L_a, L_b)[|\mathscr{Y}_{N_a}(L_a)|^2\,|\mathscr{Z}_{N_b}(L_b)|^2+(\mathscr{Y}\leftrightarrow\mathscr{Z})]\}, \quad (43)$$

where the coefficients $C_{even}{}^\infty(L_a, L_b)$ and $C_{odd}{}^\infty(L_a, L_b)$ are defined as

$$C^\infty{}_{even/odd}(L_a, L_b) = \frac{(L_a+1)(L_b+1)}{L_aL_b(2L_a+2L_b+1)!}\left[\frac{(L_a+L_b)!}{(2L_a+1)!!(2L_b+1)!!}\right]^2$$

$$\times \sum_L \delta_{L_a+L_b+L,\,even/odd}(2L+1)\begin{pmatrix}L_a & L_b & L \\ 1 & -1 & 0\end{pmatrix}^2 (2L_a+2L_b+2L+1)!!$$

$$\times (2L_a+2L_b-2L-1)!!. \quad (44)$$

For the 3-j symbols of the type occurring here closed-form expressions exist containing factorials [11]. Thus the asymptotic coefficient $C^\infty{}_{even/odd}(L_a, L_b)$ can be written as a finite sum of terms that are functions of factorials. For the lowest-order interactions the numerical values of $C^\infty{}_{even/odd}(L_a, L_b)$ are given in the table. In particular one recognizes for the electric-dipole dispersion energy the well-known coefficient 23/81.

The asymptotic coefficients $C^\infty{}_{even/odd}(L_a, L_b)$ for L_a, $L_b \leqslant 3$.

L_a	L_b	$C^\infty{}_{even}$	$C^\infty{}_{odd}$
1	1	$\dfrac{23}{81}$	$\dfrac{7}{81}$
2	1	$\dfrac{59}{200}$	$\dfrac{11}{200}$
2	2	$\dfrac{5591}{10000}$	$\dfrac{583}{10000}$
3	1	$\dfrac{10582}{33075}$	$\dfrac{286}{6615}$
3	2	$\dfrac{210379}{220500}$	$\dfrac{611}{8820}$
3	3	$\dfrac{253374}{108045}$	$\dfrac{4202}{36015}$

APPENDIX A

An auxiliary integral relation

In the formulae (13) and (33) of the main text integrals of the type

$$I_p \equiv \int_0^\infty dz\, z^{p+1}\exp(-2zR)\int_0^1 dx\, F(zx) \qquad (A\,1)$$

occur for integer $p \geqslant 0$. With the new variable $y = zx$ this double integral may be written as

$$I_p = \int_0^\infty \mathrm{d}z \, z^p \exp(-2zR) \int_0^z \mathrm{d}y \, F(y), \qquad (A\,2)$$

whereupon partial integration with respect to z yields the recurrence relation

$$I_p = \frac{p}{2R} I_{p-1} + \frac{1}{2R} \int_0^\infty \mathrm{d}z \, z^p \exp(-2zR) F(z). \qquad (A\,3)$$

When this relation is applied iteratively the double integral I_p can be written as a sum of single integrals by means of the formula

$$I_p = \sum_{k=0}^p \frac{p!}{(p-k)!(2R)^{k+1}} \int_0^\infty \mathrm{d}z \, z^{p-k} \exp(-2zR) F(z), \qquad (A\,4)$$

which is used in the main text.

Appendix B

An identity for squares of modified Bessel functions

The modified Bessel functions of the third kind $K_{m+1/2}(z)$, with positive integer m, can be obtained from $K_{1/2}(z)$ by means of the formula

$$(\tfrac{1}{2}z)^{-m-1/2} K_{m+1/2}(z) = \frac{1}{m!} \left(\frac{\mathrm{d}^2}{\mathrm{d}z^2} - 1 \right)^m (\tfrac{1}{2}z)^{-1/2} K_{1/2}(z), \qquad (B\,1)$$

which may be proved with the help of the recurrence relations for Bessel functions [12]. Let us multiply this identity by the Hankel coefficient

$$(L + \tfrac{1}{2}, m) \equiv (L+m)! / [m!(L-m)!] \qquad (B\,2)$$

and take the summation over m. Since the Hankel coefficient equals $(-1)^{L+m} m! [\![P_L]\!]_m$, with the bracket symbol defined in (24), one gets in this way

$$\sum_{m=0}^L (L + \tfrac{1}{2}, m)(\tfrac{1}{2}z)^{-m-1/2} K_{m+1/2}(z) = P_L \left(2\frac{\mathrm{d}^2}{\mathrm{d}z^2} - 1 \right) (\tfrac{1}{2}z)^{-1/2} K_{1/2}(z). \qquad (B\,3)$$

If on both sides the equation

$$\pi^{1/2} \sum_{m=0}^L (L + \tfrac{1}{2}, m)(\tfrac{1}{2}z)^{-m-1/2} K_{m+1/2}(z) = [K_{L+1/2}(\tfrac{1}{2}z)]^2 \qquad (B\,4)$$

is substituted, which follows by inverting the well-known duplication formula [12], we finally obtain the identity

$$[K_{L+1/2}(\tfrac{1}{2}z)]^2 = P_L \left(2\frac{\mathrm{d}^2}{\mathrm{d}z^2} - 1 \right) [K_{1/2}(\tfrac{1}{2}z)]^2 ; \qquad (B\,5)$$

it shows that the differential operator $P_L(2\mathrm{d}^2/\mathrm{d}z^2 - 1)$ can be looked upon as the generator of the squares of modified Bessel functions of half-integer order. Of course, once this result has been derived it may be verified independently by induction with respect to L.

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