

## Sum Rule for Modified Spontaneous Emission Rates

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We show that the possible modifications of the spontaneous emission rate for an electric dipole transition, caused by the atomic environment, are constrained by a sum rule expressed as an integral over the transition frequency. This rule is derived on the basis of causality requirements as expressed in the Kramers-Kronig relation. [S0031-9007(96)01234-3]

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It is now well established that the rate at which an excited atom or molecule undergoes spontaneous emission depends on its environment [1]. The existence of material boundaries in the vicinity of the radiating species changes the density of field modes and the spontaneous emission rate [2]. The boundaries often take the form of an optical cavity, but more generally any material object in the vicinity of the atom changes the emission rate. These studies show that the inhibition of spontaneous emission rates for one range of transition frequencies tends to be accompanied by enhancement of the rates at other frequencies. More recently, attention has been focused on the practical application of the phenomenon in the development of efficient semiconductor devices [3], and it has been suggested that nearly complete control over spontaneous emission rates might be achieved by developing photonic band-gap materials [4]. Spontaneous emission rates are also modified when an excited atom is embedded in a dielectric host; the free-space rate is then scaled by the real part of the refractive index of the host at the frequency of the transition [5].

In this Letter we show that the allowed modifications in the variation of spontaneous emission rates with transition frequency  $\omega_a$  are constrained in all cases by the simple sum rule

$$\int_0^\infty d\omega_a \frac{\Gamma_m(\mathbf{r}, \omega_a) - \Gamma_0(\omega_a)}{\Gamma_0(\omega_a)} = 0. \quad (1)$$

Here  $\Gamma_0(\omega_a)$  is the spontaneous emission rate in free space and  $\Gamma_m(\mathbf{r}, \omega_a)$  is the emission rate of an atom or molecule at position  $\mathbf{r}$  as modified by the environment, whose effect is assumed to vary by a negligible amount across the extent of the emitting object. It follows that any reduction in spontaneous emission rate over some range of frequencies  $\omega_a$  must necessarily be compensated by increases over some other range of transition frequencies.

The spontaneous emission rate for an electric dipole transition is calculated using Fermi's golden rule. The resulting expression involves the vacuum expectation value of a product of electromagnetic field operators in the form [6]

$$\begin{aligned} \Gamma(\mathbf{r}, \omega_a) &= \frac{1}{\hbar^2} \int_0^\infty d\omega \int_0^\infty d\omega' \mu_i \mu_j \langle 0 | \hat{E}_i^+(\mathbf{r}, \omega) \hat{E}_j^-(\mathbf{r}, \omega') | 0 \rangle \delta(\omega' - \omega_a) \\ &= \frac{1}{\hbar^2} \int_0^\infty d\omega \mu_i \mu_j \omega \omega_a \langle 0 | \hat{A}_i^+(\mathbf{r}, \omega) \hat{A}_j^-(\mathbf{r}, \omega_a) | 0 \rangle, \end{aligned} \quad (2)$$

where  $\mu$  is the dipole matrix element for the transition. We adopt the convention that repeated indices  $i$  and  $j$  are summed over the three Cartesian coordinates. If the field operators for an unbounded region of free space are inserted into this expression, we recover the familiar free-space rate

$$\Gamma_0(\omega_a) = \frac{\mu^2 \omega_a^3}{3\pi \epsilon_0 c^3}, \quad (3)$$

which is of course independent of position.

The fluctuation-dissipation theorem [7,8] provides a simple relationship between the vacuum expectation value in Eq. (2) and the vector potential Green's function in the

form

$$\begin{aligned} \langle 0 | \hat{A}_i^+(\mathbf{r}, \omega_a) \hat{A}_j^-(\mathbf{r}, \omega) | 0 \rangle &= 2\hbar \text{Im} G_{ij}^T(\mathbf{r}, \mathbf{r}, \omega_a) \\ &\times \delta(\omega - \omega_a), \end{aligned} \quad (4)$$

where the superscript  $T$  denotes that this is the transverse Green's function. It follows immediately that the spontaneous emission rate and the Green's function are related by

$$\Gamma(\mathbf{r}, \omega_a) = \frac{2\omega_a^2}{\hbar^2} \mu_i \mu_j \text{Im} G_{ij}^T(\mathbf{r}, \mathbf{r}, \omega). \quad (5)$$

The form of the Green's function is restricted by the requirements of causality, in particular it can have no poles in the upper half of the complex  $\omega$  plane. However, this observation is not immediately useful as the leading term in an asymptotic expansion of the Green function for  $\omega \rightarrow \infty$  in powers of  $1/\omega$  is a constant. The Green's function is not therefore square integrable and this precludes the use of the standard dispersion relations [9]. We can circumvent this difficulty by working with  $D = G - G_0$ , that is, the difference between the Green's function  $G$  and that valid for free space  $G_0$ . As the dielectric function for any material object must tend to the free-space value of unity as  $\omega \rightarrow \infty$ , the constants in the asymptotic forms of  $G$  and  $G_0$  are the same. The function  $D$  is thus square integrable in addition to having no poles in the upper half of the complex  $\omega$  plane. It follows, therefore, that it obeys conditions of the familiar Kramers-Kronig form, in particular,

$$2 \int_0^\infty d\omega_a \frac{\text{Im } D_{ij}^T(\mathbf{r}, \mathbf{r}, \omega_a)}{\omega_a} = \pi \text{Re } D_{ij}^T(\mathbf{r}, \mathbf{r}, 0). \quad (6)$$

The Green's function is the well-behaved solution of the partial differential equation

$$-\left(\nabla^2 + \frac{\omega_a^2 \varepsilon(\mathbf{r}, \omega_a)}{c^2}\right) G_{ij}^T(\mathbf{r}, \mathbf{r}', \omega_a) = \frac{1}{\varepsilon_0 c^2} \delta_{ij}^T(\mathbf{r} - \mathbf{r}'), \quad (7)$$

where  $\delta_{ij}^T(\mathbf{r} - \mathbf{r}')$  is the transverse part of the delta function [10] and  $\varepsilon(\mathbf{r}, \omega_a)$  is the complex dielectric function [11]. It follows that at zero frequency the Green's function is independent of the surrounding medium and hence that  $\text{Re} D_{ij}^T(\mathbf{r}, \mathbf{r}, 0) = 0$ . The sum rule (1) then follows from Eq. (6) on using the relation (5) together with the explicit form of the free-space decay rate (3). The simplest example of the sum rule is given by the rate of decay for an atom embedded in an unbounded uniform dielectric for which  $\Gamma_m(\omega_a) = \eta(\omega_a)\Gamma_0(\omega_a)$ , where  $\eta(\omega_a)$  is the real part of the refractive index [5]. The sum rule then takes the form

$$\int_0^\infty d\omega_a [\eta(\omega_a) - 1] = 0, \quad (8)$$

which is well-established property of dielectrics [12].

We should point out two subtleties associated with the sum rule (1). First, it is important to note that we have considered only the contribution to the decay process associated with the *transverse* electric field. Transitions can also occur by excitation of the longitudinal field, but the sum rule applies only to that part of the total decay rate associated with the transverse electric field. The contribution of the longitudinal field can be important, for example, in absorbing materials having dielectric functions with significant imaginary parts [13].

Second, apparent violations of the sum rule can be obtained from the results of model calculations that

do not respect the general restrictions on the form of the dielectric function. Consider, for example, the spontaneous emission rate calculated for a dipole in front of a mirror which reflects light perfectly at all frequencies. The resulting expression for the spontaneous emission rate [14] leads to a violation of the sum rule. Evaluation of the integral in Eq. (1) can, depending on the orientation of the dipole, lead to a term inversely proportional to the distance between the dipole and the perfect mirror. In particular, for a dipole at a distance  $z$  from a perfectly reflecting plane and oriented perpendicular to the plane of the mirror we find that the integral (1) gives the result  $3\pi c/8z$  rather than zero. However, this departure from the sum rule can be accounted for within the more general result (6). For a perfectly reflecting surface  $\text{Re} D_{ij}^T(\mathbf{r}, \mathbf{r}, 0)$  does not vanish. This is a consequence of the fact that a transverse delta function cannot be accommodated within a half space, but must be replaced by delta functions involving both points in the half space and their image points in the reflecting surface [15]. The resulting modification of the equation for the Green's function in this case produces the nonzero value of  $\text{Re} D_{ij}^T(\mathbf{r}, \mathbf{r}, 0)$  in accord with the violation of the sum rule. Nevertheless, the idea of a reflecting surface that is perfect at all frequencies is unphysical, and it is the cause of the departure from the sum rule in this case. For more physical models of reflecting surfaces incorporating both absorption and high-frequency transparency, the sum rule (1) should be valid. We will return to this point elsewhere.

Our sum rule should not be confused with more familiar rules such as the Thomas-Reiche-Kuhn (TRK) sum rule, which can be expressed as a relationship between the total cross sections for absorption and stimulated emission [16]. The TRK sum rule constrains the dipole matrix elements for all induced transitions from a given atomic state and it is therefore a property of the atom. The sum rule in Eq. (1), however, applies to spontaneous emission from a fixed excited state to a fixed lower level as the frequency of this given transition is swept from zero to infinity, keeping the dipole matrix element constant. The spontaneous emission sum rule constrains the allowed transitions from the vacuum for any possible distribution of field modes. It is therefore a property of the transverse electromagnetic field at the position of the atom.

Finally, we emphasize that the sum rule in Eq. (1) applies to the spontaneous emission by an atom or molecule in a completely arbitrary environment, which may include, for example, metallic mirrors, Bragg reflectors, photonic band-gap materials, and absorptive dielectrics or semiconductors. In all cases, the sum rule applies to model calculations of the modified spontaneous emission rates only if they use dielectric functions that conform to general causality and asymptotic requirements.

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