RETARDATION IN THE ATOMIC PAIR POLARIZABILITY

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The atomic pair polarizability for hydrogen atoms is calculated within the framework of covariant quantum electrodynamics. Retardation effects are shown to change the dependence on the interatomic separation R from R^{-6} to R^{-7} for R large compared with a characteristic wavelength of the atomic spectrum. For harmonic oscillators the pair polarizability is proved to be independent of the interparticle interaction.

The polarizability of a pair of atoms is non-additive, owing to the interactions between the atoms. This phenomenon, which manifests itself in the density dependence of the Clausius—Mossotti function, has been discussed extensively in the literature. In fact, both the long-range dispersion [1–7] and the short-range overlap [8,9] contributions to the pair polarizability have been studied. On the basis of a perturbation-theoretical treatment of the instantaneous electrostatic interaction between the atoms, the long-range pair polarizability has been found to fall off as an inverse sixth power of the interatomic separation R [1,2]. However, at distances comparable with a characteristic wavelength of the atomic spectrum retardation effects may be expected [10], in close analogy with those showing up in the interatomic pair potential; for the latter case the radial dependence at very large separations is given by R^{-7} rather than R^{-6} [11]. Such retardation effects may be obtained in the pair polarizability if the exchange of virtual photons is included in the interaction, as will be shown in the present letter.

The induced electric-dipole moments $\langle d \rangle$ of a set of atoms in the presence of an external electrostatic field E_0 are interrelated by the equation

$$\langle d_a \rangle = \alpha_a \cdot \left[E_0 - \sum_{b(\neq a)} T_{ab} \cdot \langle d_b \rangle \right] , \qquad (1)$$

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with α the atomic polarizability and $T_{ab} \equiv \nabla_a \nabla_b$ $(1/4\pi R_{ab})$ the static dipole—dipole propagator. Following ref. [1] we also introduce tensors β by writing:

$$\langle d_a \rangle = \beta_a \cdot E_0 ; \qquad (2)$$

from (1) and (2) the relationship between α and β is found to be:

$$\beta_a = \alpha_a \cdot \left[U - \sum_{b(\neq a)} T_{ab} \cdot \beta_b \right] \qquad (3)$$

Hence, to derive the polarizability one may as well start by evaluating β.

We shall consider a pair of hydrogen atoms, with fixed nuclei, of which the electrons are described by a relativistic Dirac hamiltonian H_D. In the presence of a quantized radiation field A^μ and a static external field A_0^μ, with $-\nabla A_0^0 = E_0$ and $A_0 = 0$, the total hamiltonian of the system can be split up into a free part and a part that takes into account the interaction of the atoms and the total electromagnetic field $A^\mu + A_0^\mu$. In accordance with (1)–(3) this interaction will be treated in the electric-dipole approximation. Perturbation theory then leads to an expression for $V(R, E_0)$, which is the interatomic potential energy averaged over the degenerate ground states of both atoms independently. Subsequently, the polarizability follows through the relation $\beta_a + \beta_b = -\partial^2 V/\partial E_0 \partial E_0$, for $E_0 = 0$.

In lowest, i.e. second-order perturbation theory,

β is the polarizability of a free atom, which can be written as:

$$\beta_a^{(2)} = \alpha_a^{(2)} = \sum_\alpha 2k_\alpha^{-1} D_a^{(2)} \mathbf{U} ; \tag{4}$$

here the sum over α runs over both positive- and negative-energy excited atomic states α, while k_α is the energy difference between these states and the g-fold degenerate ground states α_0. Rotation-invariance arguments permitted us to introduce in (4) the invariant part

$$D_\alpha^{(2)} = \tfrac{1}{3} g^{-1} \sum_{\alpha_0} |d_{\alpha_0\alpha}|^2 \tag{5}$$

of a product of dipole transition matrix elements.

In fourth order the interaction energy $V(R, E_0)$ is due to the exchange of one photon between the atoms. It may be calculated in the framework of covariant perturbation theory by using the connection with the scattering matrix, viz.

$$S_{\mathrm{fi}}^{(4)} = -2\pi i \delta(E_{\mathrm{f}} - E_{\mathrm{i}}) V_{\mathrm{fi}}^{(4)} , \tag{6}$$

where the delta function expresses energy conservation between the final and initial states f and i of the system; in fact $V(R, E_0)$ is the averaged eigenvalue of the matrix $V_{\mathrm{fi}}^{(4)}$. The one-photon exchange processes are represented by the Feynman diagrams of fig. 1, which can be evaluated by means of the standard rules of covariant quantum electrodynamics. The first diagram for instance leads to the following contribution in $\beta_a^{(4)}$:

$$-g^{-2} \sum_{\alpha_0 \alpha \beta_0 \beta} 2(2\pi)^{-3} \int \mathrm{d}k \exp(\mathrm{i}k \cdot R)(k^2 k_\alpha k_\beta)^{-1}$$

$$\times d_{\alpha_0\alpha} d_{\beta_0\beta}(kk + k_\alpha k_\beta \mathbf{U}) : d_{\alpha\alpha_0} d_{\beta\beta_0} , \tag{7}$$

with k the momentum of the exchanged photon. The leading product of dipole moments in (7) is due to the interaction with the static external field, while the last factor of (7) contains two terms, arising from the interaction with the time and space components of the quantized radiation field, respectively. Upon carrying out the integration over k, using rotation invariance for the dipole matrix elements and adding the contributions of the other diagrams one gets:
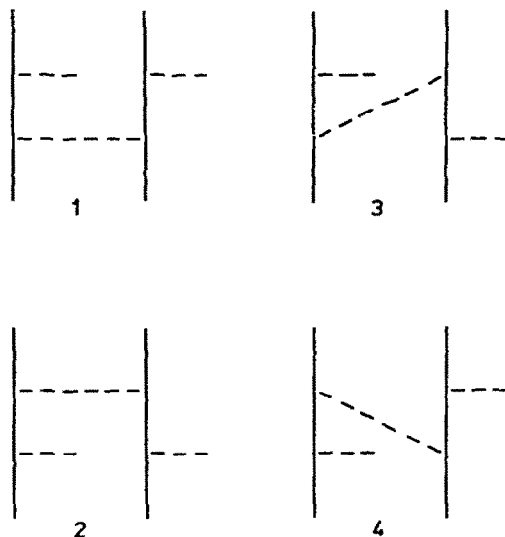

Fig. 1. Diagrams for one-photon exchange.

$$\beta_a^{(4)} = -\sum_{\alpha,\beta} 4(k_\alpha k_\beta)^{-1} D_a^{(2)} D_b^{(2)} \mathbf{T}_{ab} . \tag{8}$$

When both (8) and (4) are substituted into (3) we find $\alpha_a^{(4)} = 0$, so that in fourth order the polarizability is not influenced by the interatomic interaction, as was already known for the case of electrostatic interactions [1].

Sixth-order perturbation theory leads to the two-photon-exchange diagrams of fig. 2, together with those having crossing photon lines. The contribution of each diagram contains two dipole matrix elements for one atom and a product of four for the other; upon employing rotational invariance the former may be related to the invariant $D^{(2)}$ defined in (5), whereas the latter gives rise to three types of invariant contributions, viz.

$$D_{a,i}^{(4)} = g^{-1} \sum_{\alpha_0} (c_{i1}\delta_{kl}\delta_{mn} + c_{i2}\delta_{km}\delta_{ln} + c_{i3}\delta_{kn}\delta_{lm})$$

$$\times d_{\alpha_0\alpha}^k d_{\alpha\alpha'}^l d_{\alpha'\alpha''}^m d_{\alpha''\alpha_0}^n , \tag{9}$$

with $c_{ij} = \tfrac{1}{6}\delta_{ij} - \tfrac{1}{30}$. The quantities thus defined are connected by sum rules. In fact, the closure relation for the atomic states may be used to prove the identities
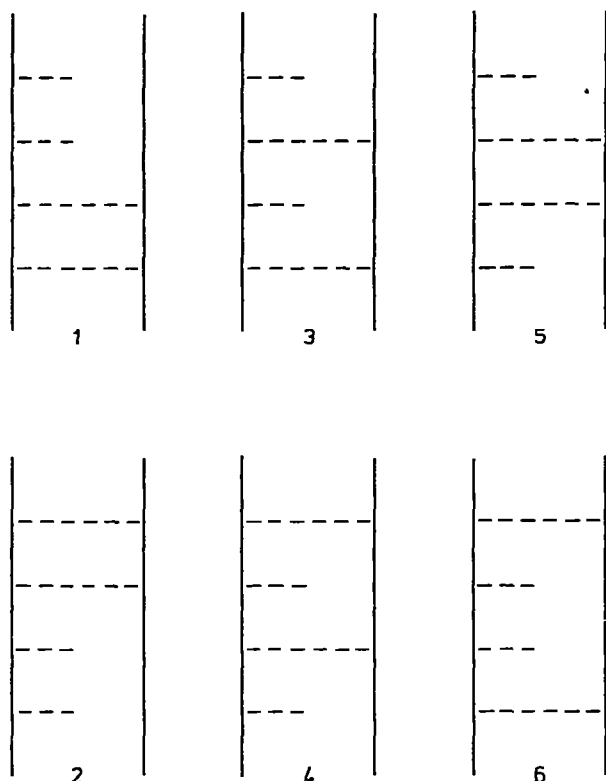
Fig. 2. Diagrams for two-photon exchange.

$$\sum_{\alpha} (D_{a,2}^{(4)} - D_{a,3}^{(4)}) = \sum_{\alpha'} (D_{a,1}^{(4)} - D_{a,2}^{(4)})$$

$$= \sum_{\alpha''} (D_{a,2}^{(4)} - D_{a,3}^{(4)}) = 0 . \qquad (10)$$

Furthermore the vanishing of the repeated commutator $[d, [H_D, d]]$ implies:

$$\sum_{\alpha} (2k_{\alpha} - k_{\alpha}') D_{a,i}^{(4)} = \sum_{\alpha'} (2k_{\alpha'} - k_{\alpha} - k_{\alpha''}) D_{a,i}^{(4)}$$

$$= \sum_{\alpha''} (2k_{\alpha''} - k_{\alpha'}) D_{a,i}^{(4)} = 0 , \qquad (11)$$

which are generalizations of the relativistic Thomas–Reiche–Kuhn sum rule $\sum_{\alpha} k_{\alpha} D_{a}^{(2)} = 0$.

The general formulae for $\beta_a^{(6)}$ and $\alpha_a^{(6)}$ that are obtained by evaluating all diagrams of fig. 2 are rather lengthy and will not be given here. The dependence

on the interatomic separation turns out to be governed by the function $P(x) = ci(x) \sin x - si(x) \cos x$, with $x = 2|k_{\alpha}|R$. The same function also occurs in the dispersion energy and indeed gives rise to retardation for very large interatomic separations. In particular, if $R \gg |k_{\alpha}|^{-1}$ the asymptotic sixth-order polarizability is found to be:

$$\alpha_a^{(6)} = \sum_{\alpha, \alpha', \alpha'', \beta} (k_{\alpha} k_{\alpha''} k_{\beta})^{-1}$$

$$\times [(1 - \delta_{\alpha', 0}) k_{\alpha'}^{-1} (D_{a,1}^{(4)} + D_{a,2}^{(4)} + D_{a,3}^{(4)})$$

$$- \tfrac{1}{2} \delta_{\alpha', 0} (k_{\alpha}^{-1} + k_{\alpha'}^{-1}) D_{a,1}^{(4)}] D_b^{(2)} (36 \mathbf{U} + 7\hat{R}\hat{R}) / 4\pi^3 R^7 . \qquad (12)$$

The nonrelativistic limit of the expressions arrived at may be obtained by making a Foldy–Wouthuysen transformation of the atomic operators. The asymptotic expression for the retarded pair polarizability then retains the same form as in (12), except that the sums are extended over positive-energy-intermediate states only. In the electrostatic approximation, i.e. for $R \ll k_{\alpha}^{-1}$, the nonrelativistic formula of Jansen and Mazur [1] is recovered.

In ref. [1] the results for the electrostatic pair polarizability were applied to a pair of harmonic oscillators. It was found there that in this special case $\alpha^{(6)}$ vanishes; it could be proved even quite generally that the polarizability of a set of identical harmonic oscillators is not influenced by the interparticles interaction (cf. also ref. [12]). The same result may be shown to hold true for the retarded pair polarizability. In particular this may be verified for the sixth-order expressions derived here, but again a general proof may be given. The hamiltonian for a set of identical harmonic oscillators in an external field and a quantized radiation field reads:

$$H = \sum_a [\tfrac{1}{2} m^{-1} (p_a + eA_a)^2 + \tfrac{1}{2} mk^2 r_a^2 + er_a \cdot E_0]$$

$$+ \sum_{a,b} \tfrac{1}{2} e^2 r_a \cdot T_{ab} \cdot r_b + H_{rad} , \qquad (13)$$

with k the wave number of the harmonic oscillators. The Ehrenfest equations for an eigenstate of the total hamiltonian yield $\langle \partial H / \partial r_a \rangle = 0$. Since in the dipole ap-

proximation the vector potential A_α of the radiation field is independent of r_α one recovers in this way for $d_\alpha = -er_\alpha$ the relation (1) with $\alpha_\alpha = (e^2/mk^2)\,\mathbf{U}$ the free polarizability of a harmonic oscillator.

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