The retarded energy shift and pair polarizabilities of interacting atoms in an external field

Application of resummed field-theoretical perturbation theory

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The interaction energy of two atoms in the presence of an external electrostatic field is evaluated up to sixth order with the help of covariant field-theoretical perturbation theory. The divergent Feynman diagrams entering the calculation are resummed according to a systematic procedure that has been developed in a previous paper. The pair polarizability and first hyperpolarizability that give the response of the interacting atoms to the external field are subsequently obtained from the energy shift by virtue of a Hellmann-Feynman theorem. The retardation effects showing up in the pair polarizability are discussed in detail.

1. INTRODUCTION

The response of atoms to externally applied fields is influenced by the interatomic interaction. This phenomenon manifests itself in the so-called pair polarizability and pair hyperpolarizabilities. Both the long-range dispersion [1-7] and the short-range overlap (see for example [8] and references therein) contributions to the pair polarizability have been studied. In the field-free case the interaction through the quantized radiation field entails retardation effects when the distance between the atoms is of the order of a characteristic spectral wavelength [9]. As has been realized by Mackrodt [10], analogous retardation effects are expected to occur in the pair polarizability. This author considered the coupling of intermolecular interactions to a static field by means of non-covariant Rayleigh-Schrödinger perturbation theory. However, such a treatment necessitates the evaluation of a number of diagrammatic contributions which rapidly increases with perturbation order. In [10] the ensuing complex calculations have been avoided by considering in higher order only the subset of static interaction diagrams. An actual expression for the pair polarizability in the fully retarded limit has been reported by the present authors in a preliminary letter [11].

The evaluation of the large number of radiative processes that describe the interplay of the retarded interatomic interaction and the coupling to the external field becomes more feasible if a covariant field-theoretical perturbation theory is used. Even then the calculation is not straightforward, since Feynman diagrams are encountered that are divergent when considered separately. Recently we
have cast the field-theoretical perturbation theory in a form that systematically avoids these divergencies in any order [12–14]. In fact, by analysing the global block structure of the Feynman diagrams, a recipe could be given for the resummation of the divergent contributions. In the present paper we shall employ this resummed perturbation theory to evaluate the energy shift that arises up to sixth order from the coupling of the atoms with both the radiative and the external field. Subsequently it will be shown how the pair polarizability and the first hyperpolarizability follow from this energy shift.

2. THE ENERGY SHIFT OF INTERACTING ATOMS IN AN EXTERNAL FIELD.

EFFECTS OF ONE-PHOTON EXCHANGE PROCESSES

To study the influence of a homogeneous electrostatic field $E_e$ on the retarded interatomic interaction we consider a pair of ground state hydrogen atoms $a, b$ of which the nuclei are at fixed positions $R_a, R_b$. The electrons are described by the relativistic Dirac theory, so that the energy eigenstates $|\alpha\rangle$ of atom $a$ have four-spinor wavefunctions $\psi_a(x) = \psi_a(r) \exp(-iE_a t)$; the overlap of the wavefunctions $\psi_\alpha, \psi_\beta$ of the two atoms will be ignored. The total hamiltonian of the system can be split up into an unperturbed part describing the free atoms and the quantized radiation field $A^\mu$, and a perturbation involving the electric dipole coupling of the atoms with $A^\mu$ and the external field $A_e^\mu = -g_{0\mu} r \cdot E_e$. Since the atomic ground level is degenerate one has to use degenerate perturbation theory; it can be formulated by means of an effective hamiltonian $V$ that acts on the subspace of unperturbed ground states $|\alpha_0\rangle |\beta_0\rangle$.

We will be interested especially in the average $\Delta E$ of the energy shift over these ground states, so that only the trace of the effective hamiltonian is needed. In a preceding paper [12] expressions for $V$ and $\text{Tr} V$ have been derived in terms of time-ordered products of interaction operators, so that in the calculation of the energy shifts Feynman diagram techniques may be employed.

The contributions to the averaged energy shift $\Delta E$ that depend on the interatomic radius vector $R = R_a - R_b$ and the external field $E_e$ are of fourth and higher order in the coupling constant $e$. Fourth order perturbation theory leads to diagrams in which one photon is exchanged between the atoms, while two couplings to the external fields are present (see figure 1). The next contributions to $\Delta E(R, E_e)$ are of sixth order and include both one- and two-photon exchange processes (see figure 2 and 3; radiative self-energy and vertex corrections are not considered here). The general method for calculating these processes through resummed adiabatic perturbation theory has been outlined in [13]. To elucidate it we shall briefly sketch in this section how the exchange of a single photon can be dealt with; in the following section the more complicated two-photon exchange diagrams will be considered in detail.

![Figure 1. Fourth order diagrams with one-photon exchange.](image-url)
Figure 2. Sixth order diagrams with one-photon exchange. The labelling of atomic states is as indicated in diagram 5; the vertices are always labelled in the same cyclic order along the electron lines, starting with the photon vertices.

Figure 3. Sixth order diagrams with two-photon exchange. The labelling of atomic states is as indicated in diagram 17; the vertices are always labelled in the same cyclic order along the electron lines, starting with the photon vertices.
When the usual Feynman rules are employed the total averaged energy shift \( \Delta E_{1\gamma}^{(4)} = g^{-2} \text{Tr} \, V \) (with \( g \) the level degeneracy) that is associated with figure 1 can be derived straightforwardly; in terms of the scalar polarizability \( \alpha_0(B\, 3) \) of the non-interacting atoms it reads

\[
\Delta E_{1\gamma}^{(4)}(R, E_e) = -\alpha_0 \alpha_0 E_e E_e : \nabla \nabla \frac{1}{4\pi R}.
\]

As may be expected this energy shift is non-retarded, although the full electromagnetic field has been included in the perturbation. Indeed, as has been noticed already by Mackrodt [10], equation (1) may be understood as originating from the static interaction between the dipole moments induced by the external field \( E_e \).

We shall now consider the next one-photon processes contributing to \( \Delta E(R, E_e) \) in the electric dipole approximation, which are of fourth order in \( E_e \). In [13] it has been shown that in general both connected and disconnected Feynman diagrams may contribute to the averaged energy shift. In the present case these two types have been drawn in figure 2 as diagrams 5–12 and 13–16, respectively. (Of course diagrams with \( a \) and \( b \) interchanged have to be added.) They arise by taking \( N = 1 \) and \( N = 2 \) in formula (6) of [13], which represents the trace of the effective Hamiltonian.

Let us first study the diagrams 5–12. Parity arguments show that in the electric dipole approximation the intermediate atomic states \( \alpha, \alpha^* \) and \( \beta \) have energies different from that of the ground states (that is \( k_\alpha, k_\alpha^*, k_\beta \neq 0 \)). The state \( \alpha^* \), however, may be either an excited state \( (k_\alpha^* \neq 0) \) or a ground-level state \( (k_\alpha^* = 0) \). In the latter case a time ordering of the vertices can be realized such that at a fixed intermediate time the energy of the total system is equal to the initial energy. Correspondingly, the contributions of the diagrams 5–12 to the trace of the effective Hamiltonian will be divergent in the adiabatic limit if \( k_\alpha^* = 0 \). Similar divergencies occur in the diagrams 13–16, where \( \alpha = \alpha_0' \) always. It has been demonstrated in [13] how a cancellation of the divergencies can be obtained by a resummation of the diagrams. In particular, the terms with \( k_\alpha = 0 \) from diagrams 5 and 9 have to be taken together with 13, which has an identical trace of products of dipole moments. In the following the contributions \( \text{Tr} \, V^0 \) (with \( k_\alpha = 0 \)) and \( \text{Tr} \, V^* \) (with \( k_\alpha = 0 \)) will be evaluated separately.

The contributions with \( k_\alpha = 0 \) of the diagrams 5, 9 and 13 follow by applying the Feynman rules; when in 9 the labels \( (\alpha_0, \alpha) \) and \( (\alpha_0', \alpha^*) \) are interchanged we get

\[
\text{Tr} \, V^0_{5+9+13} = \lim_{\epsilon \to 0} \left\{ \sum_{x_\alpha, x_\alpha', x_\beta} -ie^4 \int d^4 x_1 \ldots d^4 x_6 \, e^{-\epsilon|t_1|\ldots-\epsilon|t_4|}\delta(t_{\text{max}}) \psi_{\alpha_0}(x_0) \right.
\]

\[
\times \gamma^\alpha S_{F\alpha}(x_0, x_4) \gamma^\alpha \psi_{\alpha_0}(x_4) \bar{\psi}_{\alpha_0}(x_5) \gamma^\beta S_{F\beta}(x_5, x_1) \gamma^\beta \psi_{\alpha_0}(x_1) \left. \times \bar{\psi}_{\beta_0}(x_6) \gamma^\beta S_{F\beta}(x_6, x_2) \gamma^\gamma \psi_{\beta_0}(x_2) g_{\alpha\beta} D_F(x_1 - x_2) A_\mu^\gamma(x_3) \right.
\]

\[
\times A_\nu^\delta(x_4) A_\rho^\epsilon(x_5) A_\sigma^\tau(x_6) [\theta(t_{45}) + \theta(t_{13}) - 1].
\]
[13] we now write
\[ \theta(t_{45}) + \theta(t_{13}) - 1 = \theta(t_{45}) \theta(t_{13}) - \theta(t_{54}) \theta(t_{31}). \] (3)
In contrast to the terms at the left-hand side those at the right-hand side each lead to separately convergent time integrals in the adiabatic limit; consequently we may put \( \epsilon = 0 \) explicitly in (2). When the \( \theta \) functions in (3) are Fourier transformed, the expression obtained from (2) may be evaluated along the familiar lines, with the result
\[ \text{Tr} \ V^0_{5+9+13} = - \sum_{a, b, a', \beta} \sum_{x, x'} d_{a_\alpha} \cdot E_x d_{a_\alpha} - E_x d_{a_\alpha} \cdot E_x d_{b_{\beta}} \cdot E_x \\ \times d_{a'_{\alpha}} \cdot \left( \nabla \nabla - k_{a'} k_{\beta} U \right) \cdot d_{b_{\beta}} F^0(R). \] (4)
The radial function \( F^0(R) \) contains the intermediate excitation energies \( k_{a}, k_{a'} \) inside a contour integral; evaluation of this integral gives
\[ F^0(R) = \delta_{k_{a'}, 0} \int_{-\infty}^{\infty} d\Omega \left\{ \{ k_{a} (1 - i0) + \Omega \} \{ k_{a'} (1 - i0) + \Omega \} k_{\beta} \right\}^{-1} \left\{ (\Omega - i0)^{-2} \right\} \frac{1}{4\pi R} \\
= \delta_{k_{a'}, 0} \left( \frac{\partial}{\partial k_{a}} + \frac{\partial}{\partial k_{a'}} \right) \frac{1}{k_{a} k_{a'} k_{\beta}} \frac{1}{4\pi R}. \] (5)
The parts of the diagrams 5 and 9 having \( k_{a} \neq 0 \) can be evaluated straightforwardly. In that case the radial function becomes
\[ F'(R) = 2(1 - \delta_{k_{a'}, 0}) \frac{1}{k_{a} k_{a'} k_{\beta}} \frac{1}{4\pi R}. \] (6)
Comparison of (5) and (6) shows a general feature of the radial functions that arise in the present problem; for the diagrams with \( k_{a} = 0 \) the singular energy denominator \( k_{a}^{-1} \) is replaced by a differentiation with respect to other, non-vanishing, excitation energies.

The remaining groups of diagrams (6, 10, 14), (7, 11, 15) and (8, 12, 16) in figure 2 may be treated likewise, whereupon all diagrams can be added. As a natural extension to (1) the total averaged sixth order energy shift due to one-photon exchange then takes the simple form
\[ \Delta E_{1_6}^{(0)}(R, E) = -\frac{1}{8} (\gamma_0 \alpha_{0b} + \alpha_{0a} \gamma_{0b}) E_{e}^2 E_{e} : \nabla \nabla \frac{1}{4\pi R} \] (7)
with \( \gamma_0 \) the free atomic hyperpolarizability (B 7). As in the fourth order one-photon process the energy shift shows no retardation, as may be understood on general grounds.

3. THE SIXTH ORDER ENERGY SHIFT FROM TWO-PHOTON EXCHANGE
The radial dependence of the fourth and sixth order interaction energies obtained so far is governed by the electrostatic dipole–dipole tensor \( \nabla \nabla (4\pi R)^{-1} \). A more complicated radial function may be expected when different types of processes are included, namely those in which two photons are exchanged between the ground state atoms; for the field-free case such processes are known
to lead to retardation effects \[9, 15\]. The first field-dependent contributions to the averaged energy shift involve sixth order perturbation theory. The relevant Feynman diagrams are those drawn in figure 3 and their crossed counterparts; they result from formula (6) of [13] by putting \(N=1\) (diagrams 17–22) and \(N=2\) (diagram 23). The diagrams 17, 18 and 23 are divergent for \(k_{\alpha}=0\) and have to be taken together in order to ensure a finite answer; in the diagrams 19–22 no such divergence can occur, since parity arguments imply \(k_{\alpha}, k_{\alpha'} \neq 0\).

The three singular diagrams 17, 18 and 23 are dealt with as in the preceding section. We first consider the part \(\text{Tr} \, V^0_{17+18+23} \) having \(k_{\alpha}=0\). If in diagram 18 the labels \((\alpha_0, \alpha)\) and \((\alpha_0', \alpha')\) are interchanged all three contributions can be added. The part of the electron propagator \(S_F\) that is associated with ground-level intermediate states \(\alpha = \alpha_0'\) leads to \(\theta\) functions that may be grouped together in the following way

\[
\theta(t_{61}) + \theta(t_{35}) - 1 = \theta(t_{61})\theta(t_{35}) - \theta(t_{16})\theta(t_{53}).
\]

This equation is completely analogous to (3); again each of the terms at the left-hand side leads to divergences in the adiabatic limit, while the two terms at the right-hand side can be treated separately for \(\epsilon \to 0\). Along the same lines that led to (4) we then get from the diagrams with non-crossing photon lines

\[
\text{Tr} \, V^0_{17+18+23,nc} = - \sum_{\alpha_0, \alpha_1} \sum_{\alpha_0', \alpha_1'} \sum_{\alpha, \alpha'} d_{\alpha \alpha} \cdot E_\epsilon d_{\alpha \alpha'} \cdot E_\epsilon d_{\alpha' \alpha} \cdot (\nabla \nabla - k_{\alpha} - k_{\beta} U) \cdot d_{\beta \alpha} d_{\beta \alpha'} \cdot (\nabla' \nabla' - k_{\alpha'} - k_{\beta} U) \cdot d_{\beta \alpha} \cdot \mathcal{F}^0(R, R').
\]

For book-keeping reasons we formally introduced here two different radius vectors \(R\) and \(R'\); they are to be put equal after the operations \(\nabla\) and \(\nabla'\) have been performed. The radial function \(\mathcal{F}^0(R, R')\) is obtained by carrying out the integrals over the four-momenta \(k^\alpha\) and \(k'^\beta\) with the help of appendix A

\[
\mathcal{F}^0(R, R') = \delta_{k_{\alpha}, 0} \left( \frac{1}{16\pi^3 k_{\alpha}(k_{\alpha} + k_{\beta}) RR'} \right)
\]

\[
\times [\text{sgn} \left( E_{\alpha} \right) P(|k_{\alpha} R + k_{\beta} R'|) + \text{sgn} \left( E_{\beta} \right) P(|k_{\beta} R + k_{\alpha} R'|)],
\]

with \(P(x)\) defined in (A 5).

The parts of the non-crossed diagrams 17 and 18 with \(k_{\alpha'} \neq 0\) pose no problem in the adiabatic limit. The result for \(\text{Tr} \, V^0_{17,nc}\) has the same general form as (9), albeit with a different radial function and different coefficients in front of the two tensors \(U\). The latter now read \((k_{\alpha'} - k_{\alpha})k_{\beta}\) and \(-k_{\alpha} - k_{\beta}\) respectively; the radial function is again a double four-momentum integral, which may be calculated with the help of (A 8)

\[
\mathcal{F}'(R, R') = (1 - \delta_{k_{\alpha'}, 0}) \left( \frac{1}{16\pi^3 k_{\alpha} k_{\alpha'}(k_{\alpha'} + k_{\beta}) RR'} \right)
\]

\[
\times [\text{sgn} \left( E_{\alpha} \right) P(|k_{\alpha} R + k_{\beta} R'|) + \text{sgn} \left( E_{\beta} \right) P(|k_{\beta} R + k_{\alpha} R'|)],
\]

The term \(\text{Tr} \, V^0_{18,nc}\) is equal to \(\text{Tr} \, V^0_{17,nc}\) apart from an interchange of the labels \(\alpha\) and \(\alpha''\).

The contributions \(\text{Tr} \, V^0\) and \(\text{Tr} \, V'\) of the diagrams 17, 18 and 23 with crossing photon lines may be derived along the same lines as followed above. When all
products of atomic dipole matrix elements are written in their rotation-invariant combinations $D_{a1}^{(4)} (B 5)$ and $D_{b}^{(2)} (B 2)$, it turns out that the crossed and non-crossed contributions only differ by a number of minus signs and can simply be added. The trace of the total effective hamiltonian arising from the diagrams 17, 18 and 23 then becomes

$$\text{Tr} V_{17+18+23}$$

$$= - g^2 \sum_{\sigma = \pm 1} \sum_{\alpha', \beta} \{E_\sigma^2 \{\nabla \nabla + \sigma (k_{\alpha'} - k_{\alpha}) \cdot \nabla \nabla' - \sigma k_{\alpha} \cdot k_{\beta} \cdot \nabla \nabla' - \sigma k_{\alpha} \cdot k_{\beta} \cdot \nabla \nabla'\}} D_{a1}^{(4)}$$

$$+ E_\sigma \cdot \{\nabla \nabla + \sigma (k_{\alpha'} - k_{\alpha}) \cdot \nabla \nabla' - \sigma k_{\alpha} \cdot k_{\beta} \cdot \nabla \nabla' - \sigma k_{\alpha} \cdot k_{\beta} \cdot \nabla \nabla'\} \cdot E_\sigma (D_{a1}^{(4)} + D_{a11}^{(4)})$$

$$\times D_{b}^{(2)} F_{\sigma} (R, R') + (\alpha \leftrightarrow \alpha'),$$

with

$$F_{\sigma} (R, R') = \left[ (1 - \delta_{k_{\alpha'}, 0}) \frac{1}{k_{\alpha'}} + \frac{1}{2} \delta_{k_{\alpha'}, 0} \left( \frac{\partial}{\partial k_{\alpha'}} + \frac{\partial}{\partial k_{\alpha'}} \right) \right] \frac{\sigma}{16 \pi^3 k_{\alpha}(k_{\alpha'} + \sigma k_{\beta}) RR'}$$

$$\times [\text{sgn} (E_\sigma) P(|k_{\alpha} R + k_{\alpha} R'|) + \sigma \text{sgn} (E_\sigma) P(|k_{\beta} R + k_{\beta} R'|)].$$

Formulæ similar to (12) with (13) hold for the remaining diagrams 19–22 of figure 3; however in these diagrams no singularities are met for $k_{\alpha'} = 0$ and accordingly the derivatives with respect to $k_{\alpha}$ and $k_{\alpha'}$ are missing. The derivation of these formulæ is straightforward and will not be given here.

A common feature of (12) and the expressions for the other diagrams is the presence of three types of terms, with four, two and no differential operators acting on the radial function. When in the leading one of these, with the product of operators $\nabla \nabla' \nabla \nabla'$, the summation over $\sigma$ is carried out, the radial function contains the following combination of $P$ functions

$$g_{a\beta} (R, R') = - \frac{1}{8 \pi^3 (k_{\alpha}^2 - k_{\beta}^2) RR'} \left[ k_{\beta} \text{sgn} (E_\sigma) P(|k_{\alpha} R + k_{\alpha} R'|) \right.$$  

$$- k_{\alpha} \text{sgn} (E_\sigma) P(|k_{\beta} R + k_{\beta} R'|)],$$

By substituting for $P(x)$ its Laplace transform (see (A 5)) we get the integral representation

$$g_{a\beta} (R, R') = \frac{k_{\alpha} k_{\beta}}{8 \pi^3 RR'} \int_0^\infty du \frac{e^{-u(R+R')}}{(k_{\alpha}^2 + u^2)(k_{\beta}^2 + u^2)}$$

which for the case $k_{\alpha} = 0$ is defined by taking the limit $k_{\alpha} \downarrow 0$. In fact, the function $g_{a\beta} (R, R')$ plays a central role here, in the sense that it determines the radial dependence of all terms in $\text{Tr} V$. To show this one first has to make (12) and the analogous expressions homogeneous in $\nabla$ and $\nabla'$ with the help of the differential equations (A 6) for $P(x)$. Subsequently the part of $\text{Tr} V$ that can not be written in terms of $g_{a\beta} (R, R')$ (14) may be seen to vanish as a consequence of the sum rules (B 9)–(B 11) for the dipole matrix elements. As a result the averaged sixth order energy shift $\Delta \bar{E} = g^2 \text{Tr} V$ due to all two-photon processes
is finally found to be
\[
\Delta E_{2y}^{(6)}(\mathbf{R}, \mathbf{E}_e) = - E_e^2 (\nabla \nabla - \mathbf{U} \Delta) \cdot (\nabla' \nabla' - \mathbf{U} \Delta') \sum_{\alpha, \beta} \left[ (D_{a1}^{(4)} G_1 + D_{a11}^{(4)} G_{11}) + (D_{a11}^{(4)} G_{11}) D_{b}^{(2)} - E_e \cdot (\nabla \nabla - \mathbf{U} \Delta) \cdot (\nabla' \nabla' - \mathbf{U} \Delta') \cdot \mathbf{E}_e \right] \sum_{\alpha', \beta'}
\]
\times [(D_{a1}^{(4)} + D_{a11}^{(4)}) G_1 + (D_{a11}^{(4)} + D_{a1}^{(4)}) G_{11} + (D_{a1}^{(4)} + D_{a11}^{(4)}) G_{111}] \times D_{b}^{(2)} + (a \leftrightarrow b). \quad (16)
\]

Here we have added the contributions from diagrams in which the external field acts on atom \( b \) instead of \( a \). The radial functions \( G_i \) are linear combinations of the canonical functions \( g_{\alpha}(\mathbf{R}, \mathbf{R}') \)
\[
G_1 = \left[ (1 - 3k_{a,0}) \frac{1}{k_a} + \frac{1}{2} \delta k_{a,0} \left( \frac{\partial}{\partial k_a} + \frac{\partial}{\partial k_{a'}} \right) \right] \left( \frac{1}{k_a} g_{\alpha\beta} + \frac{1}{k_a} g_{\alpha\beta} \right), \quad (17)
\]
\[
G_{11} = \frac{1}{(k_a - k_a') g_{\alpha\beta}} + \frac{1}{k_a(k_a - k_{a'})} g_{\alpha\beta}
\]
\[
+ \left( k_a - k_{a'} \right) \frac{1}{k_a(k_a - k_{a'})} g_{\alpha\beta}, \quad (18)
\]
\[
G_{111} = \frac{1}{(k_a - k_a')(k_a' - k_{a'})} g_{\alpha\beta} + \frac{1}{(k_a - k_{a'})(k_a' - k_{a'})} g_{\alpha\beta}
\]
\[
+ \frac{1}{k_a} g_{\alpha\beta} + \frac{1}{k_a} g_{\alpha\beta}, \quad (19)
\]

The two-photon exchange contribution (16) to the averaged energy shift is much more complicated than the one-photon exchange terms given in (1) and (7). In particular, the radial function occurring here is not a simple power of \( R \); instead it is governed by the functions \( g_{\alpha\beta} \) defined in (14). Precisely the same function shows up in the expression for the retarded dispersion energy of two atoms without external fields \([9, 15]\); indeed, the latter also involves the exchange of two virtual photons. It should be noticed, however, that the present result (16) contains static terms as well, as is seen by substituting in (18) and (19)
\[
g_{\alpha\beta}(\mathbf{R}, \mathbf{R}') = (1 - \delta k_{a,0}) g_{\alpha\beta}(\mathbf{R}, \mathbf{R}') + \delta k_{a,0} \frac{1}{16\pi^2 k_R R} \quad (20)
\]
since \( P(x) = \pi/2 \) for \( x = 0 \) (\( k_a, k_{a'} \) and \( k_R \) are always non-zero). The precise role of these terms, and the detailed form of the retarded contributions at long and short interatomic distances, will be discussed further in the next section, in relation with the atomic pair polarizability.

4. THE ATOMIC PAIR POLARIZABILITY AND PAIR HYPERPOLARIZABILITY

The energy shifts that have been calculated in the preceding sections can be employed to obtain the polarizability and hyperpolarizability of a pair of atoms as a function of their separation. We start by considering the expectation value
of the dipole moments induced in the interacting atoms; they can be written in terms of the applied external field \( \mathbf{E}_e \) with the help of susceptibilities \( \beta, \delta \)

\[
\langle \psi | \mathbf{d}_a | \psi \rangle = \beta_a \cdot \mathbf{E}_e + \frac{1}{2} \delta_a : \mathbf{E}_e \mathbf{E}_e \mathbf{E}_e ,
\]

where effects of higher non-linearity are ignored. The state \( | \psi \rangle \) is an eigenstate of the hamiltonian of the interacting ground state atoms in the external field, which satisfies \( | \psi \rangle = P | \psi \rangle \), with \( P \) the projector on the perturbed states. For such a state a (generally non-unitary) one-to-one mapping \( W = P W P_0 \) exists onto an eigenstate \( | \phi \rangle = P_0 | \phi \rangle \) describing the free atoms (\( P_0 \) is the projector onto the unperturbed states). (In particular, one may choose \( W = PP_0 (P_0 P P_0)^{-1} \) and \( W^{-1} = P_0 P \), see [12].) As a consequence the left-hand side of (21) is equal to the matrix element between \( | \phi \rangle \) and \( \langle \phi | W^\dagger W \) of the transformed dipole operator \( W^{-1} \mathbf{d}_a W \). Since in the case of relativistic hydrogen atoms the set of ground states \( | \phi \rangle = | \alpha \rangle | \beta \rangle \) is degenerate we have to consider off-diagonal dipole matrix elements as well. For that reason (21) is generalized to an equation for \( W^{-1} \mathbf{d}_a W \), with susceptibility operators \( \beta_a \) and \( \delta_a \) connecting states \( | \phi \rangle \) and \( \langle \phi | \)

\[
W^{-1} \mathbf{d}_a W = \beta_a \cdot \mathbf{E}_e + \frac{1}{2} \delta_a : \mathbf{E}_e \mathbf{E}_e \mathbf{E}_e .
\]

The total dipole moment \( \mathbf{d}_a + \mathbf{d}_b \) follows from the hamiltonian \( H \) through the derivative \( - \partial H / \partial \mathbf{E}_e \). Furthermore the identities \( W^{-1} W = P_0 \) and \( WW^{-1} = P \) entail for the transform of this derivative

\[
W^{-1} \frac{\partial H}{\partial \mathbf{E}_e} W = \frac{\partial}{\partial \mathbf{E}_e} (W^{-1} HW) = \left[ W^{-1} HW, W^{-1} \frac{\partial W}{\partial \mathbf{E}_e} \right]
\]

which is an operator form of the familiar Hellmann–Feynman theorem [16]. The transformed hamiltonian \( W^{-1} HW \) itself differs from the effective hamiltonian \( V \) by a trivial term \( H_0 P_0 = E_0 P_0 \). Consequently the susceptibility operators are related to \( V \) and \( W \) by

\[
(\beta_a + \beta_b) \cdot \mathbf{E}_e + \frac{1}{2} (\delta_a + \delta_b) : \mathbf{E}_e \mathbf{E}_e \mathbf{E}_e = - \frac{\partial V}{\partial \mathbf{E}_e} + \left[ V, W^{-1} \frac{\partial W}{\partial \mathbf{E}_e} \right].
\]

This result shows how the total susceptibilities \( \beta \) and \( \delta \) can be obtained from energy level perturbation theory. If one is interested only in the averages \( \bar{\beta} \) and \( \bar{\delta} \) over the chosen set of reference states \( | \phi \rangle \) the trace of (24) has to be taken; the commutator term then drops out, while \( \text{Tr} \ V \) equals \( (\text{Tr} \ P_0) \Delta E \), so that one gets

\[
(\bar{\beta}_a + \bar{\beta}_b) \cdot \mathbf{E}_e + \frac{1}{2} (\bar{\delta}_a + \bar{\delta}_b) : \mathbf{E}_e \mathbf{E}_e \mathbf{E}_e = - \frac{\partial \Delta E}{\partial \mathbf{E}_e} .
\]

The susceptibilities of an individual atom can be found from (24) and (25) by differentiating \( V, W \) and \( \Delta E \) only with respect to the external fields that are connected to dipole matrix elements of that particular atom.

The susceptibilities \( \beta \) and \( \delta \) differ from the atomic polarizability \( \alpha \) and hyperpolarizability \( \gamma \), which are determined by the response to the local fields. The effect of the latter is expressed by writing

\[
W^{-1} \mathbf{d}_a W = \alpha_a \cdot (\mathbf{E}_e - \mathbf{T}_{ab} \cdot W^{-1} \mathbf{d}_b W) + \frac{1}{2} \gamma_a \cdot (\mathbf{E}_e - \mathbf{T}_{ab} \cdot W^{-1} \mathbf{d}_b W) \times (\mathbf{E}_e - \mathbf{T}_{ab} \cdot W^{-1} \mathbf{d}_b W) \]

\[
(\mathbf{E}_e - \mathbf{T}_{ab} \cdot W^{-1} \mathbf{d}_b W)(\mathbf{E}_e - \mathbf{T}_{ab} \cdot W^{-1} \mathbf{d}_b W)
\]

(26)
with \( T_{ab} \) the electrostatic dipole–dipole propagator \( \nabla_a \nabla_b \cdot \frac{1}{(4\pi |R_a - R_b|)} \).

Relations between the polarizabilities \( \alpha, \gamma \) and the susceptibilities \( \beta, \delta \) then follow immediately upon substitution of (22) into (26). In perturbation theory the tensors \( \alpha, \beta, \gamma, \delta \) may be written as series in powers of the coupling constant \( \epsilon \); the leading terms in \( \alpha, \beta \) and \( \gamma, \delta \) are of order \( \epsilon^2 \) and \( \epsilon^4 \), respectively. Upon insertion of these series expansions one can solve for \( \alpha \) and \( \gamma \) in successive orders of \( \epsilon \). Up to order \( \epsilon^6 \) one finds

\[
\alpha^{(2)}_a = \beta^{(2)}_a, \quad (27)
\]

\[
\alpha^{(4)}_a = \beta^{(4)}_a + \beta^{(2)}_a \cdot T_{ab} \cdot \beta^{(2)}_b, \quad (28)
\]

\[
\alpha^{(6)}_a = \beta^{(6)}_a + \beta^{(4)}_a + \beta^{(2)}_a \cdot T_{ab} \cdot \beta^{(2)}_b + \beta^{(2)}_b \cdot T_{ab} \cdot \beta^{(2)}_b. \quad (29)
\]

\[
\gamma^{(4)}_a = \delta^{(4)}_a, \quad (30)
\]

\[
\gamma^{(6)}_a = \delta^{(6)}_a + 3\delta^{(4)}_a + \delta^{(2)}_a \cdot T_{ab} \cdot \beta^{(2)}_b + \beta^{(2)}_b \cdot T_{ab} \cdot \delta^{(2)}_b, \quad (31)
\]

where in the second term at the right-hand side of (31) we used the fact that by definition \( \delta \) is symmetric in its last three indices (cf. (21)).

In the following we shall be interested only in the averages \( \bar{\alpha}_a \equiv g^{-2} \text{Tr} \alpha_a \) and \( \bar{\gamma}_a \equiv g^{-2} \text{Tr} \gamma_a \) of the polarizability and hyperpolarizability over the unperturbed energy eigenstates of the pair of atoms. These averages may be obtained in successive order of \( \epsilon \) by taking the traces of (27)–(31). Inspection of these formulae shows that one needs expressions for \( \beta^{(2)}_a, \beta^{(4)}_a, \delta^{(4)}_a \) and for the averages \( \bar{\beta}^{(6)}_a \) and \( \bar{\delta}^{(6)}_a \). Whereas according to (25) the latter follow directly by taking the derivative \( \partial \Delta E / \partial E_e \), the former involve an additional term, namely the commutator in (24). However, when \( \bar{\alpha}_a \) and \( \bar{\gamma}_a \) are calculated up to order \( \epsilon^6 \) this commutator may be ignored. In fact, it is at least of order \( \epsilon^4 \) and starts in this order with a term proportional to \( E_e^3 \), so that it contributes only in the tensors \( \delta^{(4)} \). These contributions turn out to depend exclusively on the variables of one of the atoms, and are multiplied in (31) by the polarizability \( \beta^{(2)} \) of the other atom. In evaluating \( \bar{\gamma}_a^{(6)} \) the average can therefore be taken over the ground states of each atom independently, which implies that the commutator contributions drop out.

Let us now first evaluate the averaged polarizability \( \bar{\alpha} \) with the help of (27)–(31). The tensors \( \beta^{(2)} \) and \( \beta^{(4)} \) follow from the part of the effective-hamiltonian matrix \( V_{\alpha_0 \beta_0, \alpha_0' \beta_0'} \) that is quadratic in \( E_e \) and at most of order \( \epsilon^4 \). It may be evaluated along similar lines as in § 2, with the result

\[
[V_{\alpha_0}]_{\alpha_0 \beta_0, \alpha_0' \beta_0'} = -\sum \kappa_a^{-1} d_{\alpha \alpha_0} \cdot E_e d_{\alpha \alpha_0'} \cdot E_e \delta_{\beta_0, \beta_0'} + (a \leftrightarrow b), \quad (32)
\]

\[
[V_{\gamma_0}]_{\alpha_0 \beta_0, \alpha_0' \beta_0'} = \sum \kappa_a^{-1} \kappa_\beta^{-1} E_e \cdot (d_{\alpha \alpha_0} d_{\alpha \alpha_0'} + d_{\alpha \alpha_0} d_{\alpha \alpha_0'}) \cdot T_{ab} \cdot (d_{\beta \beta_0} d_{\beta \beta_0'} + d_{\beta \beta_0'} d_{\beta \beta_0}) \cdot E_e. \quad (33)
\]

The susceptibilities \( \beta^{(2)}_a \) and \( \beta^{(4)}_a \) of atom \( a \) are obtained from these expressions by differentiation with respect to the external fields \( E_e \) that are contracted to the dipole matrix elements of that atom. When the ensuing formulae are inserted into (27), (28) and the invariant \( D^{(2)} \) is introduced by means of (B 2), the averaged
polarizabilities $\tilde{\alpha}_n^{(2)}$ and $\tilde{\alpha}_n^{(4)}$ are found as

$$\tilde{\alpha}_n^{(2)} = \alpha_0 U,$$

$$\tilde{\alpha}_n^{(4)} = 0,$$

with $\alpha_0$ the free polarizability (B 3). The expression (29) yields upon introduction of $D^{(4)}$ (B 5)

$$\tilde{\alpha}_n^{(6)} = \tilde{\beta}_n^{(6)} - \sum_{\alpha', \beta} \delta_{k_{\alpha'}, 0} k_{\alpha'}^{-1} k_{\beta}^{-1} [U(\nabla \cdot \nabla')^2(D_{aII}^{(4)} + D_{aIII}^{(4)})$$

$$+ \nabla \nabla' \nabla' (2D_{aI}^{(4)} + D_{aII}^{(4)} + D_{aIII}^{(4)})]D_{b}^{(2)} \frac{1}{4\pi^2 RR'}.$$

(36)

The averaged tensor $\tilde{\beta}_n^{(6)}$ in (36) follows by differentiation from the sixth order two-photon-exchange energy $\Delta E_2^{(6)}$ given in (16) with (17)–(19). Upon substitution it turns out that the terms with $(RR')^{-1}$ given explicitly in (36) are exactly cancelled by the static terms in $\tilde{\beta}_n^{(6)}$ that have been discussed at the end of § 3. As a consequence the polarizability tensor $\tilde{\alpha}_n^{(6)}$ has a form slightly different from that for $\tilde{\beta}_n^{(6)}$

$$\tilde{\alpha}_n^{(6)}(R) = 2(\nabla \nabla - U\Delta) \cdot (\nabla' \nabla' - U\Delta') U \sum_{\alpha', \beta} (D_{aI}^{(4)}G^{(4)}_{11} + (D_{aII}^{(4)}G^{(4)}_{II}$$

$$+ (D_{aIII}^{(4)}G^{(4)}_{III}D_{b}^{(2)} + 2(\nabla \nabla - U\Delta) \cdot (\nabla' \nabla - U\Delta') \sum_{\alpha', \beta}$$

$$\times [(D_{aII}^{(4)} + (D_{aIII}^{(4)}G^{(4)}_{11} + (D_{aII}^{(4)} + D_{aI}^{(4)})G^{(4)}_{II}$$

$$+ (D_{aI}^{(4)} + D_{aIII}^{(4)})G^{(4)}_{III}D_{b}^{(2)}].$$

(37)

The radial functions $G'_{i}$ are obtained from $G_{i}$ by suppression of the $k_{\alpha'} = 0$ contributions in the terms with $g_{\alpha' \beta'}$; in the expressions (17)–(19) this amounts to the replacement

$$g_{\alpha' \beta} \rightarrow (1 - \delta_{k_{\alpha'}, 0}) g_{\alpha' \beta}.$$

(38)

The results (34), (35) and (37) give the first few terms of the expansion of the atomic polarizability in powers of $e^2$. In fourth order the polarizability is not influenced by the interatomic interaction, as was already known for the case of electrostatic interactions [1]. A change in the atomic polarizability due to the interaction with a neighbouring atom is found only if at least sixth order perturbation theory is employed. Before discussing in detail this pair polarizability we want to study first the hyperpolarizability $\gamma$, which is connected to the processes of fourth order in the external field $E_e$. The leading terms in powers of $e$ have been written in (30) and (31).

The part $V_{\theta}^{(4)}$ of the effective hamiltonian that is of fourth order in both $E_e$ and $e$ may be evaluated by employing the same methods as used in § 2; the result is

$$[V_{\theta}^{(4)}]_{\alpha \beta \alpha' \beta'} = - \sum_{\alpha', \beta'} \left[ (1 - \delta_{k_{\alpha'}, 0}) k_{\alpha'}^{-1} + \delta_{k_{\alpha'}, 0} \frac{\partial}{\partial k_{\alpha}} \right] k_{\beta}^{-1} k_{\alpha'}^{-1}$$

$$\times d_{\alpha \beta} \cdot E_e d_{\alpha' \beta'} \cdot E_e d_{\alpha' \beta} \cdot E_e d_{\alpha' \beta} \cdot E_e \delta_{\beta \beta} + (a \leftrightarrow b).$$

(39)
As discussed before the contribution of $\delta_a^{(4)}$ that is associated to the commutator term in (24) drops out; hence the non-linear susceptibility is obtained by differentiating of (39) with respect to the fields $E_{i\alpha}$ contracted with dipole matrix elements of atom $a$. The expression for $\delta_a^{(4)}$ found in this way is independent of the variables of atom $b$ so that upon averaging (30) and (31) only the average $\bar{\delta}_a^{(4)}$ of $\delta^{(4)}$ plays a role. This average follows directly from (39). Upon introduction of the invariants $D^{(4)}$ (B 5) one recovers for $\delta_a^{(4)} = \bar{\delta}_a^{(4)}$ the diagonal form

$$\bar{\delta}_a^{(4)} = \gamma_0 U^{(4)}$$

with $\gamma_0$ the scalar hyperpolarizability (B 7) and $U^{(4)}$ the fourth-rank unit tensor (B 6).

The sixth order average hyperpolarizability $\bar{\gamma}_a^{(6)}$ follows by inserting into (31) the expressions for $\bar{\beta}^{(2)}$, $\delta^{(4)}$ and for $\delta^{(6)}$. The former have been derived already, while the latter is found by differentiating $\Delta E_{1\gamma}^{(6)}$ (7) with respect to the external fields $E_{i\alpha}$ that in the underlying Feynman diagrams are connected to atom $a$. The result for $\delta_a^{(6)}$ is

$$[\delta_a^{(6)}]_{ijk} = \frac{1}{4\pi R} \left[ \gamma_{0a} \gamma_{0b} (\delta_{ij} \nabla_k + \delta_{ik} \nabla_j + \delta_{jk} \nabla_i) + \frac{1}{2} \left( \gamma_{0a} \gamma_{0b} + \alpha_{0a} \gamma_{0b} \right) \gamma_{0a} \gamma_{0b} \right] \frac{1}{4\pi R}.$$ (41)

In (31) all these terms are precisely cancelled by the terms containing $T_{ab}$, so that one ends up with the identity

$$\bar{\gamma}_a^{(6)} = 0.$$ (42)

Hence we conclude that sixth order perturbation theory is not enough to detect effects of the interatomic interaction on the hyperpolarizability. This conclusion is analogous to that reached for the case of the polarizability, where we found $\bar{\alpha}_a^{(4)} = 0$; two-photon-exchange processes had to be included in order to obtain a non-vanishing pair polarizability. Similarly one expects a non-vanishing pair hyperpolarizability if two-photon-exchange processes of eighth order are evaluated. Such a calculation will not be undertaken here.

The pair polarizability $\bar{\alpha}_a^{(6)}$ depends on the interatomic separation through the radial functions $g_{ab}^\rho$ defined in (14). These functions, which also occur in the field-free dispersion energy, give rise to retardation effects for very large interatomic separations.

For large $R$ and $R'$ one may write $g_{ab}^\rho$ as

$$g_{ab}^\rho(R, R') = \frac{1}{8\pi^3 k_\rho R(R + R')}, \quad R, R' \gg |k_\rho|^{-1}, |k_\rho|^{-1}$$

since $P(x) = x^{-3}$ for $x \gg 1$. As a consequence the functions $G_i$ get the form

$$G_i^\rho(R, R') = \frac{4\pi^3}{2 \pi^3 R(R + R')}, \quad (i = I, II, III)$$

with the coefficients

$$c_L = \left[ (1 - \delta_{k_\rho,0}) \frac{1}{k_\rho} + \frac{1}{2} \delta_{k_\rho,0} \left( \frac{\partial^2}{\partial k_\rho^2} + \frac{\partial}{\partial k_\rho} \right) \right] \frac{1}{k_\rho |k_\rho|^2}.$$ (45)
Upon insertion of (44) into (37) the radial differentiations can be carried out straightforwardly. The averaged polarizability for large interatomic separations then becomes

\[ \bar{\alpha}_a^{(6)L}(R) = \gamma_0 \alpha_0 \left( 36U + 7 \frac{RR}{R^2} \right) \frac{1}{192 \pi^3 R^7}. \]  

(46)

So we have found that the atomic pair polarizability depends on the atomic properties through the product \( \gamma_0 \alpha_0 \) of the free atomic polarizabilities only; it falls off as an inverse seventh power of the separation \( R \) [11]. This result shows a close analogy between the asymptotic forms of the pair polarizability and the interatomic dispersion energy, since the latter is proportional to \( \alpha_0 \alpha_0 R^{-7} \) [9].

When the interatomic separation is small compared to the characteristic atomic wavelength \( |k|^{-1} \) the function \( g_{a\beta} \) may be replaced by its short-range asymptotic form

\[ g_{a\beta}(R, R') = \frac{\text{sgn} (E_a E_\beta)}{16 \pi^2 (|k_a| + |k_\beta|) RR'}, \quad R, R' \ll |k_a|^{-1}, |k_\beta|^{-1} \]

(47)

which follows by inserting in (14) \( P(x) = \pi/2 \) for \( x = 0 \). It should be borne in mind, however, that the short-range asymptotic condition \( |k| R \ll 1 \) cannot be satisfied simultaneously for all energy states occurring in the sums over \( \alpha, \alpha', \alpha'', \beta \). In fact, for the negative energy states one has \( |k| \sim 2m \) and hence \( |k| R \gg 1 \) for all \( R \) that correspond to non-overlapping atoms. As a consequence the pair polarizability for small interatomic separations will contain both limiting forms (43) and (47) of the functions \( g_{a\beta} \). Since the occurrence of negative energy intermediate states is a direct consequence of the use of a relativistic description for the electrons the short-range pair polarizability will simplify upon taking the non-relativistic limit. For the dipole matrix elements \( d_{a\alpha} \), this limit is found by performing a Foldy–Wouthuysen transformation and retaining only the leading terms in powers of \( m^{-1} \). (Actually the correct order parameter is the fine-structure constant, since one has \( p/m \sim 1/mr \sim \alpha \) and \( k/m \sim \alpha^2 \).) When these non-relativistic approximations for \( d_{a\alpha} \) are inserted in \( D^{(2)} \) and \( D^{(4)} \), the contributions of negative energy intermediate states to the pair polarizability (37) turn out to be at least a factor \( \alpha^4 \) smaller than the terms with positive energy intermediate states, so that they play no role in the non-relativistic limit. The short-range asymptotic form of the pair polarizability follows by inserting (47) in the radial functions \( G'_{i\alpha} \), which then become

\[ G'_{i\alpha} = \frac{c_{i\alpha}}{16 \pi^2 RR'} \]

(48)

with

\[ c_{i\alpha} = \left[ (1 - \delta_{k_\alpha'0}) \frac{1}{k_{\alpha'} + k_{\beta}} + \frac{1}{2} \delta_{k_\alpha'0} \left( \frac{\partial}{\partial k_x} + \frac{\partial}{\partial k_{\alpha'}} \right) \right] \left[ \frac{1}{(k_{\alpha} + k_{\beta})k_{\alpha'}} \right. 
\[ \left. \left. + \frac{1}{(k_{\alpha'} + k_{\beta})k_{\alpha}} \right] \right], \]

(49)

\[ c_{11} = (1 - \delta_{k_\alpha'0}) \frac{1}{k_{\alpha'} + k_{\beta}} \left[ \frac{1}{(k_{\alpha} + k_{\beta})k_{\alpha'}} + \frac{1}{(k_{\alpha'} + k_{\beta})k_{\alpha}} \right] - \delta_{k_\alpha'0} \frac{1}{k_{\alpha}k_{\alpha'}} \]

\[ \times \left( \frac{1}{k_{\alpha} + k_{\beta}} + \frac{1}{k_{\alpha'} + k_{\beta}} \right), \]

(50)
When the radial differentiations in (37) are performed the non-relativistic pair polarizability becomes in the short-range limit

$$
\varphi_a^{(6)}(R) = \sum_{\alpha, \beta(k > 0)} \left[ (D_{a_1}^{(4)})c_1^8 + D_{a_11}^{(4)}c_{11}^8 + D_{a_111}^{(4)}c_{111}^8 \right] D_b^{(2)} \left[ 2U + \frac{RR}{R^2} \right] \frac{1}{R^6}.
$$

This asymptotic form for the pair polarizability coincides with the result that has been found by Jansen and Mazur [1] and later by Mackrodt [10]; these authors limited themselves to the electrostatic part of the interaction diagrams and applied non-relativistic Rayleigh–Schrödinger perturbation theory.

5. CONCLUSION

In this paper we have studied the effect of an externally applied field on a pair of hydrogen atoms that interact via the quantized radiation field. This problem, which is almost forbiddingly complicated in standard non-covariant perturbation theory, could be handled by virtue of a field-theoretical method, which involves a resummation of Feynman diagrams. So the present calculation serves as a good illustration of this powerful method, which can be used quite generally. The resulting expressions for the polarizability $\alpha$ and the hyperpolarizability $\gamma$ up to sixth order in $e$ are given in (34), (35), (37) and (40), (42), respectively. It is seen that the one-photon exchange processes give no contributions to $\alpha$ and $\gamma$. In contrast, the exchange of two photons leads to a true pair polarizability that shows retardation when the interatomic separation is of the order of a characteristic atomic wavelength. In fact, the radial dependence changes from a short-range $R^{-8}$ (52) to a long-range $R^{-7}$ (46) behaviour, just as was found by Casimir and Polder for the field-free dispersion interaction.

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APPENDIX A. FEYNMAN INTEGRALS FOR THE TWO-PHOTON PROCESS

The diagrams with two-photon exchange that have been considered in the main text lead to the following Feynman integrals:

$$
I(R, R') = \frac{-i}{(2\pi)^7} \int d^4 k d^4 k' \delta(k^0 + k'^0) \exp \left( i \mathbf{k} \cdot \mathbf{R} + i \mathbf{k}' \cdot \mathbf{R}' \right)
\times \left[ \prod_{\ell=1}^n \left( E_\alpha(1 - i0) - E_{\alpha n} + \lambda_\alpha k^0 \right) \left( k'^0 - k^0 \right) \left( k'^0 - k^0 \right) \right]^{-1}
$$

(A 1)
with $\lambda_\alpha = \pm 1$ and $k = |k|$. To evaluate these integrals one starts by making an expansion in partial fractions

$$\left[ \prod_{\alpha=1}^{n} \left( E_\alpha(1-i0) - E_{\alpha_0} + \lambda_\alpha k^0 \right) \right]^{-1} = \sum_{\alpha=1}^{n} \left[ \frac{E_\alpha(1-i0) - E_{\alpha_0} + \lambda_\alpha k^0}{k_\beta - \lambda_\alpha \lambda_\beta k_\alpha} \right]^{-1}$$

(A 2)

with $k_\alpha = E_\alpha - E_{\alpha_0}$. The integral over $k^0$ in (A 1) with (A 2) may be carried out by closing the integration contour in either the upper or the lower part of the complex plane. If these contours are used in a symmetric way one gets:

$$\int dk^0 \left[ \frac{\text{sgn} (E_\alpha)}{2(k_\alpha^2 - k^2)(k_\alpha^2 - k'^2)} - \frac{1}{2k(k_\alpha - \lambda_\alpha k)(k_\alpha^2 - k'^2)} - \frac{1}{2k(k_\alpha + \lambda_\alpha k)(k_\alpha^2 - k'^2)} \right]$$

$$+ \frac{1}{2k(k_\alpha - \lambda_\alpha k)(k_\alpha^2 - k'^2)} (k\leftrightarrow k')$$

(A 3)

where $(k\leftrightarrow k')$ stands for the terms resulting from the preceding ones by an interchange of $k$ and $k'$; $k_\alpha \text{sgn} (E_\alpha)$ could be replaced by $|k_\alpha|$, since $E_{\alpha_0}$ is the lowest positive energy level.

When the trivial angular integrations in (A 1) have been performed, the term $(k-k')^{-1}$ may be used to extend the integral over $(k+k')^{-1}$ to negative values of $k'$. Complex contour integration in the $k'$ plane then yields

$$\int \frac{dk}{4\pi k} \int \frac{dk'}{4\pi k'} \exp(ik \cdot R + ik' \cdot R') \left[ \frac{1}{|k_\alpha| + k} \left( \frac{1}{k+k'} - \frac{1}{k-k'} \right) + (k\leftrightarrow k') \right]$$

$$= \pi P(|k_\alpha R + k_\alpha R'|).$$

(A 4)

Here the function $P(x)$ is defined as

$$P(x) = \int_0^\infty dt \frac{\sin t}{x+t} = \int_0^\infty dt \frac{e^{-xt}}{1+t^2} (x > 0);$$

(A 5)

it obeys the differential formulae

$$\frac{dP(x)}{dx} = -Q(x), \quad \frac{d^2 P(x)}{dx^2} = -P(x) + \frac{1}{x} (x > 0)$$

(A 6)

where $Q(x)$, on a par with $P(x)$, is given by

$$Q(x) = \int_0^\infty dt \frac{\cos t}{x+t} = \int_0^\infty dt \frac{te^{-xt}}{1+t^2} (x > 0).$$

(A 7)

The functions $P(x)$ and $Q(x)$ are related to the sine and cosine integrals [17].

Collecting the results we have found for the Feynman integrals

$$I(R, R') = \sum_{\alpha=1}^{n} \frac{\text{sgn} (E_\alpha)}{16\pi^3} \prod_{\beta(\neq \alpha)} \frac{P(|k_\alpha R + k_\alpha R'|)}{RR'}. $$

(A 8)
APPENDIX B. INVARIANCE PROPERTIES AND SUM RULES OF DIPOLE MATRIX ELEMENTS

For an atom that interacts twice with the electromagnetic field the ensuing product of dipole matrix elements \( d_{\alpha \alpha'} = -\epsilon \langle \alpha | r | \alpha' \rangle \) may be written in an invariant form as

\[
G^{-1} \sum_{\alpha_0} \sum_{a(k_0 \text{ const.})} d_{\alpha_0 a} k d_{a a_0} l = \sum_{a(k_0 \text{ const.})} D^{(2)}_{\alpha} \delta^{kl} \tag{B 1}
\]

with the abbreviation

\[
D^{(2)}_{\alpha} = \frac{1}{3} G^{-1} \sum_{\alpha_0} |d_{\alpha_0 \alpha}|^2. \tag{B 2}
\]

In particular, (B 2) occurs in the averaged polarizability tensor \( \alpha_0 U \) of a free atom, the scalar part of which reads

\[
\alpha_0 = 2 \sum_{\alpha} k_{\alpha}^{-1} D^{(2)}_{\alpha}. \tag{B 3}
\]

Similarly, the product of four dipole matrix elements can be expanded in terms of rotational invariants

\[
g^{-1} \sum_{\alpha_0} \sum_{a, a', a'', a''' (k_0, k_{a'}, k_{a''}, \text{const.})} d_{\alpha_0 a} k d_{a a'} l d_{a' a''} m d_{a'' a_0} n = \sum_{a, a', a'', a''' (k_0, k_{a'}, k_{a''}, \text{const.})} (D^{(4)}_{ai} \delta^{kl} \delta^{mn} + D^{(4)}_{ai1} \delta^{km} \delta^{ln} + D^{(4)}_{ai11} \delta^{kn} \delta^{lm}); \tag{B 4}
\]

the three invariants \( D^{(4)}_{ai} \) have the form

\[
D^{(4)}_{ai} = g^{-1} \sum_{\alpha_0} (c_{ij} \delta^{kl} \delta^{mn} + c_{i11} \delta^{km} \delta^{ln} + c_{111} \delta^{kn} \delta^{lm})
\]

\[
\times d_{\alpha_0 a} k d_{a a'} l d_{a' a''} m d_{a'' a_0} n \tag{B 5}
\]

with the coefficients \( c_{ij} = \frac{1}{6} \delta_{ij} - \frac{1}{2} \). These fourth order combinations enter in the averaged hyperpolarizability \( \gamma_0 U^{(4)} \), with \( U^{(4)} \) the fourth-rank unit tensor

\[
U_{ijkl}^{(4)} = \frac{1}{3} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \tag{B 6}
\]

and \( \gamma_0 \) the scalar hyperpolarizability

\[
\gamma_0 = 24 \sum_{a, a', a''} \left( \sum_{i=1}^{III} D^{(4)}_{ai} \right) \left[ (1 - \delta_{ka',0}) \frac{1}{k_{a'}} + \frac{1}{2} \frac{\partial}{\partial k_{a'}} \left( \frac{\partial}{\partial k_{a'}} + \frac{\partial}{\partial k_{a''}} \right) \right] \left( \frac{1}{k_{a} k_{a'}} \right). \tag{B 7}
\]

It may be remarked that for the non-relativistic hydrogen atom both the polarizability and the hyperpolarizability are known exactly [18, 19].

Both \( D^{(2)}_{\alpha} \) and \( D^{(4)}_{ai} \), as defined in (B 2) and (B 5), satisfy sum rules. Some of these may be derived from the double-commutator identity \([\left[H_{at}, r\right], r] = 0\), with \( H_{at} \) the atomic Dirac hamiltonian. Upon taking the matrix elements of this double commutator between \( \langle \alpha | \) and \( | \alpha' \rangle \) and inserting a complete set of states \( | \alpha' \rangle \) one finds

\[
\sum_{a'} (k_{a} + k_{a'} - 2k_{a'} \cdot d_{a'' a} \cdot d_{a' a'} = 0. \tag{B 8}
\]

From this relation one immediately obtains the sum rules

\[
\sum_{\alpha} k_{\alpha} D^{(2)}_{\alpha} = 0. \tag{B 9}
\]
Interacting atoms in an external field

\[ \sum_a (2k_a - k_{a'}) D_{ai}^{(4)} = \sum_{a'} (2k_{a'} - k_a - k_{a''}) D_{ai}^{(4)} = \sum_{a'} (2k_{a''} - k_a') D_{ai}^{(4)} = 0. \] (B 10)

A different type of sum rule for \( D_{ai}^{(4)} \) follows from the commutator identity 
\[ [r, r'] = 0, \] 
\[ \sum_{a} (D_{a11}^{(4)} - D_{a111}^{(4)}) = \sum_{a'} (D_{a1}^{(4)} - D_{a11}^{(4)}) = \sum_{a'} (D_{a11}^{(4)} - D_{a111}^{(4)}) = 0. \] (B 11)

The spherical tensor formalism may be employed to derive general expressions for \( D_a^{(2)} \) and \( D_a^{(4)} \) in terms of the reduced matrix elements \( d_{j',j} \) of the dipole moment. For the relativistic hydrogen atom the ground states have \( J_0 = \frac{1}{2} \); if the intermediate state \( |\alpha'\rangle \) is chosen to be one of the ground states one can prove from rotational invariance the identity
\[ \sum_{a, \alpha, \alpha'} \delta_{k_a, \alpha, \alpha'} [D_{a11}^{(4)} + D_{a111}^{(4)}] = 0. \] (B 12)

This relation has been used in [11] to give a different form for the asymptotic long-range pair polarizability (46) with (B 2) and (B 7).

References