Resonant Energy Exchange between Atoms in Dispersing and Absorbing Surroundings

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Within the framework of quantization of the macroscopic electromagnetic field, a master equation describing both the resonant dipole-dipole interaction (RDDI) and the resonant atom-field interaction (RAFI) in the presence of dispersing and absorbing macroscopic bodies is derived, with the relevant couplings being expressed in terms of the surroundings-assisted Green tensor. It is shown that under certain conditions the RDDI can be regarded as being governed by an effective Hamiltonian. The theory, which applies to both weak and strong atom-field coupling, is used to study the resonant energy exchange between two (two-level) atoms sharing initially a single excitation. In particular, it is shown that in the regime of weak atom-field coupling there is a time window, where the energy transfer follows a transfer-rate law of the type obtained by ordinary second-order perturbation theory. Finally, the spectrum of the light emitted during the energy transfer is studied and the line splittings are discussed.

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I. INTRODUCTION

It is well known that an initially excited molecule can irreversibly transfer its energy to unexcited species located nearby—a fundamental process involved in ultrafast photochemistry, excitation transport in Langmuir-Blodgett films, determination of molecular structures, etc.. For (acceptor) molecules that exhibit a sufficiently broad (quasi-)continuum of vibronic states, the energy transfer may be regarded as being irreversible, and the transfer rate can be calculated by using standard second-order perturbation theory (see, e.g., [1] and references therein). If instead of molecules, the donor and acceptor species are (two-level) atoms, the transfer can be reversed in principle, leading to a back-and-forth energy exchange between the atoms [2]. This process can be thoroughly described by a nonperturbative treatment. When the interatomic interaction is weak, however, the probability of the return transfer can be so small that the energy exchange is essentially again a one-way process. In addition to that, the atoms always feature some natural linewidths, which can be regarded as continua of states. An aim of the present article is to establish the connection between the intermolecular energy transfer and the spontaneous-decay-assisted interatomic energy exchange.

The underlying mechanism of intermolecular and interatomic energy transfer can be both RDDI and RAFI [3]. In free space and for transfer distances $R$ below the wavelength of real-photon emission, the RDDI described in terms of an instantaneous Coulomb interaction potential with the familiar $R^{-3}$ distance law is typically considered as the leading mechanism. For transfer distances exceeding the wavelength of real-photon emission, the RDDI may be thought of as resulting from an extended off-resonant atom-field interaction, and the effect of the RAFI needs to be considered carefully. In particular, in the multipolar-coupling quantum electrodynamics [4], the near-zone and far-zone results simply arise as limits of a unified theory based on the full atom-field coupling (in electric-dipole approximation).

Similar to the single-atom spontaneous decay, the interatomic energy exchange can be strongly affected by the presence of material surroundings. While RDDI and RAFI in free space have been more or less well understood, there have been a number of open problems when material surroundings are present. In particular, it is not clear whether the near-zone $R^{-3}$ law is still generally valid. Another problem that needs investigation is the regime of strong RAFI, i.e., when suitably chosen material surroundings form a high-$Q$ (micro-)resonator, which gives rise to a strong atom-field coupling accompanied by quantum Rabi oscillations. These and related problems have recently been very actual in view of proposals to entangle atoms (see, e.g., [5]) and to implement quantum logic gates (see, e.g., [6, 7]), using atoms in a cavity, impurities in the condensed phase, or quantum dots in a semiconductor.

For two atoms that interact with cavity-type modes, a Hamiltonian for treating both RDDI and RAFI was suggested in [8]. In the Hamiltonian, an effective dipole-dipole interaction energy, which may be thought of as resulting from a perturbative treatment of the off-resonant atom-field coupling, is added to the exact on-resonant atom-field interaction energy. Unfortunately, the relevant coupling strengths are introduced as parameters rather than physically determined system quantities. Moreover, the underlying mode expansion concept makes the theory inapplicable for the realistic case of absorbing
and dispersing material surroundings. Inclusion of material absorption and dispersion is especially important in designing quantum computing systems where dissipation and decoherence have to be strictly kept under control.

In what follows we give a more rigorous approach to the problem, basing on a recently developed quantization scheme for the electromagnetic field in the presence of (linear) absorbing and dispersing macroscopic bodies (see [9] and references therein). In this scheme, an operator noise polarization source is introduced into the Maxwell equations, and the electromagnetic field operators are given by a source-quantity representation in terms of the classical Green tensor and a continuous set of bosonic vector fields, which play the role of the fundamental variables of the composite system of the electromagnetic field plus the media. The Green tensor, which can be calculated in a purely classical manner, is essentially determined by the (Kramers-Kronig consistent) space- and frequency-dependent complex permittivity, which characterizes the relevant properties of the macroscopic bodies. The medium-assisted electromagnetic field can then be coupled to additional atomic systems, and the minimal-coupling Hamiltonian can be derived by means of a unitary transformation.

By using the multipolar-coupling Hamiltonian in electric-dipole approximation, in Section II an equation of motion for the reduced density operator of a system that consists of two-level atoms and that part of the medium-assisted electromagnetic field that resonantly interacts with the atoms is derived. It is shown that when the (shifted) atomic transition frequencies differ by amounts small compared to the scale of the frequency variation of the Green tensor, the system can be regarded as being governed by a Hamiltonian, with the RDDI being described by a well-defined effective interaction energy. The problem of resonant energy exchange between two two-level atoms is studied in Section III, with special emphasis on the rate regime. The spectrum of the light emitted during the energy exchange is considered in Section IV. Finally, some concluding remarks are given in Section V.

II. REDUCED DENSITY OPERATOR EQUATION

A system of $N$ two-level atoms [positions $r_A$, transition frequencies $\omega_A$, transition dipole moments $d_A$ ($A = 1, 2, \ldots, N$)] interacting with the electromagnetic field via electric-dipole transitions in the presence of dispersing and absorbing bodies can be described by the multipolar-coupling Hamiltonian [10]

$$\hat{H} = \int d^3r \int_0^\infty d\omega \ h\omega \ \hat{f}^\dagger(r, \omega) \hat{f}(r, \omega) + \sum_A \frac{1}{2} \hbar \omega_A \hat{\sigma}_A$$

and

$$- \sum_A \int_0^\infty d\omega \left[ \hat{d}_A \hat{E}(r_A, \omega) + \text{H.c.} \right],$$

where

$$\hat{d}_A = \hat{d}_A \hat{\sigma}_A + \hat{d}_A^\dagger \hat{\sigma}_A$$

and

$$\hat{E}(r, \omega) = i \sqrt{\frac{\hbar}{\pi \varepsilon_0 c}} \int d^3r' \sqrt{\varepsilon(r', \omega)} \hat{G}(r, r', \omega) \hat{f}(r', \omega).$$

Here, $\hat{f}(r, \omega)$ and $\hat{f}^\dagger(r, \omega)$ are bosonic fields which play the role of the fundamental variables of the electromagnetic field and the medium, including a reservoir necessarily associated with the losses in the medium, $\hat{G}(r, r', \omega)$ is the classical Green tensor, and $\varepsilon(r, \omega) = \varepsilon_R(r, \omega) + i \varepsilon_I(r, \omega)$ is the complex permittivity. There are no direct Coulomb forces between the particles in the multipolar-coupling Hamiltonian [11]; all interactions are mediated by the medium-assisted electromagnetic field.

With regard to the interaction of the atoms with the electromagnetic field, it is convenient to decompose the latter into an on-resonant part (denoted by $\int_0^{2\pi} d\omega \ldots$) and an off-resonant part (denoted by $\int_0^{2\pi} d\omega \ldots$). Let us consider the temporal evolution of the system that consists of the atoms and the on-resonant part of the electromagnetic field. For this purpose we formally solve the Heisenberg equation of motion for $\hat{f}(r, \omega)$ [and $\hat{f}^\dagger(r, \omega)$] and insert the result into the equation of motion for an arbitrary system operator. Applying a (coarse-grained) Markov approximation to the slowly varying atomic variables in the off-resonant frequency integrals, and assuming that the off-resonant free-field is initially $(t = 0)$ prepared in the vacuum state, after some algebra, we derive the following equation of motion for the system density operator in the Schrödinger picture:

$$\dot{\hat{\rho}} = -\frac{i}{\hbar} \left[ \hat{H}_R, \hat{\rho} \right]$$

$$+ \left\{ i \sum_{A,A'} \left[ \hat{\sigma}_A^\dagger \hat{\sigma}_A, \hat{\sigma}_A^\dagger \hat{\sigma}_A \right] \right\} + \text{H.c.},$$

where

$$\hat{H}_R = \int d^3r \int_0^{2\pi} d\omega \ h\omega \ \hat{f}^\dagger(r, \omega) \hat{f}(r, \omega) + \sum_A \frac{1}{2} \hbar \omega_A \hat{\sigma}_A^\dagger \hat{\sigma}_A$$

$$- \sum_A \int_0^\infty d\omega \left[ \hat{d}_A \hat{E}(r_A, \omega) + \text{H.c.} \right],$$

and the notation $\sum'_{A,A'}$ indicates that $A \neq A'$. In Eqs. [12] and [13], the shifted atomic transition frequencies and
the resonant dipole-dipole coupling strengths are defined according to

\[ \hat{\omega}_A = \omega_A - \delta_{A^*A}. \]  

(6)

\[ \delta_{A^*A} = \delta_{A^*A} - \delta_{A^+A^*}. \]  

(7)

\[ \delta_{A^+A^*} = \frac{\mathcal{P}}{\pi \hbar \epsilon_0} \int_0^\infty \, \frac{\omega^2 \, d_A \, \text{Im} \, G(r_A, r_{A'}, \omega)}{\omega - (\pm)\hat{\omega}_{A'}} \omega \, d\omega \]  

(8)

\[ [\mathcal{P} - \text{principal value}]. \] The notation \( A^* \) (\(^*A\)) means that the relations from each other, then \( \delta_{A^*A} \) and \( \delta_{A^+A^*} \) are (approximately) valid.

From Eq. (8) it is seen that when the transition frequencies \( \hat{\omega}_A \) and \( \hat{\omega}_{A'} \) of two atoms \( A \) and \( A' \) are different from each other, then \( \delta_{A^*A} \) and \( \delta_{A^+A^*} \) are not symmetric with respect to \( A \) and \( A' \). Only if the differences \( \hat{\omega}_A - \hat{\omega}_{A'} \) are small compared with the frequency scale of variation of the Green tensor, so that

\[ \delta_{A^*A} \approx \delta_{A^+A^*}. \]  

(11)

holds, this asymmetry can be disregarded. Then Eq. (8) reduces to

\[ \hat{\omega}_A = \omegahat_A - \delta_{A^*A} + \delta_{A^+A^*}. \]  

(9)

\[ \delta_{A^+A^*} = \frac{\mathcal{P}}{\pi \hbar \epsilon_0} \int_0^\infty \, \frac{\omega^2 \, d_A \, \text{Im} \, G(r_A, r_{A'}, \omega)}{\omega - (\pm)\hat{\omega}_{A'}} \omega \, d\omega \]  

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(11)
of the rest of the system, and \( \hat{f}(\mathbf{r}, \omega) | \{0\} \rangle \) is a state, where a single quantum is excited.

From the effective Hamiltonian given in Eq. (13), we obtain the following system of coupled integrodifferential equations for the (slowly-varying) upper-state probability amplitudes \( C_A \):

\[
\dot{C}_A(t) = \sum_{A' \neq A} i \delta_{AA'} e^{i(\omega_A - \omega_{A'}) t} C_{A'}(t) + \sum_{A'} \int_0^t dt' \int_0^{t'} d\omega K_{AA'}(t, t'; \omega) C_{A'}(t'),
\]

where

\[
K_{AA'}(t, t'; \omega) = -\frac{1}{\hbar \pi \varepsilon_0} \left[ \frac{\omega^2}{c^2} e^{-i(\omega - \omega_A)t} e^{i(\omega - \omega_{A'})t'} \right] \times \mathbf{d}_A \text{Im} \mathbf{G}(\mathbf{r}_A, \mathbf{r}_{A'}, \omega) \mathbf{d}_{A'}. \tag{18}
\]

We see that the RAfI is determined by the imaginary part of the Green tensor. In order to get insight into the atomic motion on the basis of closed solutions, let us consider two atoms and restrict our attention to the limiting cases of weak and strong RAfI.

A. Weak atom-field coupling

In the weak coupling regime, the integral expression in Eqs. (13) can be treated in a (coarse-grained) Markov approximation. We now make the simplifying assumption that the transition frequencies of the two atoms are nearly equal to each other, \( \tilde{\omega}_A \simeq \tilde{\omega}_B \), but allow for \( \Gamma_{AA'} \neq \Gamma_{BB'} \). The latter may happen, e.g., when the atoms \( A \) and \( B \) have different dipole matrix elements and/or different dipole orientations. It is then not difficult to solve Eqs. (17). In particular, if the atom \( B \) is initially in the lower state, \( C_B(t = 0) = 0 \), we obtain

\[
C_A = \frac{1}{2D} \left\{ \left[ -\frac{1}{2}(\Gamma_{AA'} - \Gamma_{BB'}) + D \right] e^{D_A t/2} + \left[ \frac{1}{2}(\Gamma_{AA'} - \Gamma_{BB'}) + D \right] e^{-D_A t/2} \right\}, \tag{19}
\]

\[
C_B = \frac{K_{BB'} A}{D} \left( e^{D_A t/2} - e^{-D_A t/2} \right), \tag{20}
\]

where

\[
\Gamma_{AA'} = \frac{2\omega_A^2}{\hbar \varepsilon_0 c^2} \mathbf{d}_A \text{Im} \mathbf{G}(\mathbf{r}_A, \mathbf{r}_{A'}, \tilde{\omega}_{A'}) \mathbf{d}_{A'}, \tag{21}
\]

\[
\mathcal{K}_{AB} = -\frac{1}{2} \delta_{AB} + i \delta_{AB}, \tag{22}
\]

\[
D = \left[ \frac{1}{2}(\Gamma_{AA'} - \Gamma_{BB'})^2 + 4\mathcal{K}_{AB} \sqrt{\mathcal{K}_{BB'}} \mathcal{K}_{AB} \right]^{1/2}, \tag{23}
\]

\[
D_\pm = -\frac{1}{2}(\Gamma_{AA'} + \Gamma_{BB'}) \pm D. \tag{24}
\]

When the two atoms are identical and have equivalent positions and dipole orientations with respect to the material surroundings such that the relations

\[
\Gamma_{AA'} = \Gamma_{BB'}, \tag{25}
\]

\[
\Gamma_{AB} = \Gamma_{BA}, \quad \delta_{AB} = \delta_{BA} \tag{26}
\]

are valid, we have \( \mathcal{K}_{AA'} = \mathcal{K}_{BB'} \), and \( \Gamma_{AB}, \Gamma_{BA}, \delta_{AB}, \text{ and } \delta_{BA} \) are real quantities due to the reciprocity of the Green tensor. Then Eqs. (19) and (20) yield

\[
P_{A(B)}(t) = \frac{1}{2} \left[ \cos(\Gamma_{AB} t) + \left(-\cos(2\delta_{AB} t)\right) e^{-\Gamma_{BB'} t} \right]. \tag{27}
\]

Eqs. (13) - (24) and thus Eq. (27) are valid for arbitrary dispersing and absorbing material surroundings of the atoms. In particular, substituting in Eqs. (21) and (22) for the Green tensor the vacuum Green tensor, Eq. (27) reduces to that one obtained in Ref. [3]. Accordingly, using the Green tensor for absorbing bulk material, the result in Ref. [4] is recognized.

From Eq. (27) a damped oscillatory excitation exchange between the two atoms is seen. For sufficiently small times, \( \Gamma_{BB'} t \ll 1 \), and strong RDDI, \( |\delta_{AB}| \gg \Gamma_{BB'} \), the oscillatory behavior dominates. This can typically be observed when the atoms are sufficiently near to each other, but can also be realized for more moderate distances with the interatom coupling being mediated by a high-Q medium-assisted field resonance [11]. In the opposite limit of weak resonant dipole-dipole coupling, \( P_A(t) \) decreases monotonously while \( P_B(t) \) features one peak which separates the regime of energy transfer from atom \( A \) to atom \( B \) at early times and the subsequent decay of the excited state of atom \( B \).

B. Rate regime

As already mentioned, for weak RDDI the energy transfer is one-way; that is, from atom \( A \) to atom \( B \). In this case, a transfer rate \( w_1 \) can be defined according to

\[
w_1 = \left. \frac{dP_B(t)}{dt} \right|_{t_0}, \tag{28}
\]

where \( t_0 \) is determined from the conditions that

\[
\left. \frac{d^2 P_B(t)}{dt^2} \right|_{t_0} = 0, \quad \left. \frac{dP_B(t)}{dt} \right|_{t_0} > 0. \tag{29}
\]

From Eq. (27) [together with Eqs. (23) and (24) for negligibly small \( \mathcal{K}_{AA'} \) and \( \mathcal{K}_{BB'} \) therein] it then follows that

\[
w_1 \simeq \frac{|K_{BB'}|^2}{D^2} e^{D_{-t_0}} \times \left[ D_+ + D_+ e^{2D_{t_0}} - (D_+ + D_-) e^{D_{t_0}} \right], \tag{30}
\]
\[ t_0 \simeq \frac{1}{D} \ln \left( \frac{1}{4D^2} \left( (D_+ + D_-)^2 - 2D \left[ (D_+ + D_-)^2 + 4D_+D_- \right]^{1/2} \right) \right). \] (31)

Let us analyze Eq. (30) for three particular cases.

(i) If \( \Gamma_{A^*A} \gg \Gamma_{B^*B} \) is valid, then from Eq. (31) it follows that \( \Gamma_{A^*A}t_0 = \ln 4 \), and Eq. (30) reduces to
\[ w_1 = |K_{B^*A}|^2 / \Gamma_{A^*A}. \] (32)

(ii) For \( \Gamma_{A^*A} = \Gamma_{B^*B} \) the relation \( \Gamma_{B^*B}t_0 = 2 - \sqrt{2} \) holds. Thus, Eq. (30) reads as
\[ w_1 \simeq |K_{B^*A}|^2 \left( \sqrt{2} - 1 \right) e^{-\left(2 - \sqrt{2}\right)} / \Gamma_{B^*B}. \] (33)

(iii) In the case where \( \Gamma_{B^*B} \gg \Gamma_{A^*A} \) is valid, one finds \( \Gamma_{B^*B}t_0 = \ln 4 \), so that Eq. (30) reduces to
\[ w_1 = |K_{B^*A}|^2 / \Gamma_{B^*B}. \] (34)

For molecules, a rate regime is commonly considered, and the transfer rate is calculated by means of Fermi's golden rule in second-order perturbation theory with regard to the molecule-field interaction,
\[ w = \sum_{f,i} p_i w_{fi}, \] (35)

where \( w_{fi} \) is proportional to the absolute square of the second-order interaction matrix element and the energy conserving \( \delta \)-function \( \delta(\omega_f - \omega_i) \), and the sum runs over the (quasi-)continuum of initial (i) and/or final (f) vibronic states. In particular, short-distance energy transfer, where the intermolecular coupling is essentially static, has been well known as Förster transfer \([4, 13]\). Later on energy transfer over arbitrary distances has been considered (see, e.g., \([1, 10]\) and references therein).

For two two-level atoms, the single-transition probability per unit time \( w_{fi} \) corresponds to \( \hat{p}_B \). Starting from the effective Hamiltonian \([13]\) and evaluating \( C_B(t) \) from Eq. (17) in first-order perturbation theory, we derive, on making the standard long-time assumption,
\[ \hat{p}_B = 2\pi |K_{B^*A}|^2 \delta(\tilde{\omega}_A - \tilde{\omega}_B), \] (36)

which is fully consistent with the result, obtained in second-order perturbation theory on the basis of the original (fundamental) Hamiltonian \([1, 10]\). The only new feature in the current treatment is that the medium-induced atomic frequency shifts are taken into account.

For establishing a rate regime, it is necessary that, according to Eq. (35), a continuum of initial and/or final states is involved in the transition. In the two-atom problem at hand, the continua of states are obviously provided by the atomic level broadening due to the spontaneous decay. Assuming Lorentzian line shapes, we may perform the integrals in Eq. (35) to obtain
\[ w = \frac{4|K_{B^*A}|^2}{\Gamma_{A^*A} + \Gamma_{B^*B}} p_A(\tilde{\omega}_A). \] (37)

Let us identify \( p_A(\tilde{\omega}_A) \) with \( P_A(t_0) \) [Eq. (27)] together with Eq. (30) and compare the result with the nonperturbative rate \( w_1 \) calculated from the exact temporal evolution of \( P_B(t) \) [Eq. (30)] together with Eq. (27). Noting that \( P_A(t_0) \simeq \exp(-\Gamma_{A^*A}t_0) \), we find for the three cases considered in Eqs. (32) – (34) the following results.

(i) \( \Gamma_{A^*A} \gg \Gamma_{B^*B}: \)
\[ P_A(t_0) \simeq \frac{1}{4}, \quad \frac{w_1}{w} \simeq 1. \] (38)

(ii) \( \Gamma_{A^*A} = \Gamma_{B^*B}: \)
\[ P_A(t_0) \simeq e^{-\left(2 - \sqrt{2}\right)}, \quad \frac{w_1}{w} \simeq \sqrt{2} - 1 \simeq 0.41. \] (39)

(iii) \( \Gamma_{B^*B} \gg \Gamma_{A^*A}: \)
\[ P_A(t_0) \simeq 1, \quad \frac{w_1}{w} \simeq \frac{1}{4}. \] (40)

Agreement between \( w_1 \) and \( w \) is observed in the first case, where \( \Gamma_{B^*B} \) is sufficiently small. With increasing value of \( \Gamma_{B^*B} \) an increasing discrepancy between \( w_1 \) and \( w \) is observed. The reason can be seen in the fact that there are two processes which simultaneously drive atom \( B \): the energy transfer from \( A \) to \( B \) and the spontaneous decay. Hence, \( w_1 \) is actually the rate of both processes combined, not the bare rate of energy transfer. This explains why \( w_1 \) is typically smaller than \( w \) and why the discrepancy between them becomes more substantial for enhanced spontaneous decay of atom \( B \). To roughly compensate for the first effect, the ratio \( w_1/w \) may be multiplied by \( \exp(\Gamma_{B^*B}t_0) \). The values of the so corrected ratio are then \( \simeq 1 \) for the cases (i) and (iii), and \( \simeq 0.74 \) for the case (ii).

C. Strong atom-field coupling

For the sake of transparency, we again consider identical atoms that have equivalent positions and dipole orientations with respect to the material surroundings so that Eqs. (23) and (26) hold. Introducing the probability amplitudes
\[ C_{\pm}(t) = 2^{-\frac{1}{2}} \left[ C_A(t) \pm C_B(t) \right] e^{\mp i\delta_{A^*B}t}, \] (41)
of the superposition states \( |\pm\rangle = 2^{-1/2} (|U_A\rangle \pm |U_B\rangle) \), from Eqs. (17) we find that the equations for \( C_+(t) \) and \( C_-(t) \) decouple,
\[ \dot{C}_\pm(t) = \int_0^t dt' \int_0^{\infty} d\omega K_\pm(t, t'; \omega) e^{\mp i\delta_{A^*B}(t-t')} C_\pm(t'), \] (42)
where

\[ K_{\pm}(t,t';\omega) = K_{A'B}(t,t';\omega) \pm K_{A'B}(t,t';\omega) \]  

(43)

Let us restrict our attention to the case when the absolute value of the two-atom term \( K_{A'B}(t,t';\omega) \) is of the same order of magnitude as the absolute value of the single-atom term \( K_{A'A}(t,t';\omega) \), so that there is a strong contrast in the magnitude of \( K_{A'A}(t,t';\omega) \) and \( K_{A'B}(t,t';\omega) \). Assuming that the imaginary part of the Green tensor in the resonance region of strong RAIF has a Lorentzian shape, with \( \omega_m \) and \( \Delta \omega_m \) being the central frequency and the half width at half maximum respectively, we can perform the frequency integral in Eq. (24) in a closed form in a similar way as in the single-atom case (14). In particular for exact resonance, i.e., \( \omega_m = \omega_A \mp \delta_{AB} \), we derive

\[ C_{\pm}(t) = 2^{-\frac{1}{2}} e^{-\Delta \omega_m t/2} \cos(\Omega_{\pm} t/2) \]  

(44)

\( (\Omega_{\pm} \gg \Delta \omega_m) \), where

\[ \Omega_{\pm} = \sqrt{2\Gamma_{\pm} \Delta \omega_m}, \quad \Gamma_{\pm} = \Gamma_{A'A} \pm \Gamma_{A'B} \]  

(45)

with \( \Gamma_{A'A} \) and \( \Gamma_{A'B} \) being defined according to Eq. (21) with \( \omega_m \) in place of \( \omega_A \). For the probability amplitudes of the remaining states \( |\mp\rangle \), which are weakly coupled to the field, we obtain

\[ C_{\mp}(t) = 2^{-\frac{1}{2}} e^{-\Gamma_{\mp} t/2} \]  

(46)

\( (\Omega_{\pm} \ll \Delta \omega_m) \). It then follows that

\[ P_{A(B)}(t) = \frac{1}{4} \left[ e^{-\Gamma_{\pm} t} + e^{-\Delta \omega_m t} \cos^2(\Omega_{\pm} t/2) \right. \]

\[ + \left. (-) e^{-(\Delta \omega_m + \Gamma_{\mp}) t/2} \cos(2\delta_{AB} t) \right] \]  

(47)

Note that in the equations given above the upper (lower) signs refer to the case where the state \( |+\rangle \ (|-\rangle) \) is strongly coupled to the medium-assisted field.

For small damping, between three typical cases can be distinguished.

(i) \(|\delta_{AB}| \gg \Omega_{\pm}, \ t \ll 2/\Omega_{\pm}:
\[ P_A(t) = \cos^2(\delta_{AB} t), \]  

(48)

\[ P_B(t) = \sin^2(\delta_{AB} t). \]  

(49)

(ii) \(|\delta_{AB}| \simeq \Omega_{\pm}, \ t \ll 1/[2\delta_{AB} - \Omega_{\pm}/2]:
\[ P_A(t) = \frac{1}{4} \left[ 1 + 3 \cos^2(\Omega_{\pm} t/2) \right], \]  

(50)

\[ P_B(t) = \frac{1}{4} \left[ 1 - \cos^2(\Omega_{\pm} t/2) \right]. \]  

(51)

(iii) \(|\delta_{AB}| \ll \Omega_{\pm}, \ t \ll 1/[2\delta_{AB}]:
\[ P_A(t) = \cos^2(\Omega_{\pm} t/4), \]  

(52)

\[ P_B(t) = \sin^4(\Omega_{\pm} t/4). \]  

(53)

From Eqs. (18) – (23) the following time-averaged probabilities \( \bar{P}_A, \bar{P}_B, \) and \( \bar{P}_L = 1 - \bar{P}_A - \bar{P}_B \) are obtained, with the respective time integral being taken over one cycle. (i) \( \bar{P}_A = \bar{P}_B = \frac{1}{2} \) and \( \bar{P}_L = 0. \) The excitation energy is periodically exchanged between the two atoms through virtual field excitations exclusively. (ii) \( \bar{P}_A = \frac{2}{3}, \bar{P}_B = \frac{1}{3}, \bar{P}_L = 0. \) The two exchange channels – one channel through virtual and the other one through real field excitations – compete with each other and destructively interfere, leading to a partial trapping of the excitation energy in atom A. (iii) \( \bar{P}_A = \bar{P}_B = \frac{2}{5}, \bar{P}_L = \frac{1}{5}. \) The interatom energy exchange is dominantly mediated by real field excitations.

IV. POWER SPECTRUM

Let us finally address the problem of the influence of the RDDI on the power spectrum of the light emitted during the decay-assisted energy exchange. To calculate the (physical) spectrum, we apply the formula (see, e.g., \( 14 \))

\[ S(\mathbf{r}, \omega_S, T) = \int_0^T dt_2 \int_0^T dt_1 \left[ e^{-i \omega_S (t_2 - t_1)} \right. \]

\[ \times \left. \langle \hat{E}(\mp)(\mathbf{r}, t_2) \hat{E}(\pm)(\mathbf{r}, t_1) \rangle \right]. \]  

(54)

where \( \omega_S \) is the setting frequency of the (ideal) spectral apparatus, \( T \) is the operating-time interval of the detector, and

\[ \hat{E}(\pm)(\mathbf{r}) = \int_0^\infty d\omega \hat{E}(\mathbf{r}, \omega), \]  

(55)

\[ \hat{E}(\mp)(\mathbf{r}) = \left[ \hat{E}(\pm)(\mathbf{r}) \right]^\dagger. \]  

(56)

A. Weak atom-field coupling

For weak RAIF, we derive, on basing on Eqs. (19), (24), (25), and (26),

\[ S(\mathbf{r}, \omega_S, T \to \infty) = \frac{1}{4} \frac{\mathbf{F}_A + \mathbf{F}_B}{\Delta \omega_S + \delta_{AB} + i\Gamma_0/2} \]

\[ + \frac{\mathbf{F}_A - \mathbf{F}_B}{\Delta \omega_S - \delta_{AB} + i\Gamma_0/2} \]  

(57)

where

\[ \Delta \omega_S = \omega_S - \omega_A \]  

(58)

and \( (A' = A, B) \)

\[ \mathbf{F}_{A'} = \frac{\tilde{\omega}_A^2}{\pi \epsilon_0 c^2} \int_0^\infty d\omega \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}_{A'}, \omega) \mathbf{d}_{A'} \xi(\tilde{\omega}_A - \omega). \]  

(59)
Note that replacing $\zeta(\tilde{\omega}_A - \omega)$ with $\pi \delta(\tilde{\omega}_A - \omega)$ would be too rough here. Equation (55) reveals that the RDDI may result in a doublet structure (two asymmetric lines at $\tilde{\omega}_A = \delta_{AB}$, with $\Gamma_\perp$ and $|F_A| = |F_B|$ being the widths and weights respectively). The line separation is seen to be twice the RDDI strength. A system of two two-level atoms, one of them initially excited, is obviously equivalent to a three-level system with two upper dressed states $|\pm\rangle$. The doublet structure can be understood as a result of the transitions of the dressed states to the ground state.

As can be seen from Eq. (57), an experimental observation of the doublet structure of the emitted light requires a delicate balancing act. The interatomic distance should not be too large to provide a reasonable level splitting, but it should not be too small to avoid $|F_A| = |F_B|$, i.e., quenching of one of the two lines. It is worth noting that the presence of macroscopic bodies may facilitate the detection of the doublet, because it offers the possibility of realizing strong RDDI even for interatomic distances much larger than the wavelength.

Another interesting feature is that, according to Eq. (45), either $\Gamma^+_\perp$ or $\Gamma^-_\perp$ can be much smaller than $\Gamma^+_A = \Gamma^-_B$. That is, the resonant dipole-dipole interaction can give rise to an ultraspectral line, albeit each time at the expense of the other line of the pair. If, e.g., a single atom is placed sufficiently near a microsphere, its spontaneous decay may be suppressed, with the emission line being accordingly narrowed. Compared to the emission line of a single atom, one line of the doublet observed for two atoms being present may be further narrowed by several orders of magnitude [1].

The RDDI-induced asymmetric splitting of the power spectrum is illustrated in Fig. 2 for two atoms near a microsphere. The solid line in Fig. 2 corresponds to an off-resonant atomic transition with not too strong RDDI and moderate contrast between $\Gamma^+_\perp$ and $\Gamma^-_\perp$. As the atomic transition frequency $\tilde{\omega}_A$ approaches (from the off-resonance side) the frequency, where the absolute value of the RDDI strength reaches its maximum, the two spectral lines move apart from each other, with one of them gradually getting so much broader that it eventually disappears (dashed and dotted lines). As $\tilde{\omega}_A$ shifts further towards the resonance line center, the RDDI weakens while the contrast between $\Gamma^+_\perp$ and $\Gamma^-_\perp$ increases even more. As a result, the singlet structure persists with the peak moving back to the central position (not shown).
where \((A' = A, B)\)

\[
\mathbf{W}_{A'} = \frac{\omega_m^2 \Delta \omega_{in}}{\epsilon_0 c^2 \Omega_\pm} \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}_{A'\pm}, \omega_m) \text{d}_{A'}. \quad (61)
\]

Here the upper (lower) signs again refer to the case where the state \(|+\rangle (| - \rangle)\) is strongly coupled to the medium-assisted field. Eq. (60) reveals that due to the strong RAFI a doublet observed for weak atom-field coupling may become a triplet, with one of the lines of the doublet being split into two lines. These lines separated by \(\Omega_\pm\) have equal widths (which are solely determined by the width of the medium-assisted field resonance) and equal weights. Note that their width and weight are different from those of the third line, which is closely related to a line of the doublet observed for weak RAFI. From Eq. (60) it is also seen that, depending on the point of observation, this line or the strong-coupling-assisted doublet can be suppressed due to the interference effects.

The effect of strong RAFI on the spectrum of the emitted light is illustrated in Fig. 3 for two atoms near a microsphere. Three typical situations are shown, namely (i) strong, (ii) moderate, and (iii) weak RDDI (cf. Subsection III C). Note that the triplet structure is most pronounced in the first case.

V. CONCLUDING REMARKS

We have developed a fully quantum mechanical theory to describe both RDDI and RAFI in the presence of arbitrarily configured dispersing and absorbing material bodies. In particular, the concept of RDDI works well for arbitrary atom-field coupling strengths. Though both the single-atom level shifts and the RDDI strengths result from the off-resonant atom-field interaction and are formally given by the similar-looking Eqs. (60) and (61), respectively, Eq. (60) applies only to the level shifts caused by the scattering part of the Green tensor. The level shifts that are related to the vacuum field fluctuations have to be dealt with separately due to the divergence of the real part of the vacuum Green tensor at equal positions. In our calculations, they have been thought of as being already included in the bare atomic transition frequencies. By contrast, the real part of the Green tensor at different positions is finite and Eq. (61) can thus be used to calculate the total RDDI strengths caused by both vacuum and scattered-field fluctuations. In the same context, it might be incorrect to apply the rotating-wave approximation in the study of the RDDI. While the (scattering-assisted) level shifts \(\delta_{A' A}^\pm\), which result from counterrotating terms, are small in general [cf. Eqs. (7) and (9)], the corresponding RDDI strengths \(\delta_{A' A}^\pm\) can be significant, especially when the mutual distances of the dipoles are very small [cf. Eq. (10)]. To demonstrate the usefulness of the theory, we have applied it to the problem of resonant energy exchange between two atoms. In particular, we have shown that the RDDI can give rise to spectral line splittings of the light emitted during the decay-assisted energy exchange process. With a locally excited dipole as a probe, the effect may be employed, e.g., in imaging single atoms on a surface by scanning near-field optical microscopy techniques. The (numerical) calculations performed for atoms near a microsphere can of course be extended to other geometries of the material surroundings such as planarly stratified or cylindrical objects. It should also be mentioned that the theory is also readily extendable to the case of externally driven atoms.

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