Microscopic analysis of spontaneous emission in absorbing dielectrics

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Abstract

Spontaneous emission has been analyzed in an absorbing dielectric. The decay rate has been obtained for an excited atom (molecule) calculating the total rate of excitation transfer to the surrounding species. The contribution due to the far-zone energy transfer has been identified as the rate of photon emission in the absorbing medium. The analysis treats the surrounding medium microscopically, so that effects due to discreteness of the medium (such as the local field effects) are reflected intrinsically in the decay rates. The microscopic approach supports the previous introduction of the local field factors on a phenomenological basis. © 1998 Elsevier Science B.V. All rights reserved.

Over the recent years, there has been a great deal of interest in modified spontaneous emission by atoms (molecules) in various environments, such as in photonic band-gap crystals [1] and near-dielectric interfaces [2]. Spontaneous emission is altered in homogeneous dielectrics as well [3–9]. The rate of the process reads, in the case of photon emission into transparent areas of a dielectric [3, 6–9]:

$$\Gamma_A^{\text{sp-em}} = \frac{|\mu^A|^2 \omega^3}{3\hbar\pi\varepsilon_0 c^3} \, n \left(\frac{n^2 + 2}{3}\right)^2, \tag{1}$$

where μ^A is the transition dipole of the emitting molecule (atom) A, and n is the refractive index of the surrounding medium (calculated at the emis-

sion frequency ω). The rate given in Eq. (1) may be obtained through a standard procedure that involves summation over the modes of emitted photons. The emitted photons are 'dressed' by polarization of the medium, the effects due to the dielectric medium being described in terms of the refractive index (see, e.g., Refs. [7–9]). Such an approach is relevant to the case where only the long-wavelength modes (with $ka \ll \pi$) are involved in the emission process, a being a characteristic distance between the species constituting the medium. Consequently, Eq. (1) does not generally hold in the case where the emission takes place into absorbing areas of the dielectric. In the latter absorbing case, an important role may be played by exciton-like modes of the medium with larger values of k, as discussed previously [8].

Spontaneous emission in lossy dielectrics may be considered in a number of ways. The phenomenon

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might be dealt with analyzing the macroscopic Maxwell equations for a classical dipole in an absorbing medium [10, 11]. Quantum mechanical analysis has also been carried out [4, 5]. Specifically, in a recent paper by Barnett et al. [5], the decay rate has been calculated for an excited atom embedded in an absorbing dielectric. The rate was separated into the 'transverse' and 'longitudinal' components: These correspond, respectively, to the rate of emission of a transverse photon and the rate of non-radiative decay via longitudinal coupling of the atom to the dielectric [5]. The absorbing medium has been described macroscopically [4, 5], so that the effects due to discreteness of the medium (such as the local-field effects) have not been intrinsically reflected. The local-field corrections have been introduced phenomenologically at later stages [4, 5]. Yet, a fully microscopic approach is desired. It is the purpose of this contribution to present such a microscopic analysis of the phenomenon.

In the initial part of the paper, the spontaneous emission will be regarded as energy transfer to distant acceptors. The approach is in a certain relationship with the absorber theory [12] in which the spontaneous emission is seen to be the result of the direct interaction between the emitting atom and the Universe, the latter acting as a perfect absorber at all emitted frequencies. In our situation, the surrounding medium does act as a perfect absorber even at extremely low concentration of absorbing molecules (or as an alternative for almost transparent condensed medium), as long as the system dimensions are large enough to ensure eventual recapture of the emitted photon.

Consider decay of an excited state of the molecule (atom) A situated in the absorbing molecular medium. The decay rate due the energy transfer to the surrounding species is:

$$\Gamma_A = \sum_{X \neq A} W_{XA}. \qquad (2)$$

where W_{XA} is the pair rate of excitation transfer between the species A and X, the summation being over all the molecules X constituting the medium.

We shall invoke the formalism of quantum electrodynamics (QED) in which the energy transfer emerges as a second-order process mediated by a virtual photon (see, e.g., Refs. [13–17]). The QED approach takes into account completely effects due to retardation, so that the formalism treats on equal grounds the energy transfer at separation distances belonging both to near and far zones [13–17]. To obtain the proper decay rate using Eq. (2), the pair transfer rates W_{XA} should not only reflect retardation effects [13–17], but also incorporate influences of the surrounding medium. A microscopic QED theory has been developed recently [18] that takes into account both effects. The approach assumes the energy transfer to be mediated by 'medium-dressed' photons (i.e., virtual polaritons), rather than by the conventional vacuum photons. Applying microscopically derived [18] pair transfer rates, the full-decay rate in Eq. (2) can be shown to split into its far-zone contribution and that due to the near-zone energy transfer [19]

$$\Gamma_A = \Gamma_A^{\text{far-zone}} + \Gamma_A^{\text{near-zone}} \qquad (3)$$

with

$$\Gamma_A^{\text{far-zone}} = \frac{|\mu^A|^2 \omega^3}{3 \hbar \pi \varepsilon_0 c^3} n' \left| \frac{n^2 + 2}{3} \right|^2. \qquad (4)$$

The former $\Gamma_A^{\text{far-zone}}$ (regarded as the rate of spontaneous emission) corresponds to the r^{-2} term in the pair transfer rates W_{XA}. The emission rate in Eq. (4) manifestly accommodates contributions due to the dielectric medium, including the local-field factor. The latter $\Gamma_A^{\text{near-zone}}$, corresponding to the r^{-6} term in the pair rates [19], represents the familiar decay rate due to the Förster energy transfer [20].

It is noteworthy that the present analysis is based on a microscopic theory [18], the relationship supporting the previous introduction of the local-field correction by Barnett et al. [4, 5] on a phenomenological basis. In the limit $n'' \to 0$, the far-zone rate (4) reduces smoothly to the usual result given in Eq. (1) for the spontaneous emission in the transparent medium, there being vanishing contribution due the near-zone decay: $\Gamma_A^{\text{near-zone}} \to 0$. In other words, the present analysis reproduces in full the rate of spontaneous emission in transparent dielectrics ($n'' = 0$), including inter alia that in the free space ($n' = 1$, $n'' = 0$). Here the free space is to be viewed as a limit where the density of absorbing species goes to zero, while the size of

the system goes to the infinity to ensure eventual recapture of the emitted photon somewhere in the system.

Next, we shall make sure that the far-zone contribution does represent the rate of spontaneous emission in the absorbing medium. Consider the flow of the emitting energy from the source molecule A. The operator of the appropriate pointing vector reads, in the second-order approximation

$$S^{(2)} = S^{(1,1)} + S^{(0,2)} + S^{(2,0)} \tag{5}$$

with

$$S^{(u,v)} = \tfrac{1}{2}[e^{(u)} \times h^{(v)}] + \text{h.c.} \tag{6}$$

Here $e^{(u)}$ and $h^{(v)}$ are the uth order electric and the vth order magnetic fields, the field-operators being expanded in terms of the operator V for interaction between the emitting molecule and the surrounding electromagnetic field

$$V = - \varepsilon_0^{-1} \mu^A \cdot d^{\perp}(r_A), \tag{7}$$

where μ_A is the electric dipole operator of the source molecule A, and $d^{\perp}(r_A)$ is the operator for the electric displacement field (calculated at the emission site r_A). For instance, the first-order operator of the electric field reads

$$e^{(1)}(r, t) = \mathrm{i}(\hbar\varepsilon_0)^{-1} \int_0^t \mathrm{d}t'\,[e(r,t), d_l^{\perp}(r_A, t')]\mu_l^A(t'), \tag{8}$$

where summation over the repeated Cartesian index l is implied. Here $d^{\perp}(r, t')$ and $e(r, t) \equiv e^{(0)}(r, t)$ are operators for the free evolution of the displacement and electric fields in a dielectric medium. Normal-mode expansions of these and other electromagnetic operators have been derived recently on a microscopic basis [9]. Exploiting the mode expansions [9], the total flow of energy over a sphere of the radius r has been calculated at times in access of the time lag, as

$$J_\gamma = \int r \, \mathrm{d}\Omega \langle \gamma | S^{(2)} | \gamma \rangle \cdot r$$

$$= \sum_\beta \hbar |\omega_{\gamma\beta}| \Gamma_A^{\text{sp-em}}(\gamma \to \beta) \Theta(\omega_{\gamma\beta})\, \mathrm{e}^{-\alpha r}, \tag{9}$$

where indices γ and β label initial and final states of the emitting atom, $\alpha = 2|\omega_{\gamma\beta}|n(\omega_{\gamma\beta})''/c$ is the Beer length absorbency (at the emission frequency $\omega_{\gamma\beta}$), $\Theta(\cdots)$ is the unit-step function, and

$$\Gamma_A^{\text{sp-em}}(\gamma \to \beta) \equiv \Gamma_A^{\text{far-zone}}, \tag{10}$$

the quantity $\Gamma_A^{\text{far-zone}}$ being as in Eq. (4) (with $\omega = \omega_{\gamma\beta}$ and $\mu^A = \mu_{\gamma\beta}^A$). It is instructive that only downwards transitions contribute to the energy flow in Eq. (9); Contributions due to the upward transitions cancel out by different terms comprising the Pointing vector in Eq. (5). This shows the importance of terms associated with the second-order fields (i.e., $S^{(0,2)}$ and $S^{(2,0)}$), the point being already discussed by Power and Thirunamachandran [21] in their analysis of quantized fields generated by a source molecule in vacuum. In our consideration, the energy flow in Eq. (9) appears to be affected by the dielectric medium both though the exponential factor $\mathrm{e}^{-\alpha r}$ (describing absorption losses at the medium), and also through the refractive modifications of the rate $\Gamma_A^{\text{sp-em}}(\gamma \to \beta)$. It is evident that the latter $\Gamma_A^{\text{sp-em}}(\gamma \to \beta)$ does represent the rate of spontaneous emission due to the molecular transition $\gamma \to \beta$.

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