Long-range tails in van der Waals interactions of excited-state and ground-state atoms

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A quantum electrodynamic calculation of the interaction of an excited-state atom with a ground-state atom is performed. For an excited reference state and a lower-lying virtual state, the contribution to the interaction energy naturally splits into a pole term and a Wick-rotated term. The pole term is shown to dominate in the long-range limit, altering the functional form of the interaction from the retarded $1/R^7$ Casimir-Polder form to a long-range tail—provided by the Wick-rotated term—proportional to $\cos[2(E_m - E_n)\,R/(\hbar c)]/R^2$, where $E_m < E_n$ is the energy of a virtual state, lower than the reference-state energy E_n, and R is the interatomic separation. General expressions are obtained which can be applied to atomic reference states of arbitrary angular symmetry. Careful treatment of the pole terms in the Feynman prescription for the atomic polarizability is found to be crucial in obtaining correct results.

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I. INTRODUCTION

Recently, the long-range tails of the interaction between an excited-state and a ground-state atom [1–5], as well as those of the interaction between an excited $2S$ state and a conducting wall [6], have received considerable attention. The question behind the investigation concerns the existence of long-range tails for excited reference states, for which partially conflicting results have been obtained in the past [7–9].

In this article, we reconsider the derivation of the long-range interaction, with particular emphasis on the interaction of an excited-state atom with another ground-state atom, their separation being large compared to the Bohr radius. We follow a method that deduces the long-range interaction from the scattering amplitude (see Chap. 85 of Ref. [10]). This method requires the use of the Feynman prescription for the Green functions of the photon field and the time-ordered product of atomic dipole operators.

We also aim to generalize the recent treatments in Refs. [1] and [2] to reference states of arbitrary symmetry and to clarify the role of the virtual-state energy in the calculation of the final expressions, without any approximations. In our formalism, we aim to calculate the long-range tails of the van der Waals and Casimir-Polder energy shifts on the basis of a unified formalism, which can be applied to both ground-state and excited-state interactions with an atomic state of arbitrary symmetry. The general idea is to use the matching of the forward scattering amplitude from quantum electrodynamics (QED) against the effective potential that describes the long-range interaction.

The paper is organized as follows. In Sec. II, we reconsider the derivation of the van der Waals and Casimir-Polder interaction from first principles, using the matching of the S-matrix element with the effective interaction potential. Applications are discussed in Sec. III. First, in order to check our results and connect them to the literature, we rederive the familiar form of the ground-state interaction in Sec. III A and verify the van der Waals close-range limit in Sec. III B. General excited states are treated in Sec. III C, and the expressions are specialized to excited S states in Sec. III D. Finally, conclusions are reserved for Sec. IV.

II. DERIVATION

A. S-matrix and matching with effective interaction

We consider two atoms in states $\psi_A(\vec{r}_A)$ and $\psi_B(\vec{r}_B)$ which scatter into states $\psi'_A(\vec{r}_A)$ and $\psi'_B(\vec{r}_B)$ under the action of a potential $U(\vec{r}_A,\vec{r}_B,\vec{R})$. Here, the absolute electron coordinates are $\vec{x}_A$ and $\vec{x}_B$; the relative coordinates are $\vec{r}_A = \vec{x}_A - \vec{R}_A$ and $\vec{r}_B = \vec{x}_B - \vec{R}_B$, where $\vec{R}_A$ and $\vec{R}_B$ are the coordinates of the nuclei. Their distance is $\vec{R} \equiv \vec{R}_A - \vec{R}_B$. We denote the initial state i (atoms are in states ψ_A and ψ_B, respectively) and the final state by the subscript f (atoms are in states ψ'_A and ψ'_B). The corresponding S-matrix element reads as [11]

$$\begin{aligned} S_{A'B'AB} &= -\frac{i}{\hbar} \int d^3r_A \int d^3r_B \; \psi'^*_A(\vec{r}_A)\, \psi'^*_B(\vec{r}_B) \\ &\quad \times U(\vec{r}_A,\vec{r}_B,\vec{R})\, \psi_A(\vec{r}_A)\, \psi_B(\vec{r}_B) \\ &\quad \times \int dt \, \exp\left[-\frac{i}{\hbar}\,(E_1 + E_2 - E'_1 - E'_2)\,t\right] \qquad (1) \\ &= -\frac{i}{\hbar}\,T \int d^3r_A \int d^3r_B \; \psi'^*_A(\vec{r}_A)\, \psi'^*_B(\vec{r}_B) \\ &\quad \times U(\vec{r}_A,\vec{r}_B,\vec{R})\, \psi_A(\vec{r}_A)\, \psi_B(\vec{r}_B), \qquad (2) \end{aligned}$$

where we have assumed energy conservation ($E_1 + E_2 = E'_1 + E'_2$) and denoted the (long) time interval over which the transition from initial to final state occurs as $\int dt = T$. The matching of the effective perturbative Hamiltonian $H_{\rm eff}$ and the S-matrix element thus is

$$\begin{aligned} \langle \psi'_A, \psi'_B | H_{\rm eff} | \psi_A, \psi_B \rangle &= \langle \psi'_A, \psi'_B | U(\vec{r}_A,\vec{r}_B,\vec{R}) | \psi_A, \psi_B \rangle \\ &= \frac{i\hbar}{T}\, S_{A'B'AB}. \qquad (3) \end{aligned}$$

On the level of a scattering matrix element, the matching is obtained in an "averaged" sense, where the "averaging" (i.e., the integration) occurs over the wave functions of the initial and final states of the two-atom system. In the following, we concentrate on forward scattering, i.e., $|\psi_{A'}\rangle = |\psi_A\rangle$, $|\psi_{B'}\rangle = |\psi_B\rangle$.

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B. Interaction Hamiltonian

We are inspired by the derivation outlined in Chap. 85 of Ref. [10]. We use time-dependent QED perturbation theory, where the interaction is formulated in the interaction picture [11,12]. This means that the second-quantized operators in the interaction Hamiltonian have a time dependence which is generated by the action of the free Hamiltonian [13]. We use a second-quantized approach for the operators describing the electromagnetic field, so that a time-ordered product of the four-vector potential operators results in the Feynman propagator of the photon [11]. For the position operators of the atomic electrons, though, we use a first-quantized approach, i.e., we treat these on the level of quantum mechanics, without the introduction of fermion creation and annihilation operators.

The interaction Hamiltonian in the dipole approximation is then

$$\begin{aligned} V(t) &= -\vec{E}(\vec{x}_A,t)\cdot\vec{d}_A(t) - \vec{E}(\vec{x}_B,t)\cdot\vec{d}_B(t) \\ &\approx -\vec{E}(\vec{R}_A,t)\cdot\vec{d}_A(t) - \vec{E}(\vec{R}_B,t)\cdot\vec{d}_B(t), \end{aligned} \tag{4}$$

where $\vec{d}_i = e\vec{r}_i$ is the dipole operator for atom i (for atoms with more than one electron, one has to sum over all the electrons in the atoms $i = A,B$). The $\vec{R}_A$ and $\vec{R}_B$ are the positions of the atomic nuclei. A clarifying remark is in order: In the standard formulation of QED, one would use the interaction Hamiltonian density $\mathcal{H} = j^\mu A_\mu$, where $j^\mu = \hat{\bar{\psi}}\,\gamma^\mu\,\hat{\psi}$ is the fermionic current operator, γ^μ are the Dirac γ matrices, and A_μ is the four-vector potential [11,12]. The fermionic field operator $\hat{\psi}$ contains the fermionic creation and annihilation operators. However, in the nonrelativistic limit, one may renounce the quantization of the fermion field and treat the electronic degrees of freedom using first quantization [13,14].

The fourth-order contribution to the S matrix is (the full matrix, not a single element)

$$\begin{aligned} S^{(4)} = \frac{(-i)^4}{4!\hbar^4}\int dt_1\int dt_2\int dt_3\int dt_4 \\ \times\,\mathbf{T}\,[V(t_1)V(t_2)V(t_3)V(t_4)], \end{aligned} \tag{5}$$

where $\mathbf{T}$ denotes the time ordering of all operators, pertaining both to the atomic and to the field degrees of freedom. According to the Wick theorem, the time-ordered product is equal to the normal-ordered product, plus all contractions. We need to calculate the fourth-order S-matrix element $\langle\psi,0|S^{(4)}|\psi,0\rangle$ for forward scattering of the atomic reference state $|\psi\rangle = |\psi_A,\psi_B\rangle = |\psi_A\rangle\otimes|\psi_B\rangle$ with the vacuum $|0\rangle$ of the electromagnetic field (the product state is $|\psi,0\rangle$). After the subtraction of terms which pertain to the self-energies of the atoms, one obtains four contributions, which are proportional to (T denotes the time ordering of dipole operators)

$$C_1 \equiv \langle\psi_A|\mathrm{T}\,d_{Ai}(t_1)\,d_{Ak}(t_3)|\psi_A\rangle\langle\psi_B|\mathrm{T}\,d_{Bj}(t_2)\,d_{B\ell}(t_4))|\psi_B\rangle, \tag{6a}$$

$$C_2 \equiv \langle\psi_A|\mathrm{T}\,d_{Ai}(t_1)\,d_{A\ell}(t_4)|\psi_A\rangle\langle\psi_B|\mathrm{T}\,d_{Bj}(t_2)\,d_{Bk}(t_3)|\psi_B\rangle, \tag{6b}$$

$$C_3 \equiv \langle\psi_B|\mathrm{T}\,d_{Bi}(t_1)\,d_{B\ell}(t_4)|\psi_B\rangle\langle\psi_A|\mathrm{T}\,d_{Aj}(t_2)\,d_{Ak}(t_3)|\psi_A\rangle, \tag{6c}$$

$$C_4 \equiv \langle\psi_B|\mathrm{T}\,d_{Bi}(t_1)\,d_{Bk}(t_3)|\psi_B\rangle\langle\psi_A|\mathrm{T}\,d_{Aj}(t_2)\,d_{A\ell}(t_4)|\psi_A\rangle. \tag{6d}$$

Contributions C_2 and C_4 correspond to the crossed-ladder diagram (in the language of Feynman diagrams; see Fig. 1), whereas C_1 and C_3 correspond to the two-photon ladder exchange. The contributions of atoms A and B to the atomic reference state are denoted $|\psi_A\rangle$ and $|\psi_B\rangle$, respectively. All terms C_1, C_2, C_3, and C_4 lead to equivalent contributions, and we finally arrive at ($\mathcal{T}$ denotes the time ordering of field operators)

$$\begin{aligned} \langle\psi,0|S^{(4)}|\psi,0\rangle = \frac{1}{2\hbar^4}\int dt_1\int dt_2\int dt_3\int dt_4\langle 0|\mathcal{T}[E_i(\vec{R}_A,t_1)\,E_j(\vec{R}_B,t_2)]|0\rangle\langle 0|\mathcal{T}[E_k(\vec{R}_A,t_3)\,E_\ell(\vec{R}_B,t_4)]|0\rangle \\ \times\,\langle\psi_A|\mathrm{T}\,d_{Ai}(t_1)\,d_{Ak}(t_3)|\psi_A\rangle\langle\psi_B|\mathrm{T}\,d_{Bj}(t_2)\,d_{B\ell}(t_4)|\psi_B\rangle. \end{aligned} \tag{7}$$

C. Temporal gauge and propagator

The time-ordered product of electric-field operators can be evaluated as follows:

$$D^E_{ik}(x_1 - x_2) = \langle 0|\mathcal{T}[E_i(\vec{R}_A,t_1)\,E_k(\vec{R}_B,t_2)]|0\rangle. \tag{8}$$

With $\vec{E} = -\partial_t\vec{A}$, we have, for the "electric-field propagator" $D^E_{ik}(x_1 - x_2)$,

$$\begin{aligned} D^E_{ik}(x_1 - x_2) = \left(-\frac{\partial}{\partial t_1}\right)\left(-\frac{\partial}{\partial t_2}\right) \\ \times\,\langle 0|\mathcal{T}[A_i(\vec{R}_A,t_1)\,A_k(\vec{R}_B,t_2)]|0\rangle. \end{aligned} \tag{9}$$

One can relate the time-ordered product of field operators to the photon propagator,

$$\langle 0|\mathcal{T}\,A_\mu(x)\,A_\nu(x')|0\rangle = -i\,D_{\mu\nu}(x - x'). \tag{10}$$

We resort to the Fourier representation for the temporal gauge (also known as the Weyl gauge, with vanishing scalar components $D_{00} = 0$ and $D_{i0} = D_{0i} = 0$). According to Eq. (76.14) of Ref. [10], one has

$$D_{ik}(\omega,\vec{k}) = -\frac{\hbar}{4\pi\epsilon_0 c^2}\,\frac{1}{\left(\frac{\omega}{c}\right)^2 - \vec{k}^2 + i\epsilon}\left(\delta_{ik} - c^2\frac{k_i\,k_k}{\omega^2}\right). \tag{11}$$

According to Eq. (76.16) of Ref. [10], the propagator in the mixed frequency-position representation is given by

$$D_{ik}(\omega,\vec{R}) = -\left(\delta_{ik} + c^2\frac{\nabla_i\,\nabla_k}{\omega^2}\right)D(\omega,\vec{R}), \tag{12}$$

where

$$D(\omega,\vec{R}) = -\frac{\hbar}{4\pi\epsilon_0 c^2}\,\frac{e^{i\sqrt{\omega^2+i\epsilon}\,R/c}}{R}, \tag{13}$$

and ϵ is an infinitesimal parameter used in the frequency-coordinate representation of the Feynman propagator. In the

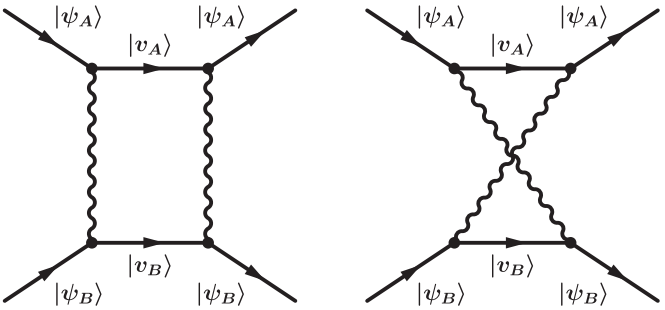

FIG. 1. Feynman diagrams for the excited-state long-range interaction of an atom in state $|\psi_A\rangle$ (excited) with a ground-state atom, B, in state $|\psi_B\rangle$. (a) Ladder diagram; (b) crossed-ladder graph. The power of using the Feynman propagator in the calculation lies in the fact that all the time orderings of the electron-photon vertices, which are otherwise relevant to time-ordered perturbation theory [14], can be summarized in only two diagrams.

following, we use the nonstandard definition

$$|\omega| \equiv \sqrt{\omega^2 + i\epsilon} \tag{14}$$

for the complex photon frequency ω. We carry out the differentiations, with the result

$$\nabla_i \nabla_k \frac{e^{i\frac{|\omega|}{c}R}}{R} = \left(\frac{\omega}{c}\right)^2 \delta_{ik}\left(-\frac{c^2}{\omega^2 R^2} + \frac{ic}{|\omega| R}\right)\frac{e^{i\frac{|\omega|}{c}R}}{R} + \left(\frac{\omega}{c}\right)^2 \frac{R_i R_k}{R^2}\left(\frac{3c^2}{\omega^2 r^2} - \frac{3ic}{|\omega| R} - 1\right)\frac{e^{i\frac{|\omega|}{c}R}}{R}. \tag{15}$$

The temporal gauge photon propagator in the mixed representation becomes

$$D_{ik}(\omega,\vec{R}) = \frac{\hbar}{4\pi\epsilon_0 c^2}\left[\delta_{ik}\left(1 + \frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2}\right)\frac{e^{i\frac{|\omega|}{c}R}}{R} + \frac{R_i R_k}{R^2}\left(-1 - \frac{3ic}{|\omega| R} + \frac{3c^2}{\omega^2 R^2}\right)\frac{e^{i\frac{|\omega|}{c}R}}{R}\right] = \frac{\hbar}{4\pi\epsilon_0 c^2}\left[\alpha_{ik} + \beta_{ik}\left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2}\right)\right]\frac{e^{i\frac{|\omega|}{c}R}}{R}, \tag{16a}$$

where

$$\alpha_{ik} = \delta_{ik} - \frac{R_i R_k}{R^2}, \quad \beta_{ik} = \delta_{ik} - 3\frac{R_i R_k}{R^2}. \tag{16b}$$

The photon propagator, which is the propagator for the vector potential $\vec{A}$, can be translated into the propagator for the electric field by differentiation with respect to time,

$$\begin{aligned} D^E_{ik}(x_1 - x_2) &= \frac{\partial}{\partial t_1}\frac{\partial}{\partial t_2}\langle 0|\mathcal{T} A_i(\vec{R}_A,t_1)\, A_k(\vec{R}_B,t_2)|0\rangle \\ &= \frac{\partial}{\partial(t_1 - t_2)}\,\frac{\partial}{\partial(t_2 - t_1)}\,(-i\, D_{ik}(x_1 - x_2)) \\ &= i\,\frac{\partial^2}{\partial t^2}\, D_{ik}(x), \quad x = x_1 - x_2. \end{aligned} \tag{17}$$

If we work in the mixed representation, we can implement the differentiation with respect to time in the Fourier integral as follows:

$$\begin{aligned} D^E_{ik}(t,\vec{R}) &= \langle 0|\mathcal{T} E_i(\vec{R}_A,t_1)\, E_k(\vec{R}_B,t_2)|0\rangle \\ &= -i\int \frac{d\omega}{2\pi}\,\omega^2\, D_{ik}(\omega,\vec{R})\, e^{-i\omega t}. \end{aligned} \tag{18}$$

Now, let us proceed to the time-ordered product of dipole operators, which is given as (for atom A)

$$\begin{aligned} \alpha_{A,ik}(t_1 - t_2) &= \frac{i}{\hbar}\,\langle\psi_A|\mathrm{T}(d_{Ai}(t_1)\, d_{Ak}(t_2))|\psi_A\rangle \\ &= \frac{i}{\hbar}\,\langle\psi_A|\mathrm{T}(d_{Ai}(t_1 - t_2)\, d_{Ak}(0))|\psi_A\rangle, \end{aligned} \tag{19}$$

and analogously for atom B.

Now, according to the prescription that Fourier transformation is a summation over exponentials with frequency factors $\exp(-i\omega t)$,

$$\alpha_{A,ik}(t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega t}\,\alpha_{A,ik}(\omega), \tag{20}$$

we write

$$\begin{aligned} &\langle\psi_A|\mathrm{T}\, d_{Ai}(t_1)\, d_{Ak}(t_2)|\psi_A\rangle \\ &\quad = -i\hbar\,\alpha_{A,ik}(t_1 - t_2) \\ &\quad = -i\hbar\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega(t_1 - t_2)}\,\alpha_{A,ik}(\omega). \end{aligned} \tag{21}$$

The time-ordered product of dipole operators can be evaluated in terms of the polarizability of the atom, with the poles being displaced according to the Feynman prescription (so that the integrals converge),

$$\begin{aligned} \alpha_{A,ik}(\omega) &= \int_{-\infty}^{\infty} dt\, e^{i\omega t}\,\alpha_{A,ik}(t) = \frac{i}{\hbar}\sum_v \int_0^{\infty} dt\, e^{-\frac{i}{\hbar}(E_v - E_A - \hbar\omega - i\epsilon)t}\langle\psi_A|d_{Ai}|v_A\rangle\,\langle v_A|d_{Ak}|\psi_A\rangle \\ &\quad + \frac{i}{\hbar}\sum_v \int_{-\infty}^{0} dt\, e^{\frac{i}{\hbar}(E_v - E_A + \hbar\omega - i\epsilon)t}\langle\psi_A|d_{Ak}\,|v_A\rangle\,\langle v_A|d_{Ai}|\psi_A\rangle \\ &= \sum_{v_A}\left(\frac{\langle\psi_A|d_{Ai}|v_A\rangle\,\langle v_A|d_{Ak}|\psi_A\rangle}{E_{v,A} - \hbar\omega - i\epsilon} + \frac{\langle\psi_A|d_{Ai}|v_A\rangle\,\langle v_A|d_{Ak}|\psi_A\rangle}{E_{v,A} + \hbar\omega - i\epsilon}\right), \end{aligned} \tag{22}$$

where $\epsilon > 0$ and

$$E_{v,A} = E_{v_A} - E_A \tag{23}$$

is the difference between the virtual-state energy E_{v_A} and the reference-state energy E_A of atom A. In the last step of Eq. (22), we have used the fact that the polarizability has to be purely real rather than complex for real driving frequency ω, thus replacing $\langle\psi_A|d_{Ak}|v_A\rangle\,\langle v_A|d_{Ai}|\psi_A\rangle \to \langle\psi_A|d_{Ai}|v_A\rangle\,\langle v_A|d_{Ak}|\psi_A\rangle$ in the second term. In assigning the time dependence of the atomic dipole operators, we have taken into account the Heisenberg equation of motion, $\hbar\frac{d}{dt}\vec{d}_A(t) = i\,[H_A,\vec{d}_A(t)]$, where H_A is the Schrödinger Hamiltonian of atom A. The poles in the polarizability $\alpha_{A,ik}$ are displaced according to the Feynman prescription. Poles occur at $\hbar\omega = E_{v,A} - i\epsilon$ and at $\hbar\omega = -E_{v,A} + i\epsilon$. If the virtual state is displaced toward a lower energy, i.e., $E_{v,A} < 0$, then the pole at $\hbar\omega = -E_{v,A} + i\epsilon$ migrates into the first quadrant of the complex plane.

The "correct" prescription for the placement of the poles of the energy denominator of the polarizability has recently been controversially discussed in the literature [15–19]. A different prescription, which puts the poles into the lower half of the complex plane, was recently used in Ref. [20]. In the latter study, one considers the relative permittivity $\epsilon_r(\omega)$ of a dilute gas and its relation to the dynamic dipole polarizability $\alpha(\omega)$ of the gas atoms,

$$\epsilon_r(\omega) = 1 + \frac{N_V}{\epsilon_0}\alpha_R(\omega), \tag{24}$$

where $\alpha_R(\omega)$ denotes the polarizability in a pole prescription corresponding to the retarded Green function, i.e., with a sign change $(-i\epsilon \to +i\epsilon)$ in the second term on the right-hand side of Eq. (22). Furthermore, N_V is the number density of atoms. These considerations are valid upon an interpretation of the dielectric constant in terms of the retarded Green function G_R, which describes the relation of the dielectric displacement $\vec{D}(\vec{r},t)$ to the electric field $\vec{E}(\vec{r},t)$:

$$\vec{D}(\vec{r},t) = \epsilon_0\,\vec{E}(\vec{r},t) + \epsilon_0\int_0^\infty d\tau\,G_R(\tau)\,\vec{E}(\vec{r},t-\tau). \tag{25}$$

The Fourier transform is

$$G_R(\omega) = \frac{N_V}{\epsilon_0}\,\alpha_R(\omega), \tag{26}$$

where $\alpha_R(\omega)$ denotes the "retarded" polarizability. The retarded prescription is thus required for the dielectric function $\epsilon_r(\omega) = 1 + G_R(\omega)$. The answer to the question regarding the correct placement of the poles of the polarizability [15–19] thus is as follows: Namely, there is no universally correct displacement for the poles from the real axis. Instead, the correct placement depends on the form of the Green function represented by the polarizability, in the context of a particular application. If the retarded Green function is needed, then all poles should be displaced into the lower half of the complex plane, while the Feynman prescription is relevant for the current calculation, in which the time-ordered product of dipole operators is sought. Neither the retarded nor the Feynman prescription is universally correct; it depends on the context in which the calculation is being performed.

We now reformulate Eq. (7), with the help of Eqs. (16) and (21):

$$\begin{aligned}\langle\psi,0|S^{(4)}|\psi,0\rangle = \frac{1}{2\hbar^4}\int dt_1\int dt_2\int dt_3\int dt_4\left(-i\int\frac{d\omega_1}{2\pi}\,\omega_1^2\,D_{ij}(\omega_1,\vec{R})\,e^{-i\omega_1(t_1-t_2)}\right)\left(-i\int\frac{d\omega_2}{2\pi}\,\omega_2^2\,D_{k\ell}(\omega_2,\vec{R})\,e^{-i\omega_2(t_3-t_4)}\right)\\ \times\left(-i\int\frac{d\omega_3}{2\pi}\,\hbar\,\alpha_{A,ik}(\omega_3)\,e^{-i\omega_3(t_1-t_3)}\right)\left(-i\int\frac{d\omega_4}{2\pi}\,\hbar\,\alpha_{B,j\ell}(\omega_4)\,e^{-i\omega_4(t_2-t_4)}\right).\end{aligned} \tag{27}$$

One now carries out the dt_i integrations one after the other, with the results $\int dt_2 \to 2\pi\,\delta(\omega_1-\omega_4)$, then $\int dt_3 \to 2\pi\,\delta(\omega_2-\omega_3)$, and $\int dt_4 \to 2\pi\,\delta(\omega_2+\omega_4)$. As a result, the condition $\omega_1 = \omega_4 = -\omega_2 = -\omega_3$ is implemented in the final result, yielding

$$\begin{aligned}\langle\psi,0|S^{(4)}|\psi,0\rangle &= \frac{1}{2\hbar^2}\int dt_1\int\frac{d\omega_1}{2\pi}\omega_1^2(-\omega_1)^2 D_{ij}(\omega_1,\vec{R})\,D_{k\ell}(-\omega_1,\vec{R})\,\alpha_{A,ik}(-\omega_1)\,\alpha_{B,j\ell}(\omega_1)\\ &= \frac{T}{2\hbar^2}\int\frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(\omega,\vec{R})\,D_{k\ell}(\omega,\vec{R})\,\alpha_{A,ik}(\omega)\,\alpha_{B,j\ell}(\omega),\end{aligned} \tag{28}$$

where we use the invariance of the photon propagator and of the polarizability under the transformation $\omega \leftrightarrow -\omega$ [see Eqs. (16) and (22)]; we reemphasize that this invariance holds only if the Feynman prescription is used.

D. Energy shift

Using Eq. (3), we obtain the diagonal matrix element of the effective Hamiltonian, and thus the direct term of the energy shift $\Delta E^{(\mathrm{dir})}$, as

$$\begin{aligned}\Delta E^{(\mathrm{dir})} &= \langle\psi_A\psi_B|H_{\mathrm{eff}}|\psi_A\psi_B\rangle\\ &= \frac{i}{2\hbar}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(\omega,\vec{R})\,D_{k\ell}(\omega,\vec{R})\\ &\quad\times\alpha_{A,ik}(\omega)\,\alpha_{B,j\ell}(\omega).\end{aligned} \tag{29a}$$

This general result can be applied to states of arbitrary symmetry and is not restricted to ground-state atoms. Invoking the full symmetry of the integrand under a sign change of ω, one may write

$$\begin{aligned}\Delta E^{(\mathrm{dir})} &= \frac{i}{\hbar}\int_0^\infty\frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(\omega,\vec{R})\,D_{k\ell}(\omega,\vec{R})\\ &\quad\times\alpha_{A,ik}(\omega)\,\alpha_{B,j\ell}(\omega).\end{aligned} \tag{29b}$$

For convenience, we recall the definition of $D_{ij}(\omega,\vec{R})$ according to Eq. (16) and the definition of $\alpha_{A,ij}(\omega)$ according to

Eq. (22):

$$D_{ij}(\omega,\vec{R}) = \frac{\hbar e^{i\frac{|\omega|}{c}R}}{4\pi\epsilon_0 c^2\,R}\left[\alpha_{ij} + \beta_{ij}\left[\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2\,R^2}\right]\right],$$

$$\alpha_{ij} = \delta_{ij} - \frac{R_i\,R_j}{R^2}, \quad \beta_{ij} = \delta_{ij} - 3\frac{R_i\,R_j}{R^2},$$

$$\alpha_{A,ij}(\omega) = \sum_{v_A}\left(\frac{\langle\psi_A|d_{Ai}|v_A\rangle\,\langle v_A|d_{Aj}|\psi_A\rangle}{E_{v,A} - \hbar\omega - i\epsilon} + \frac{\langle\psi_A|d_{Aj}|v_A\rangle\,\langle v_A|d_{Ai}|\psi_A\rangle}{E_{v,A} + \hbar\omega - i\epsilon}\right). \tag{29c}$$

Of course, the tensor structures α_{ij} and β_{ij} need to be distinguished from the polarizabilities α_A and α_B.

It is a feature of the time-ordered product of dipole and field operators that all possible time orderings in time-ordered perturbation theory (see Fig. 1 of Ref. [8]) are automatically taken into account using a single propagator.

E. Mixing term

In the case of two identical atoms, an additional interaction energy term exists which needs to be taken into account. Here, states $|\psi_A\rangle$ and $|\psi_B\rangle$ are obviously not tied to any of the atoms, but rather, atom A may assume state $|\psi_B\rangle$, and atom B may assume state $|\psi_A\rangle$ after the interaction. The eigenstates of the van der Waals Hamiltonian in this case are states of the form $(1/\sqrt{2})\,(|\psi_A,\psi_B\rangle \pm |\psi_B,\psi_A\rangle)$ with an energy

$$\Delta E = \Delta E^{(\mathrm{dir})} \pm \Delta E^{(\mathrm{mix})}, \tag{30}$$

where $\Delta E^{(\mathrm{dir})}$ is given by Eq. (29), and $\Delta E^{(\mathrm{mix})}$ is obtained by calculating the S-matrix element of the initial state $|\psi\rangle = |\psi_A\rangle\otimes|\psi_B\rangle$ and the final state $|\psi'\rangle = |\psi_B\rangle\otimes|\psi_A\rangle$. In order to calculate the mixing term, one repeats all steps leading from Eq. (1) to Eq. (29), for the out state $|\psi'\rangle$ and the in state $|\psi\rangle$. The result is

$$\Delta E^{(\mathrm{mix})} = \frac{i}{\hbar}\int_0^\infty \frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(\omega,\vec{R})\,D_{k\ell}(\omega,\vec{R}) \times \alpha_{\underline{A}B,ik}(\omega)\,\alpha^*_{A\underline{B},j\ell}(\omega). \tag{31}$$

The definition of $D_{ij}(\omega,\vec{R})$ has been recalled in Eq. (29c). The mixed polarizabilities $\alpha_{\underline{A}B,ij}(\omega)$ and $\alpha_{A\underline{B},ij}(\omega)$ are given as follows:

$$\alpha_{\underline{A}B,ij}(\omega) = \sum_{v_A}\left(\frac{\langle\psi_A|d_{Ai}|v_A\rangle\,\langle v_A|d_{Aj}|\psi_B\rangle}{E_{v,A} - \hbar\omega - i\epsilon} + \frac{\langle\psi_A|d_{Aj}|v_A\rangle\,\langle v_A|d_{Ai}|\psi_B\rangle}{E_{v,A} + \hbar\omega - i\epsilon}\right),$$

$$\alpha_{A\underline{B},ij}(\omega) = \sum_{v_B}\left(\frac{\langle\psi_A|d_{Bi}|v_B\rangle\,\langle v_B|d_{Bj}|\psi_B\rangle}{E_{v,B} - \hbar\omega - i\epsilon} + \frac{\langle\psi_A|d_{Bj}|v_B\rangle\,\langle v_B|d_{Bi}|\psi_B\rangle}{E_{v,B} + \hbar\omega - i\epsilon}\right). \tag{32}$$

Here, the designations of the dipole transition operators with regard to atoms A and B, i.e., as d_{Ai} and d_{Bi}, constitute mere conveniences; for the mixing term to exist, the two atoms have to be identical and $|\psi_A\rangle$ and $|\psi_B\rangle$ are different states of the same atom. The important feature which differentiates $\alpha_{\underline{A}B,ij}(\omega)$ from $\alpha_{A\underline{B},ij}(\omega)$, in the case of identical atoms, is the different reference-state energy in the denominator.

III. APPLICATIONS

A. Ground-state interaction

For a reference S state of atom A, denoted $|\psi_A\rangle = |n_A S\rangle$, the polarizability tensor assumes the form

$$\alpha_{A,ik}(\omega) = \frac{\delta_{ik}}{3}\sum_{v_A}\left(\frac{\langle n_A S|\vec{d}_A|v_A P\rangle\cdot\langle v_A P|\vec{d}_A|n_A S\rangle}{E_{v,A} - \hbar\omega - i\epsilon} + \frac{\langle n_A S|\vec{d}_A|v_A P\rangle\cdot\langle v_A P|\vec{d}_A|n_A S\rangle}{E_{v,A} + \hbar\omega - i\epsilon}\right) = \delta_{ik}\,\alpha_A(\omega), \tag{33}$$

where we denote the S and P states by their respective symmetry [in this case, $E_{v,A} = E_{v_A} - E_A = E(v_A\,P) - E(n_A S)$], where the reference-state energy is that of the S state with principal quantum number n_A. This leads to the following tensor structure in Eq. (29):

$$D_{ij}(\omega,\vec{R})\,D_{ij}(\omega,\vec{R}) = \left(\frac{\hbar}{4\pi\epsilon_0 c^2}\right)^2\frac{2\,e^{2i\frac{|\omega|}{c}R}}{R^2} \times\left(1 + \frac{2i\,c}{|\omega|\,R} - \frac{5c^2}{(\omega R)^2} - \frac{6i\,c^3}{(|\omega|R)^3} + \frac{3c^4}{(\omega R)^4}\right).$$

A Wick rotation of expression (29) then leads to

$$\Delta E^{(\mathrm{dir})} = -\frac{\hbar}{\pi c^4(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,e^{-2\omega R/c}\,\frac{\omega^4}{R^2} \times\left(1 + \frac{2c}{\omega\,R} + \frac{5c^2}{(\omega R)^2} + \frac{6c^3}{(\omega R)^3} + \frac{3c^4}{(\omega R)^4}\right) \times\alpha_A(1S;i\omega)\,\alpha_B(1S;i\omega), \tag{34}$$

where we indicate the atomic states relevant to the investigation, for clarity. Expression (29b) verifies known results (see Chap. 85 of Ref. [10]).

B. van der Waals (close-range) limit

A classic result which needs to be verified is the close-range limit. For $R \ll c/\omega$, where ω is a typical transition wavelength, we find, from the dominant term in Eq. (16) in this limit,

$$D_{ij}(\omega,\vec{R}) \approx -\frac{\hbar}{4\pi\epsilon_0}\frac{\beta_{ij}}{\omega^2\,R^3}. \tag{35}$$

For arbitrary angular symmetry of the reference state, we thus have

$$\Delta E^{(\mathrm{dir})} \approx \frac{i\hbar\,\beta_{ij}\,\beta_{k\ell}}{2\,(4\pi\epsilon_0)^2\,R^6}\int_{-\infty}^\infty\frac{d\omega}{2\pi}\,\alpha_{A,ik}(\omega)\,\alpha_{B,j\ell}(\omega), \tag{36}$$

where it is advantageous to keep the integration limits as $-\infty$ and ∞. In view of the general result

$$\hbar \int_{-\infty}^{\infty} d\omega \left(\sum_{\pm} \frac{1}{E_{v,A} \pm \hbar\omega - i\epsilon} \right) \left(\sum_{\pm} \frac{1}{E_{v,B} \pm \hbar\omega - i\epsilon} \right) = \frac{4\pi i}{E_{v,A} + E_{v,B}}, \tag{37}$$

we have

$$\Delta E^{(\mathrm{dir})} \approx -\frac{1}{(4\pi\epsilon_0)^2} \frac{\beta_{ij}\, \beta_{k\ell}}{R^6} \sum_{v_A} \sum_{q_B} \frac{1}{E_{v,A} + E_{q,B}} \times \langle \psi_A | d_{Ai} | v_A \rangle \langle v_A | d_{Ak} | \psi_A \rangle \times \langle \psi_B | d_{Bj} | q_B \rangle \langle q_B | d_{B\ell} | \psi_B \rangle. \tag{38}$$

We denote the virtual states of atom B as $|q\rangle$ as opposed to $|v\rangle$. This is precisely the expression which would be obtained using second-order perturbation theory with the van der Waals potential

$$\mathcal{V} = \frac{1}{4\pi\,\epsilon_0} \frac{\beta_{ij}\, d_{Ai}\, d_{Bj}}{R^3}, \tag{39}$$

which can be obtained by expanding the electrostatic potential of the bound electrons and protons in both atoms in the limit $|\vec{r}_A|, |\vec{r}_B| \ll R$.

C. General excited reference states

1. Pole term

Let $|m_A\rangle$ be a virtual state of atom A, accessible by a dipole transition, We now assume that at least one state in atom A is energetically lower than the reference state, i.e., $E_{m,A} < 0$, while atom B is in the ground state. For the pole term, in the decomposition, (22), we restrict the sum over virtual states v_A to just one state, whose quantum numbers we denote by the multi-index m_A (see Fig. 2). A Wick rotation of the integration contour $\omega \in (0, \infty)$ from Eq. (29b) to the imaginary axis then

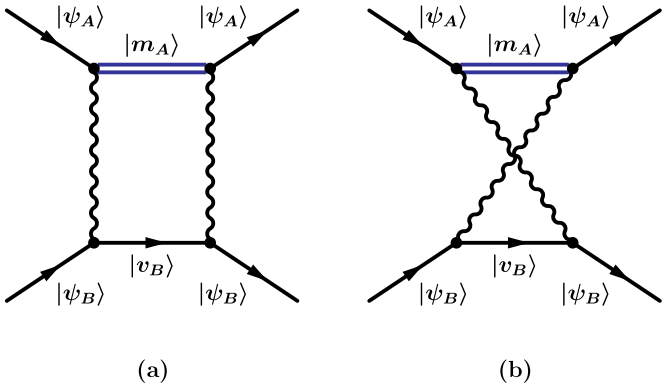

FIG. 2. The virtual resonant contribution due to a lower-lying level $|m_A\rangle$ leads to the pole term, which generates the long-range interactions for excited states [see Eqs. (43b) and (58b)].

picks up an additional pole term at

$$\hbar\omega = -E_{m,A} + i\epsilon, \quad E_{m,A} < 0, \tag{40}$$

which we need to take into account. Consequently, the interaction energy shift ΔE due to the energetically lower virtual-state energy with quantum numbers m_A (multi-index) naturally splits into a pole term $\mathcal{Q}^{(\mathrm{dir})}_{m_A}$ and a Wick-rotated term $\mathcal{W}^{(\mathrm{dir})}_{m_A}$:

$$\Delta E^{(\mathrm{dir})}_{m_A} = \mathcal{Q}^{(\mathrm{dir})}_{m_A} + \mathcal{W}^{(\mathrm{dir})}_{m_A}. \tag{41}$$

The total direct term is

$$\Delta E^{(\mathrm{dir})} = \left(\sum_{E_{m,A}<0} \mathcal{Q}^{(\mathrm{dir})}_{m_A} \right) + \mathcal{W}^{(\mathrm{dir})}, \tag{42}$$

where the Wick-rotated term $\mathcal{W}^{(\mathrm{dir})}$ is obtained after the summation over all virtual states (including those of higher energy) and enters the expression in Eq. (45). For the contribution from the pole, one finds by Cauchy's residue theorem that

$$\begin{aligned} \mathcal{Q}^{(\mathrm{dir})}_{m_A} &= -\operatorname*{Res}_{\omega=-E_{m,A}/\hbar+i\epsilon} \frac{\omega^4}{\hbar} D_{ij}(\omega,\vec{R}) D_{k\ell}(\omega,\vec{R}) \left(\sum_{\pm} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_A \rangle}{E_{m,A} \pm \hbar\omega - i\epsilon} \right) \alpha_{B,j\ell}(\omega) \\ &= -\frac{\langle \psi_A | d_{Ai} | m_A \rangle \, \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2\, R^6} \alpha_{B,j\ell}\left(\frac{E_{m,A}}{\hbar} \right) \exp\left(-\frac{2i\, E_{m,A} R}{\hbar c} \right) \left[\beta_{ij}\, \beta_{k\ell} \left(1 + 2i \frac{E_{m,A}\, R}{\hbar c} \right) \right. \\ &\quad \left. - (2\alpha_{ij}\, \beta_{k\ell} + \beta_{ij}\, \beta_{k\ell}) \left(\frac{E_{m,A} R}{\hbar c} \right)^2 - 2i \alpha_{ij}\, \beta_{k\ell} \left(\frac{E_{m,A} R}{\hbar c} \right)^3 + \alpha_{ij}\, \alpha_{k\ell} \left(\frac{E_{m,A} R}{\hbar c} \right)^4 \right] = \mathcal{P}^{(\mathrm{dir})}_{m_A} - \frac{i}{2} \Gamma^{(\mathrm{dir})}_{m_A}. \end{aligned} \tag{43a}$$

Here, $\mathcal{P}^{(\mathrm{dir})}_{m_A}$ is the real part of the interaction energy, and $\Gamma^{(\mathrm{dir})}_{m_A}$ is the induced width. The identification of the width term $\Gamma^{(\mathrm{dir})}_{m_A}$ follows the general paradigm that a bound-state energy can be written as $E = \mathrm{Re}\, E - \frac{i}{2}\Gamma$, where Γ is the width. One obtains

$$\begin{aligned} \mathcal{P}^{(\mathrm{dir})}_{m_A} &= -\frac{\langle \psi_A | d_{Ai} | m_A \rangle \, \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2\, R^6} \alpha_{B,j\ell}\left(\frac{E_{m,A}}{\hbar} \right) \left\{ \cos\left(2\frac{E_{m,A} R}{\hbar c} \right) \left[\beta_{ij}\, \beta_{k\ell} - (2\alpha_{ij}\, \beta_{k\ell} + \beta_{ij}\, \beta_{k\ell}) \left(\frac{E_{m,A}\, R}{\hbar c} \right)^2 \right. \right. \\ &\quad \left. + \alpha_{ij}\, \alpha_{k\ell} \left(\frac{E_{m,A}\, R}{\hbar c} \right)^4 \right] + 2\frac{E_{m,A} R}{\hbar c} \sin\left(2\frac{E_{m,A} R}{\hbar c} \right) \left[\beta_{ij}\, \beta_{k\ell} - \alpha_{ij}\, \beta_{k\ell} \left(\frac{E_{m,A} R}{\hbar c} \right)^2 \right] \Bigg\}. \end{aligned} \tag{43b}$$

The width term $\Gamma^{(\mathrm{dir})}_{m_A}$ can be obtained from $\mathcal{P}^{(\mathrm{dir})}_{m_A}$ by the substitution

$$\cos\left(\frac{2E_{m,A}R}{\hbar c}\right) \to \sin\left(\frac{2E_{m,A}R}{\hbar c}\right), \quad \sin\left(\frac{2E_{m,A}R}{\hbar c}\right) \to -\cos\left(\frac{2E_{m,A}R}{\hbar c}\right) \tag{43c}$$

and an overall factor 2. It reads

$$\Gamma^{(\mathrm{dir})}_{m_A} = -2\frac{\langle\psi_A|d_{Ai}|m_A\rangle\,\langle m_A|d_{Ak}|\psi_A\rangle}{(4\pi\epsilon_0)^2\,R^6}\,\alpha_{B,j\ell}\left(\frac{E_{m,A}}{\hbar}\right)\left\{\sin\left(2\frac{E_{m,A}R}{\hbar c}\right)\left[\beta_{ij}\,\beta_{k\ell} - (2\alpha_{ij}\,\beta_{k\ell}+\beta_{ij}\,\beta_{k\ell})\left(\frac{E_{m,A}\,R}{\hbar c}\right)^2 + \alpha_{ij}\,\alpha_{k\ell}\left(\frac{E_{m,A}\,R}{\hbar c}\right)^4\right] - 2\frac{E_{m,A}R}{\hbar c}\,\cos\left(2\frac{E_{m,A}R}{\hbar c}\right)\left[\beta_{ij}\,\beta_{k\ell} - \alpha_{ij}\,\beta_{k\ell}\left(\frac{E_{m,A}R}{\hbar c}\right)^2\right]\right\}. \tag{43d}$$

The result, (43b), is at variance with the corresponding result given in Eq. (14) of Ref. [7] and with Eq. (4.1) of Ref. [8]. It is in better agreement with recently published results, such as Eq. (19) of Ref. [2] and Eq. (4) of Ref. [1] (provided we average the latter over the interaction time $T > 2R/c$). We have used a symmetry of the integrand according to the replacement $\alpha_{ij}\,\beta_{k\ell} + \alpha_{k\ell}\,\beta_{ij} + \beta_{ij}\,\beta_{k\ell} \to 2\alpha_{ij}\,\beta_{k\ell} + \beta_{ij}\,\beta_{k\ell}$ in the cosine term in Eq. (43b) and $\alpha_{ij}\,\beta_{k\ell} + \alpha_{k\ell}\,\beta_{ij} \to 2\alpha_{ij}\,\beta_{k\ell}$ in the sine term. This is valid under the same assumptions as used in Eq. (22).

Written in terms of a sum over states for atom B, we have

$$\alpha_{B,j\ell}\left(\frac{E_{m,A}}{\hbar}\right) = \sum_{q_B}\langle\psi_B|d_{Bj}|q_B\rangle\,\langle q_B|d_{B\ell}|\psi_B\rangle \times\left(\frac{1}{E_{q,B}-E_{m,A}} + \frac{1}{E_{q,B}+E_{m,A}}\right). \tag{43e}$$

The authors of Ref. [1] consider a situation with two nonidentical atoms, which have resonance energies $\hbar\omega_A$ and $\hbar\omega_B$ mutually close. They define $E_{m,A} = -\hbar\omega_A$ (with manifestly positive ω_A) and write $E_{q,B} = \hbar\omega_B$, 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. (43e) to the resonant state, and they keep only the term $1/(E_{m,A}+E_{q,B})$ in Eq. (43e), because under their assumptions [see Eq. (4) of Ref. [1]],

$$\left|\frac{1}{E_{m,A}+E_{q,B}}\right| = \left|-\frac{1}{\Delta_{AB}}\right| \gg \left|\frac{1}{E_{q,B}-E_{m,A}}\right| \approx \frac{1}{2\hbar\omega_B}. \tag{44}$$

Our result, given in Eq. (43b), is much more general, as it includes nonresonant terms of atom B, which enter the expression $\alpha_{B,j\ell}(E_{m,A}/\hbar)$, and thus not restricted to the special case of distinct atoms with mutually close resonant frequencies.

2. *Wick-rotated term*

Let us now consider the Wick-rotated term in Eq. (29), which has the following tensor structure:

$$\begin{aligned}\mathcal{W}^{(\mathrm{dir})} &= -\frac{1}{\hbar}\int_0^\infty \frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(i\omega,\vec{R})\,D_{k\ell}(i\omega,\vec{R}) \\ &\quad\times\alpha_{A,ik}(i\omega)\,\alpha_{B,j\ell}(i\omega) \\ &= -\frac{\hbar}{(4\pi\epsilon_0)^2\,c^4}\int_0^\infty\frac{d\omega}{2\pi}e^{-2\omega R/c}\,\frac{\omega^4}{R^2} \\ &\quad\times\left[\alpha_{ij}+\left(\frac{c}{\omega R}+\frac{c^2}{(\omega R)^2}\right)\beta_{ij}\right]\alpha_{A,ik}(i\omega) \\ &\quad\times\left[\alpha_{k\ell}+\left(\frac{c}{\omega R}+\frac{c^2}{(\omega R)^2}\right)\beta_{k\ell}\right]\alpha_{B,j\ell}(i\omega).\end{aligned} \tag{45}$$

Here, the full polarizabilities are to be used; i.e., the sum over virtual states is not restricted to states with an energy lower than that of the reference state, for atom A. According to the nonstandard definition, (14), one has

$$|i\omega| = \sqrt{(i\omega)^2 + i\epsilon} = i\omega, \quad \omega > 0, \tag{46}$$

and the Wick rotation can be carried out as usual.

It is now crucial to verify that, in the sum of the pole term and the Wick-rotated term, the contribution of the virtual state m_A—which has a lower energy than ψ_A—to the nonretarded van der Waals energy, (38), gives the expected result. The Wick rotation performed in Eq. (45) is not "innocent"; within the Wick-rotated integral, it changes the sign of the contribution of the energetically lower state to the van der Waals energy. A compensating term is offered by the pole term, in a way discussed in the following.

First, we approximate Eq. (45) for close range using the asymptotic behavior of the photon propagator given by Eq. (35). In view of the general result

$$\hbar\int_{-\infty}^{\infty}d\omega\left(\sum_{\pm}\frac{1}{E_{m,A}\pm i\hbar\omega}\right)\left(\sum_{\pm}\frac{1}{E_{q,B}\pm i\hbar\omega}\right) = \frac{4\pi\,\mathrm{sgn}(E_{m,A})\,\mathrm{sgn}(E_{q,B})}{|E_{m,A}|+|E_{q,B}|}, \tag{47}$$

an evaluation of the Wick-rotated integral in the short-range limit leads to

$$\mathcal{W}^{(\mathrm{dir})}_{m_A} \overset{R\to 0}{=} \frac{1}{(4\pi\epsilon_0)^2 R^6} \sum_{q_B} \frac{\beta_{ij}\,\beta_{k\ell}}{|E_{m,A}| + E_{q,B}} \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle\langle\psi_B|d_{Bj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle$$
$$= \frac{1}{(4\pi\epsilon_0)^2 R^6} \sum_{q_B} \frac{\beta_{ij}\,\beta_{k\ell}}{-E_{m,A} + E_{q,B}} \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle\langle\psi_B|d_{Bj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle. \tag{48}$$

We have assumed that $E_{m,A} < 0$; the result is *not* equal to the contribution of the virtual state m_A to the van der Waals energy, (38). The compensating term is obtained by considering the short-range limit of the pole term, which is obtained from Eq. (43b) in the limit $R \to 0$:

$$\mathcal{P}^{(\mathrm{dir})}_{m_A} \overset{R\to 0}{=} -\frac{1}{(4\pi\epsilon_0)^2\, R^6} \left(\sum_{q_B,\pm} \frac{\beta_{ij}\beta_{k\ell}}{\pm E_{m,A} + E_{q,B}} \right) \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle\langle\psi_B|d_{Bj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle. \tag{49}$$

For completeness, we also note the short-range asymptotics of the width term,

$$\Gamma^{(\mathrm{dir})}_{m_A} \overset{R\to 0}{=} \frac{2[E_{m,A}/(\hbar c)]^3}{3\,(4\pi\epsilon_0)^2\, R^3} \left(\sum_{q_B,\pm} \frac{\beta_{ij}\beta_{k\ell} - 3\alpha_{ij}\,\beta_{k\ell}}{\pm E_{m,A} + E_{q,B}} \right) \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle\langle\psi_B|d_{Bj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle. \tag{50}$$

The sum of the terms in Eqs. (48) and (49) restores the van der Waals limit,

$$\Delta E^{(\mathrm{dir})}_{m_A} = \mathcal{P}^{(\mathrm{dir})}_{m_A} + \mathcal{W}^{(\mathrm{dir})}_{m_A} \overset{R\to 0}{=} -\frac{1}{(4\pi\epsilon_0)^2\, R^6} \sum_{q_B} \frac{\beta_{ij}\,\beta_{k\ell}}{E_{m,A} + E_{q,B}} \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle\langle\psi_B|d_{Bj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle. \tag{51}$$

This result precisely corresponds to what would be expected from second-order perturbation theory if the Hilbert space of atom A were restricted in the two states ψ_A and m_A. Supplementing the energetically higher states $|v_A\rangle$ for atom A, given in the Wick-rotated form, Eq. (45), one restores the full van der Waals limit.

Let us now turn our attention to the long-range limit. For the $1S$-$1S$ interaction, the classic result for very large interatomic separation [21] calls for a Casimir-Polder $1/R^7$ asymptotics. This is valid only, as we now argue, if both atoms are in their ground state. Indeed, in this situation, only the Wick-rotated contribution subsists, and its asymptotics is indeed of the Casimir-Polder form. In the general case, however, for arbitrary tensor structure, we have both the Wick-rotated term

$$\mathcal{W}^{(\mathrm{dir})} \overset{R\to\infty}{=} -\frac{\hbar c}{8\pi} \frac{\alpha_{A,ik}(0)\,\alpha_{B,j\ell}(0)}{(4\pi\epsilon_0)^2\, R^7} (3\alpha_{ij}\alpha_{kl} + 5\alpha_{ij}\beta_{kl} + 5\beta_{ij}\beta_{kl}) \tag{52}$$

and the pole term, which has the long-range asymptotics

$$\mathcal{P}^{(\mathrm{dir})}_{m_A} \overset{R\to\infty}{=} -\frac{1}{(4\pi\epsilon_0)^2\, R^2} \left(\frac{E_{m,A}}{\hbar c}\right)^4 \cos\left(2\frac{E_{m,A}R}{\hbar c}\right) \alpha_{ij}\alpha_{kl}\, \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle \alpha_{B,j\ell}\left(\frac{E_{m,A}}{\hbar}\right). \tag{53}$$

The long-range form of the width term reads as

$$\Gamma^{(\mathrm{dir})}_{m_A} \overset{R\to\infty}{=} -\frac{2}{(4\pi\epsilon_0)^2\, R^2} \left(\frac{E_{m,A}}{\hbar c}\right)^4 \sin\left(2\frac{E_{m,A}R}{\hbar c}\right) \alpha_{ij}\alpha_{kl}\, \langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_A\rangle \alpha_{B,j\ell}\left(\frac{E_{m,A}}{\hbar}\right). \tag{54}$$

This result confirms the existence of an extremely long-range van der Waals interaction for excited states.

3. Mixing terms

We now need to start from Eq. (31) for the mixing term and analyze the pole term generated for a virtual state of lower energy, in atom A, and the Wick-rotated term, as well as its nonretarded limit. The mixing term is relevant only for identical atoms. We recall that for identical atoms, the eigenstates of the van der Waals Hamiltonian are states of the form $(1/\sqrt{2})\,(|\psi_A,\psi_B\rangle \pm |\psi_B,\psi_A\rangle)$, with energy $\Delta E^{(\mathrm{dir})} \pm \Delta E^{(\mathrm{mix})}$, where $\Delta E^{(\mathrm{dir})}$ is given by Eq. (29) and $\Delta E^{(\mathrm{mix})}$ by Eq. (31). We write the contribution $\Delta E^{(\mathrm{mix})}_{m_A}$ from an energetically lower state $|v_A\rangle = |m_A\rangle$ with $E_{m,A} < 0$ as

$$\Delta E^{(\mathrm{mix})}_{m_A} = \mathcal{Q}^{(\mathrm{mix})}_{m_A} + \mathcal{W}^{(\mathrm{mix})}_{m_A}. \tag{55}$$

The total mixing term is obtained as the sum

$$\Delta E^{(\mathrm{mix})} = \left(\sum_{E_{m,A}<0} \mathcal{Q}^{(\mathrm{mix})}_{m_A} \right) + \mathcal{W}^{(\mathrm{mix})}, \tag{56}$$

where $\mathcal{W}^{(\mathrm{mix})}$ is the total mixing term, summed over all states, energetically lower as well as higher.

The generalization of Eq. (43a) to the mixed pole term reads as follows:

$$\begin{aligned}\mathcal{Q}^{(\mathrm{mix})}_{m_A} &= -\operatorname*{Res}_{\omega=-E_{m,A}/\hbar+i\epsilon} \frac{\omega^4}{\hbar}\, D_{ij}(\omega,\vec{R}) D_{k\ell}(\omega,\vec{R}) \left(\frac{\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_B\rangle}{E_{m,A}-\hbar\omega-i\epsilon} + \frac{\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_B\rangle}{E_{m,A}+\hbar\omega-i\epsilon} \right) \alpha_{A\underline{B},j\ell}(\omega) \\ &= \mathcal{P}^{(\mathrm{mix})}_{m_A} - \frac{i}{2}\Gamma^{(\mathrm{mix})}_{m_A}. \end{aligned} \tag{57}$$

For the pole term generated at $\omega = -E_{m,A} + i\epsilon$, we need the second term in parentheses, with the result

$$\begin{aligned}\mathcal{Q}^{(\mathrm{mix})}_{m_A} = &-\frac{\langle\psi_A|d_{Ai}|m_A\rangle\,\langle m_A|d_{Ak}|\psi_B\rangle}{(4\pi\epsilon_0)^2\,R^6}\,\alpha_{A\underline{B},j\ell}\left(\frac{E_{m,A}}{\hbar}\right)\exp\left(-\frac{2i\,E_{m,A}R}{\hbar c}\right)\left[\beta_{ij}\,\beta_{k\ell}\left(1+2i\,\frac{E_{m,A}\,R}{\hbar c}\right)\right. \\ &\left.-(2\alpha_{ij}\,\beta_{k\ell}+\beta_{ij}\,\beta_{k\ell})\left(\frac{E_{m,A}R}{\hbar c}\right)^2-2i\alpha_{ij}\,\beta_{k\ell}\left(\frac{E_{m,A}R}{\hbar c}\right)^3+\alpha_{ij}\,\alpha_{k\ell}\left(\frac{E_{m,A}R}{\hbar c}\right)^4\right] = \mathcal{P}^{(\mathrm{mix})} - \frac{i}{2}\Gamma^{(\mathrm{mix})}. \end{aligned} \tag{58a}$$

The real part of the pole contribution to the mixing term is

$$\begin{aligned}\mathcal{P}^{(\mathrm{mix})}_{m_A} = &-\frac{\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_B\rangle}{(4\pi\epsilon_0)^2\,R^6}\alpha_{A\underline{B},j\ell}\left(-\frac{E_{m,A}}{\hbar}\right)\left\{\cos\left(2\frac{E_{m,A}R}{\hbar c}\right)\left[\beta_{ij}\,\beta_{k\ell}-(2\alpha_{ij}\,\beta_{k\ell}+\beta_{ij}\,\beta_{k\ell})\right.\right. \\ &\left.\times\left(\frac{E_{m,A}\,R}{\hbar c}\right)^2+\alpha_{ij}\,\alpha_{k\ell}\left(\frac{E_{m,A}\,R}{\hbar c}\right)^4\right]+2\frac{E_{m,A}R}{\hbar c}\,\sin\left(2\frac{E_{m,A}R}{\hbar c}\right)\left.\left[\beta_{ij}\,\beta_{k\ell}-\alpha_{ij}\,\beta_{k\ell}\left(\frac{E_{m,A}R}{\hbar c}\right)^2\right]\right\}. \end{aligned} \tag{58b}$$

The corresponding width term is

$$\begin{aligned}\Gamma^{(\mathrm{mix})}_{m_A} = &-2\frac{\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_B\rangle}{(4\pi\epsilon_0)^2\,R^6}\alpha_{A\underline{B},j\ell}\left(-\frac{E_{m,A}}{\hbar}\right)\left\{\sin\left(2\frac{E_{m,A}R}{\hbar c}\right)\left[\beta_{ij}\,\beta_{k\ell}-(2\alpha_{ij}\,\beta_{k\ell}+\beta_{ij}\,\beta_{k\ell})\right.\right. \\ &\left.\times\left(\frac{E_{m,A}\,R}{\hbar c}\right)^2+\alpha_{ij}\,\alpha_{k\ell}\left(\frac{E_{m,A}\,R}{\hbar c}\right)^4\right]-2\frac{E_{m,A}R}{\hbar c}\,\cos\left(2\frac{E_{m,A}R}{\hbar c}\right)\left.\left[\beta_{ij}\,\beta_{k\ell}-\alpha_{ij}\,\beta_{k\ell}\left(\frac{E_{m,A}R}{\hbar c}\right)^2\right]\right\}. \end{aligned} \tag{58c}$$

The mixed polarizability $\alpha_{A\underline{B},j\ell}(\omega)$ has been defined in Eq. (32). The (total) Wick-rotated term from Eq. (56) is

$$\mathcal{W}^{(\mathrm{mix})} = -\frac{1}{\hbar}\int_0^\infty \frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(i\omega,\vec{R})\,D_{k\ell}(i\omega,\vec{R})\alpha_{A\underline{B},ik}(i\omega)\,\alpha_{\underline{A}B,j\ell}(i\omega). \tag{59}$$

The generalization of the energy shift ΔE given in Eq. (51) to the mixing term, in the van der Waals range, reads as follows:

$$\Delta E^{(\mathrm{mix})}_{m_A} \overset{R\to 0}{=} -\frac{1}{(4\pi\epsilon_0)^2\,R^6}\sum_{q_B}\frac{\beta_{ij}\,\beta_{k\ell}}{E_{m,A}+E_{q,B}}\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Bk}|\psi_B\rangle\langle\psi_A|d_{Aj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle. \tag{60}$$

The mixing contribution to the width term, at close range, is

$$\Gamma^{(\mathrm{mix})}_{m_A} \overset{R\to 0}{=} \frac{2[E_{m,A}/(\hbar c)]^3}{3\,(4\pi\epsilon_0)^2\,R^3}\left(\sum_{q_B,\pm}\frac{\beta_{ij}\beta_{k\ell}-3\alpha_{ij}\,\beta_{k\ell}}{\pm E_{m,A}+E_{q,B}}\right)\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Bk}|\psi_B\rangle\langle\psi_A|d_{Aj}|q_B\rangle\langle q_B|d_{B\ell}|\psi_B\rangle. \tag{61}$$

In the long-range limit, the mixed Wick-rotated term is

$$\mathcal{W}^{(\mathrm{mix})} \overset{R\to\infty}{=} -\frac{\hbar c}{8\pi(4\pi\epsilon_0)^2R^7}(3\alpha_{ij}\alpha_{kl}+5\alpha_{ij}\beta_{kl}+5\beta_{ij}\beta_{kl})\,\alpha_{A\underline{B},ik}(0)\,\alpha_{A\underline{B},j\ell}(0). \tag{62}$$

The mixed pole term has the leading long-range asymptotics

$$\mathcal{P}^{(\mathrm{mix})}_{m_A} \overset{R\to\infty}{=} -\frac{1}{(4\pi\epsilon_0)^2\,R^2}\left(\frac{E_{m,A}}{\hbar c}\right)^4\cos\left(\frac{2E_{m,A}R}{\hbar c}\right)\alpha_{ij}\alpha_{kl}\,\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_B\rangle\alpha_{A\underline{B},j\ell}\left(-\frac{E_{m,A}}{\hbar}\right). \tag{63}$$

Finally, the mixed width term is

$$\Gamma^{(\mathrm{mix})}_{m_A} \overset{R\to\infty}{=} -\frac{2}{(4\pi\epsilon_0)^2\,R^2}\left(\frac{E_{m,A}}{\hbar c}\right)^4\sin\left(\frac{2E_{m,A}R}{\hbar c}\right)\alpha_{ij}\alpha_{kl}\,\langle\psi_A|d_{Ai}|m_A\rangle\langle m_A|d_{Ak}|\psi_B\rangle\alpha_{A\underline{B},j\ell}\left(-\frac{E_{m,A}}{\hbar}\right). \tag{64}$$

Due to the symmetry of the wave function, the total interaction energy $\Delta E^{(\mathrm{dir})} \pm \Delta E^{(\mathrm{mix})}$ and, also, the Wick-rotated term

$$\mathcal{W} = \mathcal{W}^{(\mathrm{dir})} \pm \mathcal{W}^{(\mathrm{mix})} \tag{65}$$

and the pole and width terms

$$\mathcal{P}_{m_A} = \mathcal{P}^{(\mathrm{dir})}_{m_A} \pm \mathcal{P}^{(\mathrm{mix})}_{m_A}, \quad \Gamma_{m_A} = \Gamma^{(\mathrm{dir})}_{m_A} \pm \Gamma^{(\mathrm{mix})}_{m_A} \tag{66}$$

are the sums of the direct and an exchange (mixing) contribution.

D. Excited reference *S* states

1. Pole term for S states

For S states (i.e., when atom A is in a state with S symmetry), a number of simplifications are possible, as we can replace $\alpha_{A,ik}(\omega) \to \delta_{ik}\,\alpha_A(\omega)$ [see Eq. (33)]. We restrict the discussion to the direct term. The interaction energy, (29), becomes

$$\Delta E^{(\mathrm{dir})} = \frac{i}{\hbar}\int_0^\infty \frac{d\omega}{2\pi}\,\omega^4\,D_{ij}(\omega,\vec{R})D_{ji}(\omega,\vec{R})\,\alpha_A(\omega)\,\alpha_B(\omega). \tag{67}$$

The pole term for an energetically lower $|m_A P\rangle$ state becomes

$$\begin{aligned}\mathcal{Q}^{(\mathrm{dir})} = &-\frac{2}{3(4\pi\epsilon_0)^2R^6}\langle n_A S|\vec{d}_A|m_A P\rangle\cdot\langle m_A P|\vec{d}_A|n_A S\rangle\alpha_B\left(\frac{E_{m,A}}{\hbar}\right)\exp\left(-\frac{2i\,E_{m,A}R}{\hbar c}\right)\\ &\times\left[3+6i\frac{E_{m,A}R}{\hbar c}-5\left(\frac{E_{m,A}R}{\hbar c}\right)^2-2i\left(\frac{E_{m,A}R}{\hbar c}\right)^3+\left(\frac{E_{m,A}R}{\hbar c}\right)^4\right].\end{aligned} \tag{68}$$

The real part is

$$\begin{aligned}\mathcal{P}^{(\mathrm{dir})} = &-\frac{2}{3(4\pi\epsilon_0)^2R^6}\langle n_A S|\vec{d}_A|m_A P\rangle\cdot\langle m_A P|\vec{d}_A|n_A S\rangle\alpha_B\left(\frac{E_{m,A}}{\hbar}\right)\left\{\cos\left(\frac{2E_{m,A}R}{\hbar c}\right)\right.\\ &\left.\times\left(3-5\left(\frac{E_{m,A}R}{\hbar c}\right)^2+\left(\frac{E_{m,A}R}{\hbar c}\right)^4\right)+\frac{2E_{m,A}R}{\hbar c}\sin\left(\frac{2E_{m,A}R}{\hbar c}\right)\left(3-\left(\frac{E_{m,A}R}{\hbar c}\right)^2\right)\right\}.\end{aligned} \tag{69}$$

The corresponding width term is

$$\begin{aligned}\Gamma^{(\mathrm{dir})} = &-\frac{4}{3(4\pi\epsilon_0)^2R^6}\langle n_A S|\vec{d}_A|m_A P\rangle\cdot\langle m_A P|\vec{d}_A|n_A S\rangle\alpha_B\left(\frac{E_{m,A}}{\hbar}\right)\left\{\sin\left(\frac{2E_{m,A}R}{\hbar c}\right)\right.\\ &\left.\times\left(3-5\left(\frac{E_{m,A}R}{\hbar c}\right)^2+\left(\frac{E_{m,A}R}{\hbar c}\right)^4\right)-\frac{2E_{m,A}R}{\hbar c}\cos\left(\frac{2E_{m,A}R}{\hbar c}\right)\left(3-\left(\frac{E_{m,A}R}{\hbar c}\right)^2\right)\right\}.\end{aligned} \tag{70}$$

We recognize a number of prefactors also present in Eq. (19) of Ref. [2] and recall the definition of the S-state polarizability from Eq. (33). In the sum-over-states representation, the polarizability relevant to the pole term reads

$$\alpha_B\left(\frac{E_{m,A}}{\hbar}\right) = \frac{1}{3}\sum_{q_B}\langle n_B S|\vec{d}_B|q_B P\rangle\cdot\langle q_B P|\vec{d}_B|n_B S\rangle\left(\frac{1}{E_{q,B}-E_{m,A}}+\frac{1}{E_{q,B}+E_{m,A}}\right). \tag{71}$$

We recall that the pole term persists only for $E_{m,A} < 0$.

2. Wick-rotated term for S states

For S states, the Wick-rotated term, (45), becomes

$$\begin{aligned}\mathcal{W}^{(\mathrm{dir})} = &-\frac{\hbar}{\pi c^4(4\pi\epsilon_0)^2}\int_0^\infty\frac{d\omega}{\pi}\,e^{-2\omega R/c}\,\frac{\omega^4}{R^2}\\ &\times\left(1+\frac{2}{\omega R}+\frac{5c^2}{(\omega R)^2}+\frac{6c^3}{(\omega R)^3}+\frac{3c^4}{(\omega R)^4}\right)\\ &\times\alpha_A(i\omega)\,\alpha_B(i\omega).\end{aligned} \tag{72}$$

Irrespective of whether the virtual state $|m_A\rangle$ is energetically lower or higher than the reference state, the long-range limit of $\mathcal{W}$ due to the virtual P state $|m_A P\rangle$ is given as follows:

$$\begin{aligned}\mathcal{W}^{(\mathrm{dir})}_{m_A} \approx &-\frac{23}{9\pi}\frac{\hbar c}{(4\pi\epsilon_0)^2}\frac{1}{R^7}\\ &\times\frac{\langle\psi_A S|\vec{d}_A|m_A P\rangle\cdot\langle m_A P|\vec{d}_A|\psi_A S\rangle}{E_{m,A}}\\ &\times\sum_{q_B}\frac{\langle\psi_B S|\vec{d}_B|q_B P\rangle\cdot\langle q_B P|\vec{d}_B|\psi_B S\rangle}{E_{q,B}}, \quad R\to\infty.\end{aligned} \tag{73}$$

Restoring the sum over m_A, one verifies that

$$\mathcal{W}^{(\mathrm{dir})} \approx -\frac{23}{4\pi}\frac{\hbar c}{(4\pi\epsilon_0)^2}\frac{1}{R^7}\,\alpha_A(0)\,\alpha_B(0), \quad R\to\infty, \quad (74)$$

where the static S-state polarizabilities are given by

$$\alpha_A(0) = \frac{2}{3}\sum_{v_A}\frac{\langle\psi_A S|\vec{d}_A|v_A P\rangle\cdot\langle v_A P|\vec{d}_A|\psi_A S\rangle}{E_{vn,A}}, \quad (75a)$$

$$\alpha_B(0) = \frac{2}{3}\sum_{q_B}\frac{\langle\psi_B S|\vec{d}_B|q_B P\rangle\cdot\langle q_B P|\vec{d}_B|\psi_B S\rangle}{E_{q,B}}. \quad (75b)$$

IV. CONCLUSIONS

We have investigated the van der Waals interaction between two atoms in a general setting, allowing for one of the (conceivably identical) atoms to be in an excited state. The expressions obtained are widely applicable. We employed the Feynman prescription propagators for the electromagnetic field, a prescription which we saw naturally arises out of time-dependent perturbation theory. Time-ordered expectation values of the atomic dipole operators are used. Our result, (29), has been kept in fully tensorial form. Our derivation can be applied to arbitrary angular symmetry of the atomic reference states involved. The general result given in Eq. (29) allows us to split the contribution of an energetically lower state $|m_A\rangle$ of the excited atom A into a pole and a width term, given in Eqs. (43b) and (43d), and a Wick-rotated term, given in Eq. (45). For an energetically lower virtual state $|m_A\rangle$, the short-range limit of the Wick-rotated term has an interesting sign change [see Eq. (48)] and would lead to a repulsive contribution to the van der Waals interaction. However, the pole term compensates this unphysical behavior and restores the correct short-range limit [see Eqs. (49) and (51)]. The additional mixing term incurred for identical atoms is discussed in Eqs. (58b), (58c), and (59).

The formalism used here involves the matching of the scattering amplitude to the effective Hamiltonian. The use of Feynman propagators allows us to drastically reduce the number of diagrams which need to be considered (Fig. 1) in comparison to time-ordered perturbation theory [1,5], because all the possible time orderings of the electron-photon vertices are already contained in the Feynman formalism. The fully retarded result, and the gerade-ungerade mixing term including all nonresonant states, is included in one single, coherent formalism. Indeed, it was the tremendous simplifications incurred by the use of Feynman propagators which allowed the simplified evaluation of loop integrals in the early days of QED [22].

We confirm that for a system involving an atom in an excited state, the "retarded" $1/R^7$ Casimir-Polder asymptotics [21] is never fully reached. Indeed, this $1/R^7$ behavior originates in the Wick-rotated version of the integral over photon frequencies, which gives the interaction energy [see Eq. (52) for the general tensorial structure of this Wick-rotated long-range limit]. However, if one of the atoms (say, atom A) is excited, then poles in the complex energy plane are picked up upon a Wick rotation of the integration contour. These poles correspond to virtual states energetically lower than the reference state and, therefore, are not present in the ground state. In the large-interatomic-separation limit, these pole contributions exhibit a surprising $1/R^2$ asymptotics [see Eq. (53)]. When the interatomic distance becomes longer than the wavelength $\hbar c/|E_{m,A}|$ (where $|E_{m,A}|$ is the transition energy between the reference state and a lower-energy level accessible through a dipole transition), the pole contribution becomes larger than the Wick-rotated contribution (the latter corresponding to the usual Casimir-Polder $1/R^7$ asymptotics), with the rule of thumb that

$$\frac{\mathcal{P}}{\mathcal{W}_{m_A}} \sim \alpha^5\left(\frac{R}{a_0}\right)^5 \quad (76)$$

in the Casimir-Polder range. Let us conclude with a few remarks on the interaction of a metastable $2S$ state in hydrogen with a ground-state atom [23–25]. The $2P_{1/2}$ states are energetically lower than the reference $2S$ state but displaced only by the Lamb shift $\mathcal{L}$. Their contribution is suppressed, even in the oscillatory terms, due to the $E_{m,A}^4 = \mathcal{L}^4$ prefactor. In the Lamb shift range $R\sim\hbar c/\mathcal{L}$ (when R becomes commensurate with the Lamb shift wavelength), the static polarizability of the $2S$ state has the Lamb shift in the denominator, so that the $1/R^7$-Wick-rotated term of the interaction energy shift is of the order $1/(\hbar c/\mathcal{L})^7\,(\mathcal{L}/\hbar c)^{-1} = [\mathcal{L}/(\hbar c)]^6$. For $R\sim\hbar c/\mathcal{L}$, it competes with the oscillatory term which is of the same order of magnitude, namely, $[\mathcal{L}/(\hbar c)]^4/[R/(\hbar c)]^2 = [\mathcal{L}/(\hbar c)]^4/[\mathcal{L}/(\hbar c)]^2 = [\mathcal{L}/(\hbar c)]^6$. In the given distance range, the interaction energy is of order $\alpha^{24}m_e c^2$, where m_e is the electron mass, and thus is negligible. The oscillatory term exists for the $2S$-$1S$ interaction, but it dominates only for distances so long that no drastic surprises can be expected for frequency shifts due to long-range interactions, within high-precision spectroscopy [26]. The suppression mainly is due to the smallness of the Lamb shift; analogous observations have recently been made in Ref. [6], where the $2P$ admixtures to a reference $2S$ state in hydrogen have been calculated for atom-wall interactions: A parametrically interesting long-range tail has been identified, but it was found to be suppressed due to the smallness of the Lamb shift.

The situation is different for highly excited states, where the energy shift naturally splits into a pole term, a width term, and a Wick-rotated term. This is applicable both to the "direct" and to the "mixing" term [see Eqs. (41) and (55)]. Our general results, (29), (43b), (43d), and (53), are applicable to the direct term. The corresponding results, for the mixing term which is relevant for van der Waals interactions among identical atoms, can be found in Eqs. (31), (58b), (58c), and (63).

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APPENDIX: SIGNIFICANCE OF NONRESONANT STATES

We should clarify the relation of our work to other recent studies [1,3] which are based on a restricted subset of atomic states, for the two atoms participating in the interaction, and the reference work [8] which uses time-ordered perturbation theory. Let us start with the latter endeavor. The Feynman

propagators [see Eq. (22)], which are used in our derivation, capture different time orderings of the electron-photon interactions in one full sweep. As the propagator captures different time orderings of electron-photon interactions in one single expression, it was possible in the early days of QED [27] to carry out the so-called virtual loop integrals of the vacuum polarization and self-energy [28,29]. Using the Feynman formalism, the 12 time-ordered diagrams for the van der Waals interaction (given in a number of places in the literature, including Fig. 1 of Ref. [8]) can be replaced by just two diagrams, given in Fig. 1, which involve Feynman propagators. The latter approach also eliminates any guesswork on where to place the infinitesimal imaginary parts in the denominators which determine the location of the poles.

Our result interpolates between the close-range nonretarded van der Waals regime and the long-range tails. When one adds the pole term and the Wick-rotated term, in our approach, then one gets the van der Waals result back, in the close-range limit [see Eq. (51)]. In order for this to happen, one has to include the nonresonant virtual states in the formalism right from the start. In the long range, the pole term dominates [see Eq. (52)]. In the van der Waals limit, on the other hand, all the nonresonant, virtual states of the atom become relevant.

The alternative approach, as outlined in Refs. [1,3], restricts the discussion to a few "active" states, namely, to the ground state and a single excited state, for each of the atoms. Based on this approximation, the quantum dynamics can be formulated within the few-state approximation (for an outline of the formalism used, see also Ref. [30]). The validity of this treatment is restricted to nonidentical atoms with two close resonances.

Our approach is much more general. It would be quite difficult, if not impossible, to generalize the treatment outlined in Refs. [1,3] to an infinite number of virtual states. This endeavor would inevitably result in an infinite number of coupled differential equations. Our general formulas, on one hand, capture the tensor structure of the pole terms due to energetically lower virtual states (the $1/R^2$ long-range tail) and, on the other hand, yield the correct van der Waals close-range result (proportional to $1/R^6$).

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