

Einstein Relations Connecting Broadband Emission and Absorption Spectra

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Relations described by Einstein connecting the rates of spontaneous emission, stimulated emission, and absorption of radiation by an atomic system in free space are generalized to apply to broadband spectra of quantized systems dilutely distributed in a dielectric medium. Although the gross features of the broadband emission and absorption spectra can be qualitatively different (especially at low temperatures), the various spectra are connected at any specific frequency by simple expressions. For a two-level system imbedded in a medium at temperature T , typical equations connecting stimulated-emission and absorption cross sections $\sigma(\omega)$ to the rate $f(\omega)$ of spontaneous emission of photons per unit solid angle per unit frequency interval are: $\sigma_e(\omega) = \sigma_a(\omega) \exp[\hbar(\mu - \omega)/kT] = f(\omega)(2\pi c/\omega n)^2$, where $\hbar\mu$ is a temperature-dependent excitation potential and n is the index of refraction of the host material.

IN a classic paper, Einstein¹ described relations connecting the rates of spontaneous emission, stimulated emission, and absorption of radiation by an atomic system in free space having two sharp energy levels. In the present paper we derive generalizations of Einstein's relations which pertain to broadband spectra of systems dilutely distributed in a dielectric medium such as a liquid, a solid, or a dense gas. As we have indicated elsewhere,^{2,3} these generalizations are of considerable practical importance for the analysis of laser systems⁴ in which the spectra might typically derive from a dilute concentration of impurity centers in an insulating solid and for which the spectral width reflects the interaction of the discrete impurity "electronic" levels with the quantized vibrations of the host lattice. Although the gross features of the emission and absorption spectra of such systems can be qualitatively different (especially at low temperatures),⁵ we shall verify that at any specific frequency the various spectra are connected by relatively simple expressions. For a pair of sharp levels in free space our results reduce to those previously given by Einstein. Our results are not inconsistent with the work of Fowler and Dexter⁵ since those authors compare spectra at *different* frequencies whereas we compare spectra at the *same* frequency.

Let us briefly summarize Einstein's results relevant to a two-level quantum system (energies E_1 and E_2 with $E_2 > E_1$, level degeneracies g_1 and g_2) in free space interacting with radiation of angular frequency

$$\omega = 2\pi\nu = (E_2 - E_1)/\hbar. \quad (1)$$

If $u(\omega)$ is the energy density per unit volume of radiation per unit frequency interval $\Delta\nu = \Delta\omega/2\pi$, then in free space in thermal equilibrium at temperature T that density is given by the Planck expression

$$u(\omega) = 8\pi \frac{2\pi\hbar}{\exp(\hbar\omega/kT) - 1} \left(\frac{\omega}{2\pi c}\right)^3. \quad (2)$$

¹ A. Einstein, *Physik Z.* **18**, 121 (1917); cf. also, A. Einstein and P. Ehrenfest, *Z. Physik* **19**, 301 (1923).

² D. E. McCumber, *Bull. Am. Phys. Soc.* **9**, 280 (1964).

³ D. E. McCumber, *Phys. Rev.* **134**, A299 (1964).

⁴ L. F. Johnson, R. E. Dietz, and H. J. Guggenheim, *Phys. Rev. Letters* **11**, 318 (1963).

⁵ W. B. Fowler and D. L. Dexter, *Phys. Rev.* **128**, 2154 (1962).

If for this density the average rate of radiation absorption by systems in each lower state (energy E_1) is $B_{12}u(\omega)$, the rate of stimulated emission by systems in each excited state (energy E_2) is $B_{21}u(\omega)$, and the rate of spontaneous emission per unit frequency interval by systems in those excited states is A_{21} , Einstein found that

$$g_1 B_{12} = g_2 B_{21} \quad (3a)$$

and that

$$A_{21} = 16\pi^2 \hbar (\omega/2\pi c)^3 B_{21}. \quad (3b)$$

To generalize these expressions, we consider an ensemble of independent quantized "impurity" systems uniformly distributed in a homogeneous dielectric medium filling a box of large but finite volume V . We assume that the impurity energy levels can be grouped into metastable sets whose total populations N_j per unit volume can be independently specified (perhaps to within the trivial constraint that $\sum_j N_j$ be fixed). Within each set all states are in equilibrium at some common average temperature $T \geq 0$. Although we neglect nonradiative transitions in our analysis, we expect our results to apply to all systems for which the time required for thermal equilibration within each metastable set is short compared to the lifetimes (total) of the different sets.

Radiation in the doped dielectric can be characterized by an angular frequency ω and by wave-vector and polarization indices (\mathbf{k}, λ) which specify the plane-wave spatial eigenmodes of the box. In degenerate cases λ can indicate either plane or circular polarization. We define a dimensionless function $f_\lambda(\mathbf{k}, \omega)_{ji}$ such that $f_\lambda(\mathbf{k}, \omega)_{ji} d\Omega_{\mathbf{k}\lambda}$ is the average intensity in photons/sec per unit frequency interval of λ -polarized frequency- ω radiation emitted into the solid angle $d\Omega_{\mathbf{k}\lambda}$ as a result of the spontaneous radiative decay of an impurity in the excited metastable set j to the lower lying set $i < j$. If τ_{ji} is the spontaneous-emission lifetime for the transition, then

$$\tau_{ji}^{-1} = \sum_\lambda \int_{4\pi} d\Omega_{\mathbf{k}\lambda} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f_\lambda(\mathbf{k}, \omega)_{ji}. \quad (4)$$

We define $\sigma_a(\mathbf{k}, \omega)_{ij}$ to be the cross section for a single

impurity in the metastable set i to be excited to the set j by the absorption of a plane-wave $(\mathbf{k}, \lambda, \omega)$ photon. We take $\sigma_{e\lambda}(\mathbf{k}, \omega)_{ji}$ to be the cross section for an impurity in the set j to decay to the set i by the stimulated emission of a $(\mathbf{k}, \lambda, \omega)$ photon. If we multiply the absorption cross section, say, by the density N_i of initial-set impurities, we obtain an inverse absorption length characteristic of the impurity-doped material. Further multiplication by the *group* velocity of light gives the time rate of photon absorption.

In order to determine the relations connecting the two cross sections, we label the energy eigenstates (in the absence of interaction with any perturbing external radiation field) of each impurity *plus* any surrounding dielectric with which it interacts by the metastable-set index j and by a second index α ranging over all (possibly degenerate) states within the set j . If the state $(j\alpha)$ has an energy $E_{j\alpha}$, then the probability $\rho_{j\alpha}$ for that state to be occupied in true thermal equilibrium at temperature T is

$$\rho_{j\alpha} = \exp(-E_{j\alpha}/kT) / \sum_i \sum_{\beta} \exp(-E_{i\beta}/kT). \quad (5)$$

Consider next the interaction of the impurity-doped dielectric with radiation. We restrict ourselves to the lowest order "linear" interactions (implicit in our previous cross section and fluorescence-function definitions) of any radiation mode with any given dielectric-perturbed impurity.⁶ We characterize the perturbing effects of any particular radiation mode $(\mathbf{k}, \lambda, \omega)$ by the set of matrix elements $M_{j\alpha, i\beta}(\mathbf{k}, \lambda, \omega)$ connecting the different states $(j\alpha)$ and $(i\beta)$. Using these matrix elements with the definitions given previously, we can relate the absorption and stimulated-emission cross sections by the ratio

$$\frac{N_i \sigma_{e\lambda}(\mathbf{k}, \omega)_{ij}}{N_j \sigma_{a\lambda}(\mathbf{k}, \omega)_{ji}} = \frac{\sum_{\alpha, \beta, \rho, \rho'} |M_{j\alpha, i\beta}(\mathbf{k}, \lambda, \omega)|^2 \delta(E_{j\alpha} - E_{i\beta} - \hbar\omega)}{\sum_{\alpha, \beta, \rho, \rho'} |M_{i\beta, j\alpha}(\mathbf{k}, \lambda, \omega)|^2 \delta(E_{j\alpha} - E_{i\beta} - \hbar\omega)}, \quad (6)$$

where here $N_j = \sum_{\alpha} \rho_{j\alpha}$. We have used the fact that whatever frequency-dependent or mode-dependent factors and local-field corrections are relevant to the absorption cross section are also relevant to the emission cross section. This is an immediate consequence of the fact that the component of the total system Hamiltonian which describes the interaction of radiation with the impurity-doped dielectric is necessarily Hermitian (real). This same fact ensures that

$$|M_{j\alpha, i\beta}(\mathbf{k}, \lambda, \omega)|^2 = |M_{i\beta, j\alpha}(\mathbf{k}, \lambda, \omega)|^2. \quad (7)$$

⁶ In this paper we do not consider spectral functions characteristic of nonlinear optical processes. Generalized Einstein relations do exist for such functions but they are less useful and somewhat more complicated than the relations we consider here for the linear spectral functions.

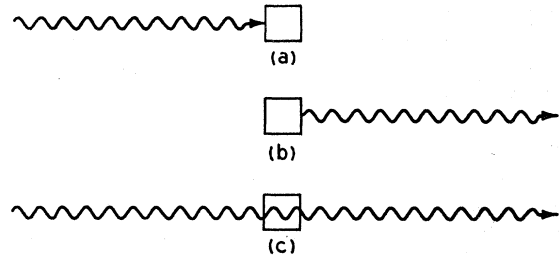


FIG. 1. Absorption and emission processes appropriate to a photon wave packet traveling from left to right. Parts (a) and (b), respectively, indicate photon absorption and emission by the small material body indicated by the open rectangle. The net result of successive absorption and emission processes is equivalent (except for a time delay and a concomitant loss of phase coherence) to process (c) in which the photon passes right through the body without interaction. It is clear that process (b) is *not* the time reverse of process (a) because in the time-reversed process the photon wave packet would be traveling from right to left, a different radiation mode combination from that relevant to (a). The general Einstein relations (9) and (19) of the text apply separately to each radiation mode, not to pairs of modes connected by time reversal.

If we further note from Eq. (5) that

$$\rho_{i\beta} \delta(E_{j\alpha} - E_{i\beta} - \hbar\omega) = \rho_{j\alpha} \exp(\hbar\omega/kT) \delta(E_{j\alpha} - E_{i\beta} - \hbar\omega), \quad (8)$$

then it follows from (6) that⁷

$$\sigma_{a\lambda}(\mathbf{k}, \omega)_{ij} = \sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} \exp[\hbar(\omega - \mu_{ji})/kT], \quad (9)$$

where, if $(N_j/N_i)_{eq}$ is the ratio of the total set- j and set- i populations in *true* thermal equilibrium at temperature T ,

$$\exp(-\hbar\mu_{ji}/kT) = (N_j/N_i)_{eq}. \quad (10)$$

Equivalently, the temperature-dependent excitation potential $\hbar\mu_{ji}$ equals the net free energy required to excite one impurity from the set i to the set $j > i$ while maintaining the initial dielectric temperature T .⁸

Equation (9) is the generalization of Eq. (3a) we have been seeking. It correctly reduces to Eq. (3a) when the spectral linewidth is less than kT/\hbar and B_{jk} is defined as in Eq. (20) below. In deriving Eq. (9), we used the facts that the desired cross sections relate to the lowest order radiation-impurity interaction and that the system Hamiltonian must be Hermitian. Since our proof does *not* depend upon time-reversal invariance, the results also obtain for systems in equilibrium in static magnetic fields and for systems described by equilibrium ensembles having net linear or angular momentum. The irrelevance of time-reversal invariance to the arguments of this paper is apparent in Fig. 1 where we have schematically indicated absorption and emission processes for a photon wave packet incident upon an absorbing medium.

Einstein was able to infer his relation (3a) from detailed-balance relations of the type we shall use

⁷ Compare the more formal but essentially equivalent operator statements of this result given in Secs. 2 of D. E. McCumber, *J. Math. Phys.* 5, 221 (1964); 5, 508 (1964).

below to determine the function $f_\lambda(\mathbf{k}, \omega)_{ji}$. This was possible because his parameters A_{ji} and B_{ji} refer only to a single pair of energy levels and do not depend upon the detailed thermal occupation of different energy levels within metastable sets—that is, they are temperature-independent. This temperature independence, used in conjunction with the fact that thermal-equilibrium blackbody radiation is described by the celebrated Planck formula, is sufficient to determine the *two* coefficient ratios of Eq. (3) from a *single* detailed-balance relation. Because our functions are implicitly temperature-dependent (when the spread of energies within a metastable set is large relative to kT), we cannot proceed in precisely the same way but must supplement the detailed-balance relation by the microscopic arguments of Eqs. (6)–(8) above.

To generalize Eq. (3b), we relate the emission cross section to the fluorescence function $f_\lambda(\mathbf{k}, \omega)_{ji}$. Using microscopic arguments, we can easily verify that for fixed $j > i$ the function $f_\lambda(\mathbf{k}, \omega)_{ji}$ is only related to that emission cross section $\sigma_{e\lambda}(\mathbf{k}, \omega)_{ji}$ which belongs to the same metastable sets $j > i$ as $f_\lambda(\mathbf{k}, \omega)_{ji}$. The specific relation connecting these spectral functions can be inferred from Eq. (9) and Einstein's detailed-balance argument¹ that at thermal equilibrium the total rate of spontaneous plus stimulated emission of $(\mathbf{k}, \lambda, \omega)$ radiation in $j \rightarrow i$ transitions must equal the rate of absorption of such radiation in $i \rightarrow j$ transitions, the equilibrium radiation density being given by a generalized Bose-Einstein-Planck distribution function for temperature T .

In our derivation we assume that the radiation frequency ω is uniquely related to the mode indices (\mathbf{k}, λ) by

$$\omega = \omega_\lambda(\mathbf{k}) \equiv ck/n_\lambda(\mathbf{k}, \omega), \quad (11)$$

where $n_\lambda(\mathbf{k}, \omega)$ is the real part of the index of refraction of the impurity-doped dielectric. When the effective radiation-dielectric interaction is very strong (as it is, for example, near the intrinsic absorption edge of an insulator or semiconductor), the mode (\mathbf{k}, λ) will not have a unique frequency but will have a spread of frequencies (or in some cases a single complex frequency) near the frequency (11) and also frequencies near the intrinsic resonances of the impurity doped dielectric. (Equivalently, a unique real wave vector cannot be assigned to each real frequency ω .) In such cases Eq. (11) is inapplicable and special techniques are required.⁸ For essentially this reason the results we derive below relating $f_\lambda(\mathbf{k}, \omega)_{ji}$ to $\sigma_{e\lambda}(\mathbf{k}, \omega)_{ji}$ are inapplicable whenever the index of refraction $n_\lambda(\mathbf{k}, \omega)$ of the impurity-doped dielectric varies rapidly over the interval characteristic of the frequency wave vector uncertainty. For example, if at the frequency ω the doped dielectric is characterized by the absorption constant $\alpha(\text{cm}^{-1})$, then our results

⁸ J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

are strictly valid only if

$$n_\lambda(\mathbf{k}, \omega) \gg \Delta_\alpha \omega \quad n_\lambda(\mathbf{k}, \omega) = \frac{\alpha c}{n_\lambda(\mathbf{k}, \omega)} \frac{d}{d\omega} n_\lambda(\mathbf{k}, \omega). \quad (12)$$

Note, however, that these restrictions do *not* apply to the more general relations (9).

If $\rho_\lambda(\mathbf{k}, \omega) d\Omega_{\mathbf{k}\lambda}$ is the unit-volume density per unit frequency interval of modes of λ -polarized frequency- ω radiation propagating in the solid angle $d\Omega_{\mathbf{k}\lambda}$, then, when Eq. (11) obtains,

$$\rho_\lambda(\mathbf{k}, \omega) = \left[\frac{\omega n_\lambda(\mathbf{k}, \omega)}{2\pi c} \right]^2 \left[\frac{d\omega_\lambda(\mathbf{k})}{dk} \right]^{-1}. \quad (13)$$

At temperature T the average photon occupation of each radiation mode is given by the Bose-Einstein-Planck distribution function

$$n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}, \quad (14)$$

which is a function only of the frequency ω of the mode. Combining Eqs. (13) and (14), we have in $\rho_\lambda(\mathbf{k}, \omega) n(\omega)$ the average density per unit solid angle per unit frequency interval of λ -polarized frequency- ω photons. Multiplying this density by the photon energy $\hbar\omega$, summing over the two polarizations λ , and integrating over the solid angle 4π , we obtain an expression for the radiation energy density per unit frequency interval which for free space with $n_\lambda(\mathbf{k}, \omega) \equiv 1$ correctly reduces to the $u(\omega)$ of Eq. (2).

At thermal equilibrium the density of $(\mathbf{k}, \lambda, \omega)$ radiation is a constant of the motion. For the $i \leftrightarrow j$ transition the rate at which spontaneous emission acts to increase this density is

$$f_\lambda(\mathbf{k}, \omega)_{ji} N_j |_{\text{eq}}, \quad (15)$$

where $N_j |_{\text{eq}}$ is defined as in Eq. (10). The rate of stimulated emission of $(\mathbf{k}, \lambda, \omega)$ radiation equals the density $\rho_\lambda(\mathbf{k}, \omega) n(\omega)$ of $(\mathbf{k}, \lambda, \omega)$ photons times the *group* velocity $d\omega_\lambda(\mathbf{k})/dk$ of light in the material, the emission cross section $\sigma_{e\lambda}(\mathbf{k}, \omega)_{ji}$, and the upper state population $N_j |_{\text{eq}}$:

$$\sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} \rho_\lambda(\mathbf{k}, \omega) n(\omega) [d\omega_\lambda(\mathbf{k})/dk] N_j |_{\text{eq}}. \quad (16)$$

The rate of absorption is similarly

$$\sigma_{a\lambda}(\mathbf{k}, \omega)_{ij} \rho_\lambda(\mathbf{k}, \omega) n(\omega) [d\omega_\lambda(\mathbf{k})/dk] N_i |_{\text{eq}}. \quad (17)$$

Equating emission and absorption rates, we require for detailed balance that

$$\begin{aligned} & \left[f_\lambda(\mathbf{k}, \omega)_{ji} + \sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} \rho_\lambda(\mathbf{k}, \omega) n(\omega) \frac{d\omega_\lambda(\mathbf{k})}{dk} \right] N_j |_{\text{eq}} \\ & = \sigma_{a\lambda}(\mathbf{k}, \omega)_{ij} \rho_\lambda(\mathbf{k}, \omega) n(\omega) \frac{d\omega_\lambda(\mathbf{k})}{dk} N_i |_{\text{eq}}. \end{aligned} \quad (18)$$

Using Eqs. (9)–(14) in Eq. (18), we find after some straightforward algebra that

$$f_\lambda(\mathbf{k}, \omega)_{ji} = \sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} \rho_\lambda(\mathbf{k}, \omega) d\omega_\lambda(\mathbf{k}) / dk \quad (19a)$$

$$= \sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} [\omega n_\lambda(\mathbf{k}, \omega) / 2\pi c]^2, \quad (19b)$$

which results are the desired generalization of Eq. (3b).

For a narrow spectral line centered at frequency $\bar{\omega}$, Eqs. (9) and (19b) correctly reduce in free space to Eqs. (3) provided we identify

$$A_{21} = \sum_\lambda \int_{4\pi} d\Omega_{k\lambda} \int \frac{d\omega}{2\pi} f_\lambda(k, \omega)_{21} \quad (20a)$$

and

$$B_{21} = \frac{1}{u(\bar{\omega})} \sum_\lambda \int_{4\pi} d\Omega_{k\lambda} \int \frac{d\omega}{2\pi} \times \sigma_{e\lambda}(\mathbf{k}, \omega)_{21} \rho_\lambda(\mathbf{k}, \omega) n(\omega) d\omega_\lambda(\mathbf{k}) / dk \\ = \frac{\sigma_{e\lambda}(\mathbf{k}, \bar{\omega})}{\hbar\omega} \frac{d\omega_\lambda(\mathbf{k})}{dk} \Big|_{av}, \quad (20b)$$

etc. Note that, as Fowler and Dexter have observed,⁵ Eqs. (3) do *not* obtain with the definitions (20) unless the spectral line is narrow. The generalization of Einstein's results is not to be found in the definitions (20) but rather in Eqs. (9) and (19) above.

An application of the preceding results to spectra in solids has been discussed elsewhere.³ As another simple but instructive illustration of the general validity of Eq. (9), let us briefly consider the Doppler broadening of a spectral line of a dilute molecular gas of temperature T . We consider the radiative transitions between two sharp levels of separation $\hbar\omega_{21} = E_2 - E_1$ for a molecule of mass M . The molecular velocities are described by a Maxwell-Boltzmann distribution for which the probability for velocity \mathbf{v} is proportional to $\exp(-Mv^2/2kT)$. If the matrix element for the molecular transition is independent of velocity, the cross sections for the absorption and emission of frequency- ω radiation are, respectively,

$$\sigma_{a\lambda}(\mathbf{k}, \omega)_{12} = C_\lambda(\mathbf{k}, \omega) \int (dv)(dv') \\ \times \exp(-Mv^2/2kT) \delta(M\mathbf{v} + \hbar\mathbf{k} - M\mathbf{v}') \\ \times \delta(v^2M/2 + \hbar\omega - (v')^2M/2 - \hbar\omega_{21}) \quad (21a)$$

and

$$\sigma_{e\lambda}(\mathbf{k}, \omega)_{21} = C_\lambda(\mathbf{k}, \omega) \int (dv)(dv') \\ \times \exp(-Mv^2/2kT) \delta(M\mathbf{v} - M\mathbf{v}' - \hbar\mathbf{k}) \\ \times \delta(v^2M/2 + \hbar\omega_{21} - (v')^2M/2 - \hbar\omega), \quad (21b)$$

where the unspecified factor $C_\lambda(\mathbf{k}, \omega)$ is a slowly varying function of the parameters $(\mathbf{k}, \lambda, \omega)$ and is the same in both cross sections. As is well known, the Doppler line-shape results automatically from the energy and momentum δ functions present in Eqs. (21). Performing the \mathbf{v} and \mathbf{v}' integrations in Eqs. (21), we obtain the results ($|\mathbf{k}| = \omega/c$):

$$\sigma_{a\lambda}(\mathbf{k}, \omega)_{12} \\ = \bar{C}_\lambda(\mathbf{k}, \omega) \exp\left[-\frac{Mc^2}{2kT} \left(1 - \frac{\omega_{21}}{\omega} - \frac{\hbar\omega}{2Mc^2}\right)^2\right], \quad (22a)$$

$$\sigma_{e\lambda}(\mathbf{k}, \omega)_{21} \\ = \bar{C}_\lambda(\mathbf{k}, \omega) \exp\left[-\frac{Mc^2}{2kT} \left(1 - \frac{\omega_{21}}{\omega} + \frac{\hbar\omega}{2Mc^2}\right)^2\right], \quad (22b)$$

where we have introduced a new coefficient $\bar{C}_\lambda(\mathbf{k}, \omega)$. Comparing Eqs. (22), we find that

$$\sigma_{a\lambda}(\mathbf{k}, \omega)_{12} = \sigma_{e\lambda}(\mathbf{k}, \omega)_{21} \exp[\hbar(\omega - \omega_{21})/kT]. \quad (23)$$

This is of the form (9) with $\mu_{21} = \omega_{21}$, the unshifted molecular frequency expected from Eq. (10). Note that a result of the type (9) obtains only when we retain the recoil energy corrections $\pm\hbar\omega/2Mc^2$ in the second factor of the exponents of Eq. (22).

The exponential factor in Eq. (23) is important only if the Doppler spectral width $\omega(kT/Mc^2)^{1/2}$ is large compared to kT/\hbar —that is, if

$$\hbar\omega \geq (Mc^2kT)^{1/2}. \quad (24)$$

If the molecular mass is one atomic mass unit and if $T = 300^\circ\text{K}$, the right-hand side of Eq. (24) equals 4.91×10^3 eV, an x-ray energy. While the exponential factor in Eq. (9) thus does not have a significant frequency dependence in the usual Doppler-broadened optical spectra, it is often significant in the much broader vibrationally perturbed optical spectra of solids and liquids.^{3,4}

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