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Phys. Rev. Lett. 118, 123001 — Published 20 March 2017
DOI: 10.1103/PhysRevLett.118.123001
Virtual Resonant Emission and Oscillatory Long–Range Tails in van der Waals Interactions of Excited States: QED Treatment and Applications

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We report on a quantum electrodynamics (QED) investigation of the interaction between a ground state atom with another atom in an excited state. General expressions, applicable to any atom, are indicated for the long-range tails which are due to virtual resonant emission and absorption into and from vacuum modes whose frequency equals the transition frequency to available lower-lying atomic states. For identical atoms, one of which is in an excited state, we also discuss the mixing term which depends on the symmetry of the two-atom wave function (these evolve into either the gerade or the ungerade state for close approach), and we include all nonresonant states in our rigorous QED treatment. In order to illustrate the findings, we analyze the fine-structure resolved van der Waals interaction for \( nD–1S \) hydrogen interactions with \( n = 8, 10, 12 \) and find surprisingly large numerical coefficients.

PACS numbers: 31.30.jh,12.20.Ds,31.15.-p,34.20.Cf

Introduction.—While the long-range interaction between two ground state atoms has been fully understood in all interatomic separation regimes since the work of Casimir and Polder [1], a completely new situation arises when one of the atoms is in an excited state [2–7]. In particular, several recent studies [8–12] have reported when one of the atoms is in an excited state [2–7]. In this case, one has to treat a mixing term [2], which describes a scattering process in which the state \( |\psi_A,\psi_B\rangle \) is scattered into the state \( |\psi_B,\psi_A\rangle \); the two atoms in this case “interchange” their quantum states. The eigenstates of the van der Waals Hamiltonian [2] are states of the form \((1/\sqrt{2})\ (|\psi_A,\psi_B\rangle \pm |\psi_B,\psi_A\rangle)\), and the interaction energy \(\Delta E\) is the sum of a direct term (which is contained in the canonical derivations, e.g., Ref. [18]), and a mixing term, which is added here and whose sign depends on the symmetry of the two-atom state (±). We find the following general expression (further details can be found in the supplementary material, Ref. [19]), including retardation, for the electrodynamical interaction between two atoms \(A\) and \(B\) in arbitrary states,

\[
\Delta E = \frac{i}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \tilde{R}) D_{kl}(\omega, \tilde{R}) \times \left[ \alpha_{A,ik}(\omega) \alpha_{B,ij}(\omega) \pm \alpha_{A,ik}(\omega) \alpha_{B,ij}(\omega) \right],
\]

where the last term describes the mixing and is present only for identical atoms. The photon propagator (in the
temporal gauge) and the tensor polarizabilities are given by

\[ D_{ij}(\omega, \vec{R}) = \frac{\hbar}{4\pi\epsilon_0 c^2} \left[ \alpha_{ij} + \beta_{ij} f(\omega, \vec{R}) \right] \frac{1}{\omega^2 + i\epsilon} R, \] (3a)

\[ \alpha_{A,ij}(\omega) = \sum_v \left( \frac{\langle \psi_A | d_{Ai} | v_A \rangle \langle v_A | d_{Aj} | \psi_A \rangle}{E_{v,A} - \hbar\omega - i\epsilon} + \frac{\langle \psi_A | d_{Ai} | v_A \rangle \langle v_A | d_{Aj} | \psi_A \rangle}{E_{v,A} + \hbar\omega - i\epsilon} \right), \] (3b)

\[ \alpha_{AB,ij}(\omega) = \sum_v \left( \frac{\langle \psi_A | d_{Ai} | v_A \rangle \langle v_B | d_{Bj} | \psi_B \rangle}{E_{v,A} - \hbar\omega - i\epsilon} + \frac{\langle \psi_A | d_{Ai} | v_A \rangle \langle v_B | d_{Bj} | \psi_B \rangle}{E_{v,A} + \hbar\omega - i\epsilon} \right). \] (3c)

Here, \( f(\omega, R) = \frac{e^2}{\hbar c R} - \frac{\epsilon_0 R^2}{2\pi^2}, \) and the tensor structures are \( \alpha_{ij} = \delta_{ij} - \frac{\beta_{ij}}{R^2} \) and \( \beta_{ij} = \delta_{ij} - 3\frac{R_i R_j}{R^4}. \) The speed of light is \( c, \) and \( \epsilon_0 \) is the vacuum permittivity. The (excited) state of atom \( A \) is \( |\psi_A\rangle, \) and \( d_A \) is the electric dipole operator for the same atom. We also write \( E_{v,A} \equiv E_v - E_A \) and \( E_{v,B} \equiv E_v - E_B. \) As usual, the dipole polarizability is given by a sum over all virtual states of atom \( A \) which are accessible from \( |\psi_A\rangle \) through an electric dipole transition. The tensor polarizability \( \alpha_{AB,ij}(\omega) \) is obtained from \( \alpha_{AB,ij}(\omega) \) by a replacement \( E_{v,A} \rightarrow E_{v,B} \) in the propagator denominators. For excited reference states, it is crucial that the polarizabilities (3b) and (3c) have the poles placed according to the Feynman prescription; this follows from the time-ordered dipole operators which naturally occur in time-ordered products of the interaction Hamiltonian which enter the S matrix.

If atom \( A \) is in an excited state and \( B \) in the ground state, then the interaction energy \( \Delta E = Q + W \) [see (2)] can be split into a Wick-rotated term \( \omega \rightarrow i\omega \)

\[ W = -\frac{1}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{kl}(\omega, \vec{R}) \]

\[ \times \left[ \alpha_{A,ik}(i\omega) \alpha_{B,j\ell}(i\omega) + \alpha_{A,B,ik}(i\omega) \alpha_{A,B,j\ell}(i\omega) \right], \]

and a pole term from the residues at \( \omega = -E_{m,A}/\hbar + i\epsilon, \)

\[ Q = \sum_{E_{m,A} c < 0} \frac{\langle \psi_A | d_{Ai} | m_A \rangle}{(4\pi\epsilon_0)^2 R^6} \left[ \langle m_A | d_{Ak} | \psi_A \rangle \alpha_{B,j\ell} \left( \frac{E_{m,A}}{\hbar} \right) \pm \langle m_A | d_{Bk} | \psi_B \rangle \alpha_{A,B,j\ell} \left( \frac{E_{m,A}}{\hbar} \right) \right] f_{ij\ell k}(r_{m,A}), \] (5a)

\[ f_{ij\ell k}(r) = -\exp(-2ir) \left[ \beta_{ij} \beta_{kl} (1 + 2i r) - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) r^2 - 2i \alpha_{ij} \beta_{kl} r^3 + \alpha_{ij} \alpha_{kl} r^4 \right], \] (5b)

\[ \text{Re} f_{ij\ell k}(r) = -\cos(2r) \left[ \beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) r^2 + \alpha_{ij} \alpha_{kl} r^4 \right] - 2r \sin(r) \left[ \beta_{ij} \beta_{kl} - \alpha_{ij} \beta_{kl} r^2 \right], \] (5c)

\[ \text{Im} f_{ij\ell k}(r) = -\frac{1}{2} \left[ -2 \sin(2r) \left[ \beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) r^2 + \alpha_{ij} \alpha_{kl} r^4 \right] + 4r \cos(r) \left[ \beta_{ij} \beta_{kl} - \alpha_{ij} \beta_{kl} r^2 \right] \right], \] (5d)

where

\[ r_{m,A} = \frac{E_{m,A} R}{\hbar c}, \quad E_{m,A} \equiv E_{m_A} - E_A. \] (6)

Here, the sum is taken over all states \( m \) that are accessible from \( |\psi_A\rangle \) by a dipole transition and of lower energy than \( |\psi_A\rangle. \) For a general atom, the generalization is trivial: one simply sums the dipole operators of atom \( A \) over the electrons.

The pole term induces both a real, oscillatory, distance-dependent energy shift as well as a correction to the width of the excited state,

\[ Q = P - \frac{i}{2} \Gamma, \] (7)

where \( \Gamma \) is obtained from Eq. (5a) by substituting for \( f_{ij\ell k}(r) \) the expression in curly brackets in Eq. (5d).

From a QED point of view, the real part of the energy shift corresponding to the pole term is due to a very peculiar process, namely, resonant virtual emission into vacuum modes whose angular frequency matches the resonance condition \( \omega = -E_{m,A} = |E_{m,A}|. \) The resonant emission is accompanied by resonant absorption, and therefore leads to a real rather than imaginary energy shift. In the ladder and crossed-ladder Feynman diagrams (see Fig. 1), the virtual electron line of atom

\[ \cdots \]

| \[|\psi_A\rangle \] | \[|m_A\rangle \] | \[|\psi_A\rangle \]
|---|---|---|
| \[|\psi_n\rangle \] | \[|m_A\rangle \] | \[|\psi_n\rangle \]
| \[|\psi_n\rangle \] | \[|m_A\rangle \] | \[|\psi_n\rangle \]
A, in state $|\psi_A\rangle$, would turn into a resonant lower-lying virtual state, whereas the ground-state atom line is excited into a “normal” energetically higher virtual state $|v_B\rangle$. The imaginary part of the pole term describes a process where the virtual photon becomes real and is emitted by the atom, in analogy to the imaginary part of the self energy [20, 21]. Feynman propagators allow us to reduce the calculation to only two Feynman diagrams, which capture all possible time orderings (in contrast to time-ordered perturbation theory).

In Ref. [11], a situation of two non-identical atoms is considered, with mutually close resonance energies $\hbar \omega_A$ and $\hbar \omega_B$. Setting $E_{m,A} = -\hbar \omega_A$ and $E_{q,B} = \hbar \omega_B$, the authors of Ref. [11] assume that $\omega_A \approx \omega_B$, and define $\Delta_{AB} = \hbar \omega_A - \hbar \omega_B$ with $|\Delta_{AB}| \ll \hbar \omega_A, \hbar \omega_B$. Furthermore, they restrict the sum over virtual states in Eq. (5) to the resonant state only, and they only keep the term $1/(E_{m,A} + E_{q,B})$ in the sum over states, in the polarization $\alpha(B(E_{m,A}/\hbar))$ [see Eq. (5)]. Under their assumptions [see Eq. (4) of Ref. [11]], $|1/(E_{m,A} + E_{q,B})| = \left| -1/\Delta_{AB} \right| \gg \left| 1/(E_{q,B} - E_{m,A}) \right| \approx \sqrt{2}\hbar \omega_B$.

Under the restriction to the resonant virtual states, the direct term in Eq. (5) [proportional to $\alpha_{B,j\ell}(E_{m,A}/\hbar)$] matches that reported in Ref. [11] if we average the latter over the interaction time $T > 2R/c$. Our result adds the contribution from nonresonant virtual states, which allow us to match the result with the close-range (van der Waals) limit, as well as the mixing term [proportional to $\alpha_{AB,j\ell}(E_{m,A}/\hbar)$] and the imaginary part of the energy shift (width term). For the mixing term to be nonzero, we need the orbital angular momentum quantum numbers to fulfill the relation $\ell_A = \ell_B$ or $|\ell_A - \ell_B| = 2$, by virtue of the usual selection rules of atomic physics. Furthermore, we find that the full consideration of the Wick-rotated term and the pole term is crucial for obtaining numerically correct results for the interaction energies, for surprisingly large interatomic distances.

**Numerical Calculations.**—In the following, we aim to apply the developed formalism to $nD$–$1S$ atomic hydrogen systems. The interaction energy depends both on the spin orientation of the electron (total angular momentum $J$) as well as its projection $\mu$ onto the quantization axis [19]. One may eliminate this dependence by evaluating the average over the fine-structure resolved states.

**Short Range.**—For interatomic separations in the range $a_0 \ll R \ll a_0/\alpha$ (where $a_0$ is the Bohr radius), the interaction energy (2) is well approximated

$$\Delta E \approx \Delta E_{\text{vdW}} \text{ where}$$

$$\Delta E_{\text{vdW}} = -\frac{1}{(4\pi\epsilon_0)^2} \frac{\beta_{kj} \beta_{kt}}{R^6} \sum_v \sum_q \frac{1}{E_{v,A} + E_{q,B}}$$

$$\times \left[ |\psi_A \rangle \langle d_{A|i} | v_A \rangle \langle v_A | d_{A|k} | \psi_A \rangle \times \langle v_B \rangle | d_{B|j} \rangle \langle q_B | d_{B|t} \rangle | \psi_B \rangle$$

$$\pm \langle v_A \rangle | d_{A|i} \rangle \langle v_B \rangle | d_{B|j} \rangle \langle q_B | d_{B|t} \rangle | \psi_B \rangle$$

$$\times \langle v_B \rangle | d_{B|j} \rangle \langle q_B | d_{A|i} \rangle | \psi_A \rangle \right],$$

**TABLE I.** Van der Waals $D_6$ (direct) coefficients, for $nD$–$1S$ interactions, averaged over the total angular momenta and magnetic projections of the excited D state. The coefficients are given in units of $\hbar E_h^6$.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Virtual $P$</th>
<th>Virtual $F$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle D_6(8D;1S) \rangle$</td>
<td>17459.439</td>
<td>26156.866</td>
<td>43616.296</td>
</tr>
<tr>
<td>$\langle D_6(10D;1S) \rangle$</td>
<td>43476.563</td>
<td>65182.580</td>
<td>108659.144</td>
</tr>
<tr>
<td>$\langle D_6(12D;1S) \rangle$</td>
<td>91115.328</td>
<td>136640.733</td>
<td>227756.061</td>
</tr>
</tbody>
</table>

where $D_6$ is the direct, and $M_6$ is the mixing van der Waals coefficient [2–7]. For energetically lower states in atom $A$ (with $E_{v,A} = E_{m,A} < 0$), the representation (8) is obtained by carefully considering the contributions from the Wick-rotated term $\mathcal{W}$ and the pole term $\mathcal{P}$.

For the fine-structure average of the direct term $D_6$, we have

$$\langle D_6(nD;1S) \rangle = \langle D_6^{(P)}(nD;1S) \rangle + \langle D_6^{(F)}(nD;1S) \rangle ,$$

where the virtual-$P$-state contribution ($\langle D_6^{(P)}(nD;1S) \rangle$) and the virtual-$F$-state contribution ($\langle D_6^{(F)}(nD;1S) \rangle$) are given in Table I. Numerically, we find that the mixing term $M_6$ is smaller than the direct term $D_6$, by at least four orders of magnitude, for all fine-structure resolved $nD$ states, for all distance ranges investigated in this Letter. This trend follows the pattern observed for the van der Waals coefficients (Table I) and is in contrast to the $2S$–$1S$ system, where both terms are of comparable magnitude [2, 4].

**Long Range.**—One might think that the $1/R^2$ pole term from Eq. (5) should easily dominate the interaction energy in the range $R \gg a_0/\alpha$. Indeed, power counting in the fine-structure constant $\alpha$, according to Ref. [22], shows that the cosine and sine terms in $\mathcal{P}$ are asymptotically given by

$$\frac{\mathcal{P}_{\text{cos}}}{\hbar E_h} \sim \left\{ \frac{\alpha^4}{\rho^2} \cos(\alpha \rho), \frac{\alpha^2}{\rho^4} \cos(\alpha \rho), \frac{1}{\rho^6} \cos(\alpha \rho) \right\} ,$$

$$\frac{\mathcal{P}_{\text{sin}}}{\hbar E_h} \sim \left\{ \frac{\alpha^3}{\rho^3} \sin(\alpha \rho), \frac{\alpha}{\rho^5} \sin(\alpha \rho) \right\} ,$$

where $\rho = R/a_0$ and $E_h$ is the Hartree energy. A comparison to the van der Waals term, given in Eq. (8), and the Wick-rotated term (4),

$$\Delta E_{\text{vdW}} \approx \frac{E_h}{\rho^6}, \quad W_{\rho \gg 1/\alpha} \sim \frac{\hbar E_h}{\alpha \rho^7} ,$$

(10c)
1 GHz (see Ref. [4]), the Wick-rotated contribution attains the familiar $1/R^7$ asymptotics from the Casimir–Polder formalism [1],

$$\mathcal{W}^{(\text{dir})} R \to \infty = -\frac{hc \alpha_{nD,ij}(0) \alpha_{1S}(0)}{8\pi} \left( 13 \delta_{ij} + 15 \frac{R_R}{R^2} \right).$$

(11)

This tail is parametrically suppressed in comparison to the leading $1/R^2$ pole contribution,

$$\mathcal{P}^{(\text{dir})} R \to \infty = -\sum_{E_m < E_{nD}} \left( \frac{E_m}{hc} \right)^4 \cos \left( \frac{2 E_m A}{hc} R \right) \left( \frac{2}{4\pi \alpha_e^2 R^2} \right) \times \alpha_{ij} \langle nD | d_{Ai} | m_A \rangle \langle m_A | d_{Aj} | nD \rangle \alpha_{1S} \left( \frac{E_m A}{\hbar} \right).$$

(12)

In the intermediate range $a_0 \ll R \ll hc/L$, the Wick-rotated contribution has a nonretarded $1/R^6$ tail, due to a nonretarded contribution from virtual $nP$ and $nF$ states which are displaced from the $nD$ state only by the Lamb shift [see Eqs. (23) and (24) of Ref. [4]],

$$\mathcal{W}^{(\text{dir})} \sim -\frac{\overline{D}_6(nD; 1S)}{R^6}, \quad \frac{a_0}{\alpha} \ll R \ll \frac{hc}{L}. \quad (13)$$

The fine-structure average of $\overline{D}_6(nD; 1S)$ is given by [19]

$$\langle \overline{D}_6(nD; 1S) \rangle = \frac{81}{8} n^2 (n^2 - 7). \quad (14)$$

For the mixing term, simplifications are scarce; the leading long-range asymptotics of the Wick-rotated term read

$$\mathcal{W}^{(\text{mix})} R \to \infty = -\frac{hc \alpha_{nD,1S,ik}(0) \alpha_{nD,1S,jf}(0)}{8\pi} \left( \frac{4\pi \alpha_e^2}{(4\pi \alpha_e^2 R^2) \times \alpha_{ij} \alpha_{kl} \alpha_{nD,1S,jf} \left( \frac{E_m A}{\hbar} \right) \times \langle nD | d_{Ai} | m_A \rangle \langle m_A | d_{Aj} | nD \rangle \alpha_{1S} \left( \frac{E_m A}{\hbar} \right) \right).$$

(15)

The leading pole contribution (in the long range) is given by a sum over virtual $P$ states which enter the mixed polarizability $\alpha_{nD,1S,jf}$,

$$\mathcal{P}^{(\text{mix})} R \to \infty = -\sum_{E_m < E_{nD}} \frac{E_m A}{\hbar} \left( \frac{4\pi \alpha_e^2}{(4\pi \alpha_e^2 R^2) \times \alpha_{ij} \alpha_{kl} \alpha_{nD,1S,jf} \left( \frac{E_m A}{\hbar} \right) \times \langle nD | d_{Ai} | m_A \rangle \langle m_A | d_{Aj} | nD \rangle \alpha_{1S} \left( \frac{E_m A}{\hbar} \right) \right).$$

(16)

In the intermediate range, one has

$$\mathcal{W}^{(\text{mix})} \sim -\frac{\overline{M}_6(nD; 1S)}{R^6}, \quad \frac{a_0}{\alpha} \ll R \ll \frac{hc}{L}, \quad (17)$$

where $\overline{M}_6(nD; 1S)$ is the generalization of $\overline{D}_6$ to the mixing term [see Ref. [19] and Eq. (67) of Ref. [4]].

In Fig. 2, we compare the magnitude of the Wick-rotated term and the pole term in the intermediate range.
multiplying the parametric estimates gives in Eq. (10).

Conclusions.—We have shown that the consistent use of Feynman propagators and the concomitant virtual photon integration contours lead to the prediction of long-range tails for excited-state van der Waals interactions. Pole terms are picked up for virtual states $|v_A\rangle = |m_A\rangle$ of lower energy than the reference state of the excited atom $A$. The pole contribution $Q$ to the energy shift is complex rather than real (includes a width term $\Gamma = -2\text{Im}(Q)$), is spacewise-oscillating and in the long-range, behaves as $\cos[2(E_m - E_A) R/(\hbar c)]/R^2$, where $E_A$ is the reference state energy and $E_m < E_A$ is of the low-energy virtual state. For excited states, both the direct as well as the exchange (gerade-ungerade mixing) term can be expressed as a sum of a Wick-rotated contribution [Eq. (4)], and a pole term [Eq. (5)]. Our inclusion of the nonresonant terms in the interaction energy enables us to match the very-long-range, oscillatory result against the well-known close-range, nonretarded van der Waals limit, and to carry out numerical calculations in the intermediate region. We also include the width term, and the gerade-ungerade mixing term which pertains to excited-state interactions of identical atoms.

For $nD–1S$ interactions, we have shown that despite parametric suppression, the Wick-rotated term, which is non-oscillatory and contains the non-resonant states, still dominates in the intermediate distance range $a_0/\alpha \lesssim R \ll \hbar c/L$ (see Fig. 2). The very-long-range, oscillatory tail of the van der Waals interaction is relevant only for very large interatomic distances. This conclusion holds for $nD–1S$ interactions as well as $nS–1S$ systems [19, 23]. The reason for the suppression is that the numerical coefficients which multiply the parametric estimates given in Eq. (10) drastically depend on the particular term in the van der Waals energy. This is in part due to the scaling of the coefficients with the principal quantum number. E.g., for $nD–1S$ interactions, the $1/R^2$ leading oscillatory tail from Eq. (5) is of order $E_n\alpha^4 \cos(\alpha \rho)/\rho^5$, yet multiplied by numerical coefficients of order $10^{-6}$ [in addition to the factor $\alpha^4$; see the supplementary material [19], Eq. (14), Table I and Fig. 2]. By contrast, the non-oscillatory terms of order $E_n/\rho^6$ are multiplied by coefficients of order $10^4 \ldots 10^6$. This behavior of the coefficients changes any predictions based on the parametric estimates given in Eq. (10) by ten orders of magnitude as compared to a situation with coefficients of order unity.

Our results are important for an improved analysis of pressure shifts, and fluctuating-dipole-induced energy shift, for atomic beam spectroscopy with Rydberg states, where these effects have been identified as notoriously problematic in recent years (see pp. 134 and 151 of Ref. [17]). An improved determination of the Rydberg constant based on Rydberg-state spectroscopy could resolve the muonic hydrogen proton radius puzzle, because the smaller proton radius measured in Ref. [24, 25] leads to a Rydberg constant which is discrepant with regard to the current CODATA value [24, 26].

Acknowledgments.—This research has been supported by the NSF (grant PHY–1403937).


