performed over "linked clusters" or "connected diagrams" only. Let us illustrate this using the example of LiF. Pershan[14] has recently shown that for fields of the order of 50 gauss the essential mechanism consists in two Li flips and one opposite F flip. Using Pershan's notations (S denotes a lithium spin operator, I a fluorine spin operator, no prime refers to an interaction between two Li, one prime refers to a LiF interaction, and two primes to two F), we have to evaluate the modulus of

$$\mathcal{V}_{rs}=\frac{1}{\hbar}\left\{\left(\frac{B'C'}{\omega_{\mathrm{Li}}}-\frac{C'B'}{\omega_{\mathrm{F}}-\omega_{\mathrm{Li}}}\right)+\left(\frac{B'C}{\omega_{\mathrm{Li}}}-\frac{CB'}{\omega_{\mathrm{F}}-\omega_{\mathrm{Li}}}\right)+\left(\frac{D'E}{2\omega_{\mathrm{Li}}}-\frac{ED'}{\omega_{\mathrm{F}}}\right)\right\}. \tag{5.9}$$

A connected diagram is associated with each term as shown in Fig. 1.

Neglecting correlations and using the approximation of the overlap of two Gaussian line shapes, one gets for the transition probability

$$W_{rs}=(2\pi/\hbar^2)g_{12}(\omega_{12})\left|\mathcal{V}_{rs}\right|^2, \tag{5.10}$$

where

$$g_{12}(\omega_{12})=\frac{1}{\{2\pi[2(\Delta\omega)_{\mathrm{Li}}{}^2+(\Delta\omega)_{\mathrm{F}}{}^2]\}^{\frac{1}{2}}}\times\exp\left(\frac{-(\omega_{\mathrm{F}}-2\omega_{\mathrm{Li}})^2}{2[2(\Delta\omega)_{\mathrm{Li}}{}^2+(\Delta\omega)_{\mathrm{F}}{}^2]}\right). \tag{5.11}$$

Using the approximation $\omega_{\mathrm{F}}=2\omega_{\mathrm{Li}}$ in (5.9), which is justified if the Gaussian is very narrow, this result coincides with the expression given by Pershan.

The temperature variation is then obtained by replacing the expression for W_{rs} in Schumacher's formula for R_{12}.

ACKNOWLEDGMENTS

We want to express our gratitude to Professor Bloembergen and Professor Prigogine for their interest and to thank Dr. Jeener and Dr. Pershan for many stimulating discussions.

---

[14] P. S. Pershan, Phys. Rev. 117, 109 (1960).

PHYSICAL REVIEW VOLUME 119, NUMBER 6 SEPTEMBER 15, 1960

Induced and Spontaneous Emission in a Coherent Field. III

I. R. SENITZKY
U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey

(Received November 9, 1959)

The theory developed in the first two articles of this series, dealing with the interaction between the electromagnetic field in a cavity resonator and a number of two-level molecules, is generalized to include a Gaussian spread in the molecular frequency. The center of the molecular frequency distribution coincides with the cavity resonant frequency. There is a coherent driving field in the cavity at the same frequency, and cavity loss is taken into account.

Using the formalism previously developed for a quantum-mechanical field in a lossy cavity, expressions are obtained by means of second-order perturbation theory for the expectation values of the field strength and field energy in the cavity, and of the power loss by the molecules. It is shown that the parts of the field energy resulting from induced and spontaneous emission, respectively, initially increase as the square of the time and approach steady-state values after (different, in general) transient periods, each of which is determined by two time constants: cavity relaxation time and inverse molecular frequency spread. It is also shown that both the induced and spontaneous emission power radiated by the molecules increase initially linearly with the time and approach steady-state values after transient periods. For the induced emission power, the transient period is determined by only one time constant, the inverse molecular frequency spread, while for the spontaneous emission power it is determined both by the inverse molecular frequency spread and the cavity relaxation time. The ratio of induced to spontaneous emission is initially n, and approaches a steady-state value

$$n[\exp(r^2)(1-\mathrm{erf}r)]^{-1},$$

where n is the driving field energy in units of the photon energy, and r is the ratio of the cavity resonance width to molecular frequency spread. The seeming inconsistency of this value with the classical value of the ratio of the Einstein coefficients is discussed.

INTRODUCTION

In the first article of this series,[1] an analysis was made of the interaction between a number of two-level quantum-mechanical systems (hereafter referred to as molecules) and a coherent cavity field, the latter as well as the former being treated quantum-mechanically. The situation considered was that of a lossless cavity, and the molecules were all in resonance with the cavity. Under these two idealizations, neither the induced nor the spontaneous emission approached a steady state. In the second article,[2] a quantum-mechanical formalism was developed for the field of a lossy cavity and applied to the interaction with the molecules. In this case the spontaneous emission approached a steady state after

---

[1] I. R. Senitzky, Phys. Rev. 111, 3 (1958), hereafter referred to as I.

[2] I. R. Senitzky, Phys. Rev. 115, 227 (1959), hereafter referred to as II.

a transient period determined by the cavity, and the induced emission did not. In the present article, the second idealization is also removed, and a spread in the resonant frequencies of the molecules is considered. It will be interesting to note that another qualitative change is produced in the results.

A generalization of the analysis to include a spread in molecular frequencies brings it into closer correspondence with many experimental situations occurring in microwave spectroscopy and in maser work. This would be justification enough for the present treatment, but actually there is further motivation. Some of the results obtained under the idealization that the molecules are all in perfect resonance with the cavity are different from those conventionally assumed.[3] It becomes, therefore, important to ascertain if this difference is due to an idealization in the theory or to a more detailed analysis than that on which conventional thinking is based.

The situation to be considered is that in which each individual molecule has two well-defined energy levels; the frequency corresponding to these levels varies among the molecules with a Gaussian distribution function. This represents inhomogeneous broadening, Doppler broadening, and possibly some other—but not all—causes of line broadening.[4] It is not the purpose of the present article to go into the details of the problem of linewidth, but rather to see how linewidth affects emission in a coherent field. We will, therefore, consider only a single cause of linewidth, the frequency spread described above, which allows a simple analytical treatment of the problem under consideration. The results are of valid interest in themselves, since frequency spread is the main cause of line broadening in some instances. It is not unreasonable to assume, however, that these results will not be altered qualitatively if we replace "frequency spread" by "linewidth."

I

The notation to be used is identical to that in I and II, except that now the molecular (angular) frequency of the mth molecule and its two energy levels are labeled with the index m: $\omega_m=(E_{m2}-E_{m1})/\hbar$. The resonant frequency of the cavity remains ω. The number of molecules per unit frequency range at ω_m is given by

$$\rho(\omega_m)=N(\alpha/\sqrt{\pi})\exp[-\alpha^2(\omega_m-\omega)^2], \tag{1}$$

where N is the total number of molecules in the cavity and α is a constant which determines the spectral width of the molecules. It is to be noted that the cavity is tuned to the peak of the molecular spectrum.

The Hamiltonian for the combined system of molecules, field, loss-mechanism, and (classical) driving mechanism is the same as that in Eq. (II, 41), except for the summation over the molecules:

$$H=H_{\text{field}}+\textstyle\sum_j H_j+\sum_m H_m+4\pi cP(\sum_j \Gamma_j U +\sum_m \gamma_m u+Du_D), \tag{2}$$

where

$$H_{\text{field}}=2\pi c^2P^2+(\omega^2/8\pi c^2)Q^2. \tag{3}$$

For the sake of completeness we repeat the definition of the notation: H_m and $\boldsymbol{\gamma}_m$ are the Hamiltonian and dipole moment of the mth molecule, H_j and $\boldsymbol{\Gamma}_j$ are the Hamiltonian and dipole moment of the dipoles of the loss mechanism (see II for a detailed discussion of the loss mechanism), D is the classical driving dipole given by $D_0\sin(\omega t+\theta)$, P and Q are the field operators (for the single pertinent mode of the cavity) obtained from

$$\mathbf{E}=-4\pi c\mathbf{u}(\mathbf{r})P(t),\quad \mathbf{H}=\boldsymbol{\nabla}\times\mathbf{u}(\mathbf{r})Q(t), \tag{4}$$

with $\mathbf{u}(\mathbf{r})$ being a normalized function describing the spatial dependence of the field in the cavity. U, u and u_D are the magnitudes of $\mathbf{u}(\mathbf{r})$ at the position of the loss dipoles, molecules, and driving mechanism, respectively. For simplicity, we assume that all molecules have the same value of $\mathbf{u}(\mathbf{r})$. The components of the dipole moments along the field are denoted by the scalar dynamical variables $\gamma_m(t)$ and $\Gamma_j(t)$ which, when uncoupled from the field, are given explicitly by

$$\begin{aligned}\Gamma_j^{(0)}(t)&=\bar{\Gamma}\begin{pmatrix}0 & e^{-i\omega_j t}\\ e^{i\omega_j t} & 0\end{pmatrix},\\ \gamma_m^{(0)}(t)&=\tilde{\gamma}\begin{pmatrix}0 & e^{-i\omega_m t}\\ e^{i\omega_m t} & 0\end{pmatrix}.\end{aligned} \tag{5}$$

The Heisenberg picture is used throughout.

As in II, the method of solution of the equations of motion is a perturbation method in which the coupling constant between the field and molecules (contained in $\tilde{\gamma}$) is a small quantity of first order. The coupling between driving mechanism and the field as well as that between the loss mechanism and the field is *not* taken to be necessarily small. The classically meaningful quantities in which we are interested are given by the expectation value of the field strength, field energy, and molecular energy, and we will obtain these up to second order. The order of coupling between molecule and field is indicated by a superscript in a square bracket.

As shown in the derivation of Eq. (II, 47), an integration of the equations motion, taking into account the effect of losses, yields

$$P(t)=P_D+P_\Gamma+P_\gamma, \tag{6}$$

---

[3] See, for instance, II, reference 11.

[4] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955); G. E. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

where

$$P_D = (\omega u_D / c\beta) D_0 \cos(\omega t + \theta) \equiv P_{D0} \cos(\omega t + \theta), \tag{6a}$$

$$P_\Gamma = -\frac{\omega}{c} U \sum_j \int_{-\infty}^{t} dt_1 \, \Gamma_j^{(0)}(t_1) e^{-\frac{1}{2}\beta(t-t_1)} \sin\omega(t-t_1), \tag{6b}$$

$$P_\gamma = -\frac{\omega}{c} u \sum_m \int_0^t dt_1 \, \gamma_m(t_1) e^{-\frac{1}{2}\beta(t-t_1)} \sin\omega(t-t_1). \tag{6c}$$

β is given in terms of the parameters of the loss mechanism by

$$\beta \equiv -4\pi^2(\omega/\hbar) U^2 \bar{\Gamma}^2 \rho_L(\omega) \langle I_j \rangle_\omega, \tag{7}$$

where $\rho_L(\omega)$ is the density of loss-dipoles per unit frequency range at ω, and $\langle I_j \rangle_\omega$ is the average expectation value of the operator

$$I \equiv \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{8}$$

for those loss-dipoles the frequency of which is in the neighborhood of ω. Macroscopically, β/ω is the "Q" of the cavity. The only difference between Eq. (6) and Eq. (II, 47) is the summation over the molecules.

In order to obtain expectation values, we must know the initial state of the system. In the formalism developed in II for the field with losses, the driving field is prescribed, the (quantum-mechanical) field which may have existed in the cavity some time in the past is damped out, and the quantum-mechanical as well as thermal fluctuations of the field are due to the loss-mechanism, the condition of the latter being determined by its temperature. We thus need only information about the initial state of the molecules. In complete generality, we have for the state of the mth molecule

$$\psi_m = a_{m1}\varphi_{m1} + a_{m2}\varphi_{m2}, \tag{9}$$

where φ_{m1} and φ_{m2} are the two energy states of the mth molecule. The a's are complex constants, of course, and the significance of their phases may be noted from the expectation value of the dipole moment of a molecule [see Eq. (I, 10)]:

$$\begin{aligned} \langle \gamma_m^{[0]}(t) \rangle &= a_{m1}^* a_{m2} \tilde{\gamma} e^{-i\omega m t} + a_{m1} a_{m2}^* \tilde{\gamma} e^{i\omega m t}, \\ &= 2|a_{m1}a_{m2}|\tilde{\gamma} \cos(\omega t + \theta_m), \end{aligned} \tag{10}$$

where θ_m is the difference in phase between a_{m1} and a_{m2}. Thus, the phase of oscillation of the expectation value of the dipole moment, which gives the coherent part of the molecular oscillations (see I for a detailed discussion of coherence) is determined by the phases of the a's. Two special distributions of the a's will be of particular interest to us. The first is a thermal equilibrium distribution, in which the average absolute values of the a's are obtained from the Boltzmann distribution, and the phases are completely random. The second is the case in which all the molecules are in the upper state; that is, $|a_{m2}| = 1$, $|a_{m1}| = 0$, for all m, and the phase is of no significance, since only phase *differences* have physical meaning.

We proceed first to calculate, in Part II, the expectation values of $P^{[0]}$, $P^{[1]}$, and $P^{[2]}$, which will give us immediately the electric field strength. Then we calculate, in Part III, the expectation value of P^2 up to second order, from which we obtain the energy of the field. Lastly, in Part IV, we study the expectation value of the average molecular energy (averaged over the molecules).

II

The zeroth order field is

$$P^{[0]} = P_D + P_\Gamma, \tag{11}$$

and, since, as shown in I,

$$\langle P_\Gamma \rangle = 0, \tag{12}$$

we have

$$\langle P^{[0]} \rangle = P_D. \tag{13}$$

The first-order field is, from (6c),

$$P^{[1]} = -\frac{\omega}{c} u \sum_m \int_0^t dt_1 \, \gamma_m^{[0]}(t_1) e^{-\frac{1}{2}\beta(t-t_1)} \sin\omega(t-t_1). \tag{14}$$

For both distributions of initial states mentioned previously, we can see from Eq. (10) that

$$\textstyle\sum_m \langle \gamma_m^{[0]}(t_1) \rangle = 0, \tag{15}$$

so that for these distributions,

$$\langle P^{[1]} \rangle = 0. \tag{16}$$

For the second-order field, we have

$$P^{[2]} = -\frac{\omega}{c} u \sum_m \int_0^t dt_1 \, \gamma_m^{[1]}(t_1) e^{-\frac{1}{2}\beta(t-t_1)} \sin\omega(t-t_1). \tag{17}$$

To obtain $\langle P^{[2]}\rangle$ we must have $\langle\gamma^{[1]}\rangle$. From (I, 12) and the immediately following discussion,

$$\gamma^{[1]}(t)=\frac{1}{i\hbar}\int_0^t dt_1[\gamma_m{}^{[0]}(t_1),H_m{}^{[1]}(t_1)], \tag{18}$$

$$H_m{}^{[1]}(t)=\frac{4\pi c}{i\hbar}u\int_0^t dt_1[H_m{}^{[0]},\gamma_m{}^{[0]}(t_1)]P^{[0]}(t_1), \tag{19}$$

$$[\gamma_m{}^{[0]}(t),[\gamma_m{}^{[0]}(t_1),H_m{}^{[0]}]]=2\hbar\omega_m I_m\tilde{\gamma}^2\cos\omega_m(t-t_1), \tag{20}$$

where I_m is given by Eq. (8), so that

$$\gamma_m{}^{[1]}=\frac{8\pi c}{\hbar}u\tilde{\gamma}^2 I_m\int_0^t dt_1\,P^{[0]}(t_1)\sin\omega_m(t-t_1). \tag{21}$$

We note the similarity of Eq. (21) to Eq. (II, 52) and also the fact that the (explicit) frequency in the integrand depends now on the molecule. Eqs. (17), (21), and (13) thus yield

$$\langle P^{[2]}(t)\rangle=-\frac{8\pi}{\hbar}\omega u^2\tilde{\gamma}^2\sum_m\langle I_m\rangle\int_0^t dt_1\int_0^{t_1}dt_2 e^{-\frac{1}{2}\beta(t-t_1)}P_D(t_2)\sin\omega(t-t_1)\sin\omega_m(t_1-t_2). \tag{22}$$

We convert the summation over m into an integration over ω_m. Thus

$$\sum_m\langle I_m\rangle\sin\omega_m\tau=\int_0^\infty d\omega_m\,\rho(\omega_m)\langle I_m\rangle\sin\omega_m\tau, \tag{23}$$

where $\rho(\omega_m)$ is given by Eq. (1). Now,

$$\langle I_m\rangle=|a_{m2}|^2-|a_{m1}|^2. \tag{24}$$

We assume it is a slowly varying function of ω_m and take its average (which is heavily weighted for $\omega_m\sim\omega$) outside of the integral sign. The result is

$$\sum_m\langle I_m\rangle\sin\omega\tau=N(\langle I_m\rangle)_{\mathrm{av}}\frac{\alpha}{\sqrt{\pi}}\int_0^\infty d\omega_m\exp[-\alpha^2(\omega_m-\omega)^2]\sin\omega_m\tau. \tag{25}$$

For $\omega\gg\alpha^{-1}$, or for the center frequency much larger than the molecular frequency width,

$$\frac{\alpha}{\sqrt{\pi}}\int_0^\infty d\omega_m\exp[-\alpha^2(\omega_m-\omega)^2]\sin\omega_m\tau\cong\int_{-\infty}^\infty d\omega'\exp(-\alpha^2\omega'^2)[\sin\omega\tau\cos\omega'\tau+\cos\omega\tau\sin\omega'\tau]$$
$$=\exp(-\tau^2/4\alpha^2)\sin\omega\tau. \tag{26}$$

We therefore have

$$\langle P^{[2]}(t)\rangle=-\frac{8\pi}{\hbar}\omega u^2\tilde{\gamma}^2 N(\langle I_m\rangle)_{\mathrm{av}}\int_0^t dt_1\int_0^{t_1}dt_2 P_{D0}\cos(\omega t_2+\theta)e^{-\frac{1}{2}\beta(t-t_1)}$$
$$\times\exp[-(t_1-t_2)^2/4\alpha^2]\sin\omega(t-t_1)\sin\omega(t_1-t_2). \tag{27}$$

We introduce a change of variables, setting

$$\xi=t_1+t_2,\quad \eta=t_1-t_2, \tag{28}$$

and noting that

$$\int_0^t dt_1\int_0^{t_1}dt_2\rightarrow\frac{1}{2}\int_0^t d\eta\int_\eta^{2t-\eta}d\xi.$$

The integrand consists now of a sum of products of trigonometric functions of ξ, η, and t, multiplied by the exponentials

$$\exp(-\eta^2/4\alpha^2)e^{-\frac{1}{2}\beta[t-\frac{1}{2}(\xi+\eta)]}. \tag{30}$$

For both $\omega\gg\alpha^{-1}$, which we have already assumed, and $\omega\gg\beta$, which is the usual requirement that the cavity relaxation time be much larger than a period (and which has been assumed in II), only those parts of the integrand which are nonoscillatory in ξ and η will contribute significantly to the integral. Thus, the product $\cos(\omega t_2+\theta)\sin\omega(t-t_1)\sin\omega(t_1-t_2)$ yields only the term $-\frac{1}{4}\cos(\omega t+\theta)$ for purposes of the integration over ξ and η. The integration over ξ can be carried out explicitly; the integration over η cannot. We therefore have

$$\langle P^{[2]}(t)\rangle=\frac{4\pi}{\beta\hbar}\omega u^2\tilde{\gamma}^2 N(\langle I_m\rangle)_{\mathrm{av}}P_D(t)F_1(t), \tag{31}$$

where

$$F_1(t)=\int_0^t dt_1 \exp\left(-\frac{t_1^2}{4\alpha^2}\right) -e^{-\frac{1}{2}\beta t}\int_0^t dt_1 \exp\left(-\frac{t_1^2}{4\alpha^2}+\frac{1}{2}\beta t_1\right).$$

(The variable of integration η has been relabeled t_1.) This is obviously the expression for the induced electric field strength [when Eq. (31) is multiplied by $-4\pi c\mathbf{u}(\mathbf{r})$], and it is interesting to compare it to the last term in Eq. (II, 55), which is the corresponding expression for the case of a molecule exactly at resonance with the cavity. We note, first, that as $\alpha^{-1}\rightarrow 0$, Eq. (31) gives the same result as the last term in Eq. (II, 55), which is what we should expect. However, the significant difference between the present case and that of exact resonance is that the induced field now approaches a steady-state value, while in the case of exact resonance it did not. We now have two transient effects. One is due to the cavity relaxation time, and the other is due to the molecular frequency spread. A steady state is achieved only for times larger than both the cavity relaxation time and the inverse molecular linewidth. (The same restriction applies here as in II: The time under discussion is short compared to the lifetime of the excited state.) A further discussion of $F_1(t)$ will be given in connection with the field energy.

III

We proceed now to calculate the expectation value of the energy of the field, which is given by Eq. (3). We have, up to second order,

$$\langle P^2\rangle=\langle P^{[0]2}\rangle+\langle P^{[1]2}\rangle+\langle\{P^{[0]},P^{[1]}\}\rangle +\langle\{P^{[0]},P^{[2]}\}\rangle, \quad (32)$$

where, as in II, we use the notation $\{A,B\}\equiv AB+BA$. $\langle P^{[0]2}\rangle$ is the same as that obtained in the absence of molecules. It leads to the zeroth order energy given by Eq. (II, 59), and is not of present interest to use. We have, further,

$$\langle\{P^{[0]},P^{[1]}\}\rangle=\{\langle P^{[0]}\rangle,\langle P^{[1]}\rangle\}=0, \quad (33)$$

from Eq. (16). The only terms with which we are presently concerned, therefore, are the second-order terms $\langle P^{[1]2}\rangle+\langle\{P^{[0]},P^{[2]}\}\rangle$. From Eq. (6c) we have

$$\langle P^{[1]2}\rangle=\frac{\omega^2u^2}{2c^2}\sum_{m,m'}\int_0^t dt_1\int_0^t dt_2\langle\{\gamma_m{}^{[0]}(t_1),\gamma_{m'}{}^{[0]}(t_2)\}\rangle e^{-\frac{1}{2}\beta(t-t_1)}e^{-\frac{1}{2}\beta(t-t_2)} \sin\omega(t-t_1)\sin\omega(t-t_2). \quad (34)$$

From Eq. (10) we see that for molecules with random initial phases,

$$\sum_{m\neq m'}\langle\gamma_m{}^{[0]}(t_1)\gamma_{m'}{}^{[0]}(t_2)\rangle=0. \quad (35)$$

Thus

$$\langle P^{[1]2}\rangle=\frac{\omega^2u^2}{2c^2}\sum_m\int^t dt_1\int_0^t dt_2\langle\{\gamma_m{}^{[0]}(t_1),\gamma_m{}^{[0]}(t_2)\}\rangle e^{-\frac{1}{2}\beta(t-t_1)}e^{-\frac{1}{2}\beta(t-t_2)} \sin\omega(t-t_1)\sin\omega(t-t_2). \quad (36)$$

From Eq. (II, 63),

$$\langle\{\gamma_m{}^{[0]}(t_1),\gamma_m{}^{[0]}(t_2)\}\rangle=2\tilde{\gamma}^2\cos\omega_m(t_2-t_1), \quad (37)$$

so that

$$\langle P^{[1]2}\rangle=\frac{\omega^2}{c^2}u^2\tilde{\gamma}^2\sum_m\int_0^t dt_1\int_0^t dt_2\cos\omega_m(t_1-t_2)e^{-\frac{1}{2}\beta(t-t_1)}e^{-\frac{1}{2}\beta(t-t_2)} \sin\omega(t-t_1)\sin\omega(t-t_2). \quad (38)$$

Using the same technique as that in carrying out the summation over $\sin\omega_m(t_1-t_2)$ [leading from Eq. (23) to Eq. (26)], we have

$$\textstyle\sum_m \cos\omega_m\eta=N\exp(-\eta^2/4\alpha^2)\cos\omega\eta. \quad (39)$$

Making the change of variables given by Eq. (28), and noting that

$$\int_0^t dt_1\int^t dt_2\rightarrow\frac{1}{2}\left\{\int_{-t}^0 d\eta\int_{-\eta}^{2t+\eta}d\xi+\int^t d\eta\int_\eta^{2t-\eta}d\xi\right\}\equiv\frac{1}{2}\int d\eta\int d\xi, \quad (40)$$

we obtain

$$\langle P^{[1]2}\rangle=\frac{1}{4}\frac{\omega^2}{c^2}u^2\tilde{\gamma}^2N\int d\eta\int d\xi\exp\left[-\frac{\eta^2}{4\alpha^2}-\beta(t-\tfrac{1}{2}\xi)\right]\cos\omega\eta[\cos\omega\eta-\cos\omega(2t-\xi)]$$

$$\cong\tfrac{1}{8}(\omega^2/c^2)u^2\tilde{\gamma}^2N\int d\eta\int d\xi\exp\left[-\frac{\eta^2}{4\alpha^2}-\beta(t-\tfrac{1}{2}\xi)\right]=\tfrac{1}{2}c^{-2}\beta^{-1}\omega^2u^2\tilde{\gamma}^2NF_2(t), \quad (41)$$

where

$$F_2(t)=\int_0^t dt_1 \exp\left(-\frac{t_1^2}{4\alpha^2}-\frac{1}{2}\beta t_1\right)-e^{-\beta t}\int_0^t dt_1 \exp\left(-\frac{t_1^2}{4\alpha^2}+\frac{1}{2}\beta t_1\right),$$

and where we have again dropped the oscillatory terms in ξ and η in the integrand.

There remains, now, the calculation of

$$\langle\{P^{[0]},P^{[2]}\}\rangle=\langle\{P_D,P^{[2]}\}\rangle+\langle\{P_\Gamma,P^{[2]}\}\rangle. \tag{42}$$

From Eqs. (11), (17), and (21), we have

$$P^{[2]}(t)=-\frac{8\pi}{\hbar}\omega u^2\tilde{\gamma}^2\sum_m I_m\int_0^t dt_1\int_0^{t_1} dt_2\, e^{-\frac{1}{2}\beta(t-t_1)}[P_D(t_2)+P_\Gamma(t_2)]\sin\omega(t-t_1)\sin\omega_m(t_1-t_2). \tag{43}$$

Since

$$\langle\{P_D(t'),P_\Gamma(t'')\}\rangle=0, \tag{44}$$

we have, immediately,

$$\begin{aligned}\langle\{P_D,P^{[2]}(t)\}\rangle&=2P_D\langle P^{[2]}\rangle\\&=(8\pi/\beta\hbar)\omega u^2\tilde{\gamma}^2N(\langle I_m\rangle)_{\mathrm{av}}P_D^2(t)F_1(t),\end{aligned} \tag{45}$$

and

$$\langle\{P_\Gamma,P^{[2]}(t)\}\rangle=-\frac{8\pi}{\hbar}\omega u^2\tilde{\gamma}^2\sum_m\langle I_m\rangle\int_0^t dt_1\int_0^{t_1} dt_2\langle\{P_\Gamma(t_2),P_\Gamma(t)\}\rangle e^{-\frac{1}{2}\beta(t-t_1)}\sin\omega(t-t_1)\sin\omega_m(t_1-t_2), \tag{46}$$

which we must yet evaluate.

From Eq. (6b) we have

$$\langle\{P_\Gamma(t_2),P_\Gamma(t)\}\rangle=\frac{\omega^2}{c^2}U^2\sum_j\int_{-\infty}^t dt_1\int_{-\infty}^{t_2} dt_3\langle\{\Gamma_j^{(0)}(t_1),\Gamma_j^{(0)}(t_3)\}\rangle e^{-\frac{1}{2}\beta(t-t_1)}e^{-\frac{1}{2}\beta(t-t_3)}\sin\omega(t-t_1)\sin\omega(t-t_3), \tag{47}$$

and since

$$\langle\{\Gamma_j^{(0)}(t_1),\Gamma_j^{(0)}(t_3)\}\rangle=2\bar{\Gamma}\cos\omega_j(t_3-t_1), \tag{48}$$

we obtain, with previously used approximations,

$$\langle\{P_\Gamma(t_2),P_\Gamma(t)\}\rangle=\frac{\omega^2}{c^2}U^2\bar{\Gamma}^2\sum_j\frac{\cos\omega_j(t_2-t)}{(\omega_j-\omega)^2+\frac{1}{4}\beta^2}, \tag{49}$$

which, when the summation is converted into an integration, becomes

$$\frac{2\pi}{c^2\beta}\omega^2U^2\bar{\Gamma}^2\rho_L(\omega)\cos\omega(t-t_2)e^{-\frac{1}{2}\beta(t-t_2)}. \tag{50}$$

Because of Eq. (7), we can write this as

$$\langle\{P_\Gamma(t_2),P_\Gamma(t)\}\rangle=(\hbar\omega/4\pi c^2)f(T)e^{-\frac{1}{2}\beta(t-t_2)}\cos\omega(t-t_2), \tag{51}$$

where

$$f(T)\equiv-(\langle I_j\rangle_\omega)^{-1}=1+2(e^{\hbar\omega/kT}-1)^{-1} \tag{52}$$

is a function of the cavity temperature, T, is derived in Eq. (II, 36), and obviously equal unity when the temperature is zero. We thus have

$$\langle\{P_\Gamma(t),P^{[2]}(t)\}\rangle=-2\frac{\omega^2}{c^2}u^2\tilde{\gamma}^2f(T)\sum_m I_m\int_0^t dt_1\int_0^t dt_2 e^{-\frac{1}{2}\beta(t-t_1)}e^{-\frac{1}{2}\beta(t-t_2)}\sin\omega(t-t_1)\cos\omega(t-t_2)\sin\omega_m(t_1-t_2). \tag{53}$$

Summing over m as we have done previously [Eq. (25)], changing the variables to ξ and η [Eq. (28)], and again retaining only nonoscillatory terms in ξ and η, we obtain

$$\langle\{P_\Gamma,P^{[2]}\}\rangle=(\omega^2u^2\tilde{\gamma}^2/2c^2\beta)N(\langle I_m\rangle)_{\mathrm{av}}f(T)F_2(t) \tag{54}$$

We note that

$$\begin{aligned}&\langle P^{[1]2}\rangle+\langle\{P_\Gamma,P^{[2]}\}\rangle\\&\quad=(\omega^2u^2\tilde{\gamma}^2/2c^2\beta)N[1+(\langle I_m\rangle)_{\mathrm{av}}f(T)]F_2(t).\end{aligned} \tag{55}$$

$\langle Q^2\rangle$ may be obtained in the same manner as $\langle P^2\rangle$, or more easily, from one of the equations of motion for the field (see I),

$$Q=-(4\pi c^2/\omega^2)\dot{P}. \tag{56}$$

From Eq. (3) we thus have for the expectation value of the field energy

$$\begin{aligned}\langle H_{\text{field}}\rangle&=\langle H^{[0]}\rangle+\langle H_{\text{field}}{}^{[2]}\rangle,\\ \langle H_{\text{field}}{}^{[2]}\rangle&=(2\pi/\beta)\omega^2u^2\tilde{\gamma}^2N[1+(\langle I_m\rangle)_{\text{av}}f(T)]F_2(t)\\ &\quad+(\omega u^2\tilde{\gamma}^2/\beta\hbar)NE_{D0}{}^2(\langle I_m\rangle)_{\text{av}}F_1(t).\end{aligned} \tag{57}$$

The zero-order energy is not due to the molecules. It is identical to that obtained in II, and will not be discussed further. The second-order energy is due to the molecules. It is obvious that the part of the field energy due to molecular emission induced by the driving field is

$$\langle H_{\text{field}}{}^{[2]}\rangle_{\text{induced}}=(\omega u^2\tilde{\gamma}^2/\beta\hbar)NE_{D0}{}^2(\langle I_m\rangle)_{\text{av}}F_1(t), \tag{58}$$

the part of the energy due to molecular emission induced by the thermal field is

$$\begin{aligned}\langle H_{\text{field}}{}^{[2]}\rangle_{\text{thermal}}&=(4\pi/\beta)N\omega^2u^2\tilde{\gamma}^2(\langle I_m\rangle)_{\text{av}}\\ &\quad\times(e^{\hbar\omega/kT}-1)^{-1}F_2(t),\end{aligned} \tag{59}$$

and the part due to spontaneous emission (zero-point vacuum—and molecular dipole-moment—fluctuations) is

$$\begin{aligned}\langle H_{\text{field}}{}^{[2]}\rangle_{\text{spontaneous}}&=(2\pi/\beta)\omega^2u^2\tilde{\gamma}^2N\\ &\quad\times[1+(\langle I_m\rangle)_{\text{av}}]F_2(t).\end{aligned} \tag{60}$$

It is interesting to examine certain characteristics of the emission energies just obtained. Some of these characteristics, such as the coherence properties (which are obtained by comparing expectation value of energy to expectation value of field strength) and the relationship of the thermal emission energy to the spontaneous emission energy, are the same as in II, and will not be discussed further here. The significant differences between these energies and the ones obtained for perfect molecular resonance are the magnitudes, in general, and the time dependence, in particular.

We note, first, that the emission energy for perfect molecular resonance, given by Eq. (II, 69), is a special case of the present situation, obtained by letting the molecular frequency spread approach zero. We note, furthermore—and this is probably the most significant aspect of the molecular frequency spread—that whereas the energy induced by the driving field did not approach a steady state in the case of perfect resonance, it does in the present case; and, as was mentioned in the discussion of field strength, the transient period is determined by two effects, linewidth and cavity loss. The steady-state values approached by F_1 and F_2 are, respectively,

$$\begin{aligned}F_{1\text{st}}&=\int_0^\infty dt_1\exp\left(-\frac{t_1{}^2}{4\alpha^2}\right),\\ F_{2\text{st}}&=\int_0^\infty dt_1\exp\left(-\frac{t_1{}^2}{4\alpha^2}-\frac{1}{2}\beta t_1\right).\end{aligned} \tag{61}$$

We can cast these expressions into more convenient form. We note that

$$\beta=\delta_c,\quad \alpha=2/\delta_m, \tag{62}$$

where δ_c and δ_m are the cavity width and molecular width according to conventional definitions.[5] We set

$$r\equiv\delta_c/\delta_m=\tfrac{1}{2}\alpha\beta. \tag{63}$$

Using the notation for the error function[6]

$$\text{erf}x\equiv\frac{2}{\sqrt{\pi}}\int_0^x dy\exp(-y^2), \tag{64}$$

we have

$$\begin{aligned}F_{1\text{st}}&=2\sqrt{\pi}/\delta_m,\\ F_{2\text{st}}&=(2\sqrt{\pi}/\delta_m)\exp(r^2)(1-\text{erf}r).\end{aligned} \tag{65}$$

For the case in which the molecules are all initially in the upper state, we have, from Eq. (24)

$$(\langle I_m\rangle)_{\text{av}}=1, \tag{66}$$

and the ratio of induced to spontaneous emission energy in the steady state, which is of interest in applications (see II), is

$$2n\frac{F_{1\text{st}}}{F_{2\text{st}}}=\frac{2n}{\exp(r^2)(1-\text{erf}r)}, \tag{67}$$

where

$$n=\frac{E_{D0}{}^2/8\pi}{\hbar\omega},$$

the ratio of energy in the driving field to the energy of a photon, or "the number of photons in the cavity." As r approaches zero (molecular width large compared to cavity width), the ratio approaches $2n$. For r large (molecular width small compared to cavity width), we use the asymptotic form[7]

$$\text{erf}r\approx1-[\exp(-r^2)/r\sqrt{\pi}], \tag{68}$$

to obtain for the steady-state ratio of induced to spontaneous emission energy in the cavity field

$$2nr\sqrt{\pi}. \tag{69}$$

This quantity may be compared with expression (II, 74), $n\beta t$, which is the same ratio for zero molecular frequency spread.

IV

So far, the energy under consideration has been that of the field. We consider now the energy of the molecules themselves. This energy is of fundamental interest since it is directly related to the molecular transition probabilities.

---

[5] δ_c is the width between the half-power points on the cavity resonance curve and δ_m is the width between the e^{-1} points on the (angular) frequency distribution curve for the molecules.

[6] See, for instance, E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1943).

[7] H. B. Dwight, *Tables of Integrals* (The Macmillan Company, New York, 1934), Eq. (592).

We set out to calculate the expectation value of the power emitted by the molecules. This is given by

$$\sum_m \left\langle \frac{dH_m}{dt} \right\rangle = -4\pi cu \sum_m \left\langle P\frac{d\gamma_m}{dt} \right\rangle, \tag{70}$$

as obtained from the Hamiltonian of Eq. (2). We have, for the first and second orders of this quantity

$$\sum\nolimits_m \langle \dot{H}_m{}^{[1]} \rangle = -4\pi cu \sum\nolimits_m \langle P^{[0]} \dot{\gamma}_m{}^{[0]} \rangle, \tag{71}$$

$$\sum\nolimits_m \langle \dot{H}_m{}^{[2]} \rangle = -2\pi cu \sum\nolimits_m [\langle \{P^{[0]}, \dot{\gamma}_m{}^{[1]}\} \rangle + \langle \{P^{[1]}, \dot{\gamma}_m{}^{[0]}\} \rangle], \tag{72}$$

where, in the last equation, we have written the product of $P(t)$ and $\dot{\gamma}(t)$ as a symmetrized product, for convenience. [$P(t)$ and $\dot{\gamma}(t)$ commute; $P^{[0]}(t)$ and $\dot{\gamma}^{[1]}(t)$ do not.] From Eq. (10) we can see that the first-order power vanishes for the case in which the molecules have random initial phases.

Equations (6c) [with $\gamma_m(t)$ replaced by $\gamma_m{}^{[0]}(t)$] and (21) give us the operator expression for $P^{[1]}$ and $\gamma^{[1]}$. The techniques used in the evaluation of the right side of Eq. (72) are the same as those used in evaluating the expectation value of the field energy, and it is therefore unnecessary to go through the details of the calculation. The result is

$$-\sum_m \langle \dot{H}_m{}^{[2]} \rangle = \frac{\omega u^2 \tilde{\gamma}^2}{2\hbar} N E_{D0}{}^2 (\langle I_m \rangle)_{\mathrm{av}} \int_0^t dt_1 \exp\left(-\frac{t_1{}^2}{4\alpha^2}\right) + 2\pi\omega^2 u^2 \tilde{\gamma}^2 N [1 + (\langle I_m \rangle)_{\mathrm{av}} f(T)] \int_0^t dt_1 \exp\left(-\frac{t_1{}^2}{4\alpha^2} - \frac{1}{2}\beta t_1\right). \tag{73}$$

We can break up this expression into spontaneous and induced emission, the latter consisting of emission induced by the driving field and thermally-induced emission. For comparison with results obtained in II and with conventional expressions, we give the power emitted *per molecule* (averaged over the molecules). Setting

$$\int_0^t dt_1 \exp\left(-\frac{t_1{}^2}{4\alpha^2}\right) = \frac{2\sqrt{\pi}}{\delta_m} \operatorname{erf}(\tfrac{1}{4}\delta_m t) \equiv f_1(t), \tag{74}$$

and

$$\int_0^t dt_1 \exp\left(-\frac{t_1{}^2}{4\alpha^2} - \frac{1}{2}\beta t_1\right) = \frac{2\sqrt{\pi}}{\delta_m} \exp(r^2)[\operatorname{erf}(\tfrac{1}{4}\delta_m t + r) - \operatorname{erf} r] \equiv f_2(t), \tag{75}$$

we note the following: The induced emission power per molecule due to driving field is

$$(\omega u^2 \tilde{\gamma}^2 / 2\hbar) E_{D0}{}^2 (\langle I_m \rangle)_{\mathrm{av}} f_1(t); \tag{76}$$

the spontaneous emission power per molecule is

$$2\pi\omega^2 u^2 \tilde{\gamma}^2 [1 + (\langle I_m \rangle)_{\mathrm{av}}] f_2(t); \tag{77}$$

and the thermally-induced emission power per molecule is

$$4\pi\omega^2 u^2 \tilde{\gamma}^2 (\langle I_m \rangle)_{\mathrm{av}} (e^{\hbar\omega/kT} - 1)^{-1} f_2(t). \tag{78}$$

For molecules in the upper state, thermally-induced emission is $(e^{\hbar\omega/kT} - 1)^{-1}$ times as large as the spontaneous emission, and need not be discussed further for present purposes. In the following discussion, we mean signal-induced emission when we refer to induced emission.

We note that, as in the case of the field energy, the induced emission power approaches a steady state as a result of a spread in molecular frequencies. The transient period is determined only by the molecular frequency spread, and the induced emission power reaches 0.84 of its steady-state value for $t = 4\delta_m{}^{-1}$. In the case of the spontaneous emission, the transient period is determined by both the molecular frequency spread and cavity loss. For molecules in the upper state, the steady-state value for induced emission power is

$$\frac{\sqrt{\pi}}{\delta_m} \frac{\omega}{\hbar} u^2 \tilde{\gamma}^2 E_{D0}{}^2 = \frac{\sqrt{\pi}}{\delta_m} 8\pi n \omega^2 u^2 \tilde{\gamma}^2, \tag{79}$$

and the steady-state value for the spontaneous emission power is

$$(\sqrt{\pi}/\delta_m) 8\pi\omega^2 u^2 \tilde{\gamma}^2 \exp(r^2)[1 - \operatorname{erf} r]. \tag{80}$$

We can compare the result of Eq. (79) with that obtained from conventional application of time-dependent perturbation theory. For a sinusoidally varying perturbation term in the Hamiltonian with amplitude H_0 and frequency corresponding to the energy difference between initial and final state of unperturbed system, the transition probability per unit time is given by[8]

$$w = \tfrac{1}{2}(\pi/\hbar)\rho(k)\,|H_{0km}|^2, \tag{81}$$

where m refers to the initial state, k refers to the final state, and $\rho(k)$ is the density of final states in energy space. A system with a number of final states may be considered as a number of systems, each one with a single final state, where the distribution of final states is the same as in the single system, and where the initial states coincide. (Actually, it is only the distribution of energy *differences* between initial and final state that

---

[8] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), Eqs. (29.17), (29.9), and (29.12).

enters in the calculation of transition probability.) If we consider our N molecules and set $N=\frac{1}{2}\sqrt{\pi}\hbar\delta_m\rho(k)$, one can see easily from Eq. (1) (recalling that $\alpha=2\delta_m{}^{-1}$) that the density of lower (or upper) states in $\hbar\omega_m$ space, at $\omega_m=\omega$, is $\rho(k)$, if we let the upper (or lower) states coincide. The steady-state transition probability may be obtained from Eq. (79) by multiplying by N and dividing by $\hbar\omega$. The result is

$$\tfrac{1}{2}(\pi/\hbar)u^2\tilde{\gamma}^2\rho(k)E_{D0}{}^2. \tag{82}$$

Since $H_{0km}=-u\tilde{\gamma}E_{D0}$, this is also the result obtained from Eq. (81).

For a given number of molecules, it is obvious that the narrower the frequency spread, the larger the induced steady-state power emitted; but as the frequency becomes narrower, the transient period becomes longer, and if the time of interest is not sufficiently long, the steady state will not give the correct result. In that event, Eq. (81) cannot be used, and one must resort to the more general expression (76).

As far as the spontaneous transition probability inside the cavity is concerned, this has been given by Purcell[9] for a molecule in resonance with the cavity. In II, it is shown that Purcell's formula, Eq. (II, 87), is really the steady-state value of the spontaneous transition probability averaged over the volume of the cavity. Comparing Eq. (80) with Eq. (II, 87), we see that in the case of a molecular frequency spread, we must multiply Purcell's formula by the factor

$$A(r)\equiv\sqrt{\pi}r\exp(r^2)[1-\mathrm{erf}r], \tag{83}$$

thus obtaining

$$8\pi\text{“}Q\text{”}\tilde{\gamma}^2A(r)/\hbar V, \tag{84}$$

as the steady-state spontaneous transition probability averaged over the volume V of the cavity. By means of Eq. (68) it is easy to see that $A(r)$ approaches unity as r becomes large. Also, for $r=1$, $A(r)\cong0.66$, and for small r, $A(r)$ obviously becomes $r\sqrt{\pi}$. As in the case of induced emission, the transition probability during the transient period must be obtained from the more general expression (77).

We consider, finally, the ratio of induced to spontaneous emission of molecules in the upper state. This ratio is of fundamental interest and is directly connected with the ratio of the Einstein A and B coefficients. The "classical" value of $(n+1)/n$ for the latter implies that the ratio of induced to spontaneous emission is n. From Eqs. (76) and (77) we obtain for this ratio (which we call R)

$$R(t)=\frac{\mathrm{erf}(\frac{1}{4}\delta_mt)}{[\mathrm{erf}(\frac{1}{4}\delta_mt+r)-\mathrm{erf}r]\exp(r^2)}n. \tag{85}$$

It is not difficult to see that for $\delta_mt\rightarrow0$, or for $r\rightarrow0$, $R(t)$ indeed becomes equal to n. Otherwise, however, $R(t)$ is not equal to n. Thus, the steady-state value of $R(t)$ is

$$R_{\mathrm{st}}=\frac{n}{\exp(r^2)(1-\mathrm{erf}r)}.$$

For the case $r=1$, $(\delta_c=\delta_m)$, we have $\mathrm{erf}1=0.843$ and $R\cong2.4n$. As r becomes large, $R_{\mathrm{asymptotic}}\cong nr\sqrt{\pi}$. The reason the "classical" value of the ratio of the Einstein coefficients (which is the ratio of the downward to upward transition probabilities) does not hold in our case is that we are dealing with induced emission produced by a coherent field.[10] The original Einstein analysis applied to an incoherent (in fact, a thermal) field. Thus, if we take the ratio of thermally-induced emission power, given by Eq. (78), to spontaneous emission power, given by Eq. (77), we obtain $(e^{\hbar\omega/kT}-1)^{-1}$. Planck's radiation law [or Eq. (II, 40)] tells us that this is just the number of photons in the thermal field energy of the cavity.

ACKNOWLEDGMENT

The author wishes to thank Professor Julian Schwinger for his critical reading of the manuscript.

Note added in proof.—Since the completion of the present article, a more general method than that employed here has been developed for the introduction of dissipation into the quantum-mechanical formalism for the radiation field [I. R. Senitzky, Phys. Rev. **119**, 670 (1960)]. No utilization is made of a specific model for the loss mechanism in the new method. The results obtained with this method are the same as those of the present article.

---

[9] E. M. Purcell, Phys. Rev. **69**, 681 (1946).

[10] In order to avoid possible misunderstandings, due to definitions of the term "coherent field" other than that given in I, the word "coherent" should be applied, in the present article as well as in II, only to that part of the zero-order field which is specified by P_D [See Eq. (11)], namely, the driving field, or the c-number part of the zero-order field. This c-number part may be thought of as being due to a macroscopic sinusoidal oscillator which is located at an appropriate distance from the cavity, for instance, to give P_D the correct amplitude. If the term "coherent" is applied to the total zero-order field without regard to the definition in I, then one might, according to the conventional uncertainty relationship between phase and number of quanta [see, for instance, W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed.], mistakenly assume that the present considerations apply only to a strong driving field. For a sufficiently strong driving field, quantum-mechanical aspects of the field are unimportant, spontaneous emission is of no consequence, and a nonperturbation treatment such as that of I. Rabi, Phys. Rev. **51**, 655 (1937), or of R. H. Dicke and R. H. Romer, Rev. Sci. Instr. **26**, 915 (1955), where the total field is a prescribed c number, is preferable.