NONLINEAR INTERFERENCE EFFECTS IN SPONTANEOUS EMISSION WITH ALLOWANCE FOR COLLISIONS

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Equations for the density matrix are derived, which describe spontaneous emission by atoms located in an external field, with collisions taken into account in the impact approximation. It is shown that the spontaneous emission probability cannot be expressed in terms of the density matrix derived under some definite initial conditions. Expressions for the spontaneous emission spectrum for various atomic transitions are derived within the framework of the model of three relaxation constants. A general analysis as well as an investigation of a concrete collision model show that changes in the spontaneous emission spectrum are due to 1) changes in the atom velocity distribution, 2) the characteristics of the collision processes, and 3) interference effects due to the presence of an external field that intermixes the stationary states of isolated atoms.

In [1-3] we considered the question of spontaneous emission of atoms situated in an external electromagnetic field. In the case of immobile atoms, the external monochromatic field leads to line splitting if the energy of interaction between the atom and the field exceeds the level width. When account is taken of the motion of the atoms and of the corresponding Doppler broadening, a relatively sharp line structure also appears (with radiation width), not masked by the thermal motion of the atoms.

Recent papers [4,5] reported experimental observation of these effects in gas systems. It turns out that the line structure due to the external field changes appreciably with the gas pressure, i.e., it is very sensitive to atom-atom collisions. Thus, nonlinear phenomena in the spontaneous emission may turn out to be a new and interesting method of investigating different processes occurring in atomic collisions.

It was assumed in [1-3] that the only relaxation processes are spontaneous transitions from combining levels, and collisions were not taken into account. In this connection, naturally, a need arises for a suitable generalization of the theory of [1-3], which indeed is the subject of the present paper. To this end we develop first a theory based on the density-matrix formalism; we then introduce into the equation for the density matrix a collision integral, thus completing the general part. In Secs. 2 and 3 we consider certain concrete collision models and the resultant line-contour deformations.

1. GENERAL RELATIONS

Let an atom with nondegenerate levels E_0, E_1, ..., E_n, ..., E_m, ... be situated in an external electromagnetic field, whose spectrum is concentrated near the frequency ω_{mn} of one of the transitions ($m \to n$). According to [3], in the resonance approximation (distance between levels much larger than the level widths and the energy of interaction between the atom and the field), the contours of the lines corresponding to transitions in which the levels m and n take part, i.e., $l \to m$, $j \to n$, $m \to n$, etc., will depend on the external field, and in different manners for different transitions. Let us consider first the $m \to n$ transition, i.e., the one in which the external field "acts." The spectral and angular densities of the spontaneous-emission probability $w(\Omega_\mu)$ are given by the expression [3]

$$w(\Omega_\mu) = \frac{\gamma_{mn}}{2\pi^2} \mathrm{Sp}\Big\{ \mathrm{Re} \int dv \int_{t_0}^{\infty} dt \int_{t_0}^{t} dt_1 \exp\{-i(\Omega_\mu - \mathbf{k}_\mu \mathbf{v})(t-t_1)\} \times \langle \mathbf{S}^+(t, t_0)\boldsymbol{\beta}\mathbf{S}(t, t_0)\mathbf{S}^{-1}(t_1, t_0)\boldsymbol{\beta}^+\mathbf{S}(t_1, t_0)\boldsymbol{\rho}_0\rangle \Big\},$$

$$\boldsymbol{\rho}_0 = \frac{1}{Q_m + Q_n}\begin{pmatrix} q_m & 0 \\ 0 & q_n \end{pmatrix},$$

$$\boldsymbol{\beta} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad \Omega_\mu = \omega_\mu - \omega_{mn}, \quad Q_j = \int q_j \, dv. \qquad (1.1)$$

Here $2\gamma_{mn}$ is the Einstein coefficient for the $m \to n$ transition, ω_μ and $\mathbf{k}_\mu$ are the frequency and wave vector of the spontaneous emission, and q_j is the number of acts of excitation of the level j per unit time and in a unit interval of the velocity $\mathbf{v}$. The matrix $\mathbf{S}(t, t_0)$ is the fundamental matrix of the equation

$$i\hbar\left(\frac{\partial}{\partial t} + \boldsymbol{\gamma}\right)\mathbf{S} = \mathbf{H}\mathbf{S}, \quad \mathbf{S}(t_0, t_0) = \mathbf{E}, \quad \boldsymbol{\gamma} = \begin{pmatrix} \gamma_m & 0 \\ 0 & \gamma_n \end{pmatrix}, \qquad (1.2)$$

where $\mathbf{H}$ is the operator of the interaction energy of the atom with the external field, $1/2\gamma_m$ and $1/2\gamma_n$ are the lifetimes of the atoms at the levels m and n, and $\mathbf{E}$ is a unit matrix. We designate the matrices by boldface letters, and there should be no confusion with vectors.

Formula (1.1) expresses the probability of spontaneous emission in terms of the probability amplitude, and this formalism is sufficiently convenient if there are no collisions. On the other hand, if collisions are taken into account, then the matrices $\boldsymbol{\gamma}$ and $\mathbf{H}$ become random functions of the time, and the procedure of averaging over the collisions on the basis of (1.1) and (1.2) is far from simple. It is more convenient to change over to a description of the system by means of the density matrix, and to take the collisions into account in the kinetic equation with the aid of the collision integral.

Thus, our first problem is to express $w(\Omega_\mu)$ in terms

of the elements of the density matrix. We shall use the well known relations

$$\rho(t_1, t_0) = S(t_1, t_0)\rho_0 S^+(t_1, t_0); \quad S(t, t_1) = S(t, t_0)S^{-1}(t_1, t_0) \quad (1.3)$$

and expand the matrix products in (1.1). Then

$$w(\Omega_\mu) = \frac{\gamma_{mn}}{2\pi^2}\int_{t_0}^{\infty} dt \int_{t_0}^{t} dt_1 \langle \exp\{-i(\Omega_\mu - k_\mu v)(t-t_1)\}$$
$$\times\{S_{nn}(t, t_1)S^*_{mm}(t, t_1)\rho_{mm}(t_1, t_0) + S_{nn}(t, t_1)S^*_{mn}(t, t_1)\rho_{mn}(t_1, t_0)\}\rangle. \quad (1.4)$$

The products $S_{nn}S^*_{mk}$ (k = m, n) in (1.4) are the off-diagonal elements of the density matrix ρ_{mn}, and correspond to the initial conditions $\rho_{nk}(t_1, t_1) = 1$. Thus, $w(\Omega_\mu)$ cannot be expressed in terms of a density matrix obtained under certain definite initial conditions. Therefore, from the formal point of view, it is natural to go over from a two-row matrix ρ to a four-row matrix σ_{ij}, in which

$$\sigma_{1j} = \rho_{mm}, \quad \sigma_{2j} = \rho_{nn}, \quad \sigma_{3j} = \rho_{nm}, \quad \sigma_{4j} = \rho_{mn}, \quad (1.5)$$

and the second index corresponds to different initial conditions:

$$j = 1, \quad \rho_{mm}(t_0, t_0) = 1; \quad j = 2, \quad \rho_{nn}(t_0, t_0) = 1;$$
$$j = 3, \quad \rho_{nm}(t_0, t_0) = 1; \quad j = 4, \quad \rho_{mn}(t_0, t_0) = 1. \quad (1.6)$$

It is easy to verify that σ obeys the following equation and initial conditions:

$$\left(\frac{\partial}{\partial t} + \frac{i}{\hbar}\mathbf{V}\right)\sigma = -\Gamma\sigma,$$
$$\Gamma = \begin{pmatrix} 2\gamma_m & 0 & 0 & 0 \\ 0 & 2\gamma_n & 0 & 0 \\ 0 & 0 & \gamma_m + \gamma_n & 0 \\ 0 & 0 & 0 & \gamma_m + \gamma_n \end{pmatrix},$$
$$\mathbf{V} = \begin{pmatrix} 0 & 0 & H_{mn} & -H^*_{mn} \\ 0 & 0 & -H_{mn} & H^*_{mn} \\ H^*_{mn} & -H^*_{mn} & 0 & 0 \\ -H_{mn} & H_{mn} & 0 & 0 \end{pmatrix};$$
$$\sigma(t_0, t_0) = \mathbf{E}. \quad (1.7)$$

In this notation, formula (1.4) takes the form

$$w(\Omega_\mu) = \frac{\gamma_{mn}}{2\pi^2}\frac{1}{Q_m + Q_n}\mathrm{Re}\left\langle \int_{t_0}^{\infty} dt \int_{t_0}^{t} dt_1 \exp\{-i(\Omega_\mu - k_\mu v)(t-t_1)\}\right.$$
$$\times\{[q_m\sigma_{11}(t_1, t_0) + q_n\sigma_{12}(t_1, t_0)]\sigma_{33}(t, t_1)$$
$$\left. + [q_m\sigma_{41}(t_1, t_0) + q_n\sigma_{42}(t_1, t_0)]\sigma_{32}(t, t_1)\}\right\rangle. \quad (1.8)$$

Formulas (1.7), (1.8) and (1.1), (1.2) are obtained from one another by identical transformations, and are therefore equivalent. Introduction of collisions in (1.8) and (1.7), naturally, violates this equivalence. Before we proceed to such a generalization, let us discuss certain features of (1.8).

The first term of the integrand in (1.8) is "usual": it is proportional to the probability of finding the atom at the upper level m (see (1.4)); this probability, in turn, consists of the terms $q_m\sigma_{11}$ and $q_n\sigma_{12}$, which are connected with the excitation of the atoms at the levels m and n, respectively. The factor σ_{33} is also quite "usual," being the off-diagonal element of ρ_{nm}, determined under the initial condition $\rho_{nm}(t_1, t_1) = 1$ (see (1.5) and (1.6)). Thus, the first term in (1.8) coincides qualitatively with what we are used to seeing in the analysis of the spontaneous-emission spectrum, and the external field can change some concrete characteristics of this term (the form of the dependence on t, t_1, etc.), but not its intrinsic meaning.

The second term in (1.8) is "unusual," and is proportional not to the probability of finding the atom at the level m, but to the off-diagonal elements $\varphi_{mn}(t_1, t_0)$ and $\sigma_{32}(t, t_1) = \rho_{nm}(t, t_1)$ under the condition $\rho_{nn}(t_1, t_1) = 1$. Further, if the external field tends to zero, then these two factors vanish. Finally, this term does not make any contribution whatever to the integral emission probability. Indeed, integration of (1.8) with respect to Ω_μ yields $2\pi\delta(t - t_1)$; according to (17), on the other hand, we have $\sigma_{32}(t_1, t_1) = 0$, $\sigma_{33}(t_1, t_1) = 1$, and

$$W_\mu = \int_{-\infty}^{\infty} w(\Omega_\mu)d\Omega_\mu$$
$$= \frac{\gamma_{mn}}{2\pi(Q_m + Q_n)}\mathrm{Re}\int_{t_0}^{\infty} dt_1\langle q_m\sigma_{11}(t_1, t_0) + q_n\sigma_{12}(t_1, t_0)\rangle, \quad (1.9)$$

i.e., the integrated probability (with respect to frequency) of the spontaneous emission W_μ is determined only by the first "usual" term in (1.8), and is proportional to the real population of the level m established in the given field. Thus, the second term in (1.8) has an interference character. In other words, it is due to interference between the states of the atom, occurring in an external field. Many effects predicted in[1-3,6] are due just to this interference.

It is appropriate to note that Bennett et al.[4] and Gordover et al.[5] interpreted the experimental data on the basis of concepts in which no allowance is made for interference phenomena of the type considered here. The possibility of such phenomena was ignored also by Burshteĭn[7].

We now turn to the question of the changes that must be introduced into expression (1.8) to take the collisions into account. We omit the corresponding derivation, and present only the final result, the physical meaning of which is perfectly clear. Namely, the element of the fundamental matrix $\sigma_{ij}(t, t')$ which enter in (1.8) must be replaced by elements (with the same indices) of the Green's matrix $\mathbf{G}(\mathbf{v}, t|\mathbf{v}', t')$, which are obtained by solving the equation

$$i\hbar\left\{\frac{\partial}{\partial t}\mathbf{G} - \mathbf{V}\mathbf{G} - \hat{\mathbf{S}}(\mathbf{G})\right\} = \mathbf{E}\delta(\mathbf{v} - \mathbf{v}')\delta(t - t'), \quad (1.10)$$

where $\mathbf{V}$ retains the form (1.7), and the term $\mathbf{S}(\mathbf{G})$ denotes a collision integral that includes also the spontaneous decay, i.e., the term $\Gamma\cdot\sigma$ from (1.7). The expression for the spectral probability density of the spontaneous emission is

$$w(\Omega_\mu) = \frac{\gamma_{mn}}{2\pi^2(Q_m + Q_n)}\mathrm{Re}\int dv \int dv_1 \int dv_0$$
$$\times\int_{t_0}^{\infty} dt \int_{t_0}^{t} dt_1 \exp\{-i\Omega_\mu(t - t_1)\}$$
$$\times\{G_{33}(\mathbf{v}, t|\mathbf{v}_1, t_1)[G_{11}(\mathbf{v}_1, t_1|\mathbf{v}_0\ t_0)q_m(\mathbf{v}_0) + G_{12}(\mathbf{v}_1, t_1|\mathbf{v}_0 t_0)q_n(\mathbf{v}_0)]$$
$$+ G_{32}(\mathbf{v}, t|\mathbf{v}_1, t_1)[G_{41}(\mathbf{v}_1, t_1|\mathbf{v}_0, t_0)q_m(\mathbf{v}_0) + G_{42}(\mathbf{v}_1, t_1|\mathbf{v}_0, t_0)q_n(\mathbf{v}_0)]\}. \quad (1.11)$$

The integration with respect to v and $\mathbf{v}_1$, connected with the possible change of the atom velocity following the collision, is the main and essentially the only difference between (1.11) and (1.8). If for some reason we can neglect the change of the velocity, then $G \sim \delta(\mathbf{v} - \mathbf{v}')$

and formula (1.11) has the same structure as (1.8). However, the collision integral in (1.10) may differ from that of (1.7). Such a situation will be considered by us in Sec. 2 below.

We present, likewise without proof, expressions for the probability of spontaneous emission in transitions adjacent to the m → n transition (see the figure). Unlike the m → n transition, which is resonant with the external field, two Green's matrices are of importance for the neighboring transitions m → l and n → j. One coincides with (1.10), and the other, the two-row matrix $\mathbf{G}'$, satisfies the equation

$$i\hbar\left\{\frac{\partial}{\partial t}\mathbf{G}'-\hat{\mathbf{S}}'(\mathbf{G}')+\frac{i}{\hbar}\mathbf{V}'\mathbf{G}'\right\}=\mathbf{E}\delta(\mathbf{v}-\mathbf{v}_0)\delta(t-t_0),$$

$$\mathbf{V}'=\begin{pmatrix}0 & H_{mn}\\ H_{mn}^{*} & 0\end{pmatrix} \qquad (1.12)$$

where $\hat{\mathbf{S}}'$ is the collision integral. The part of this integral connected with the spontaneous damping is equal, in the cases m → l and n → j respectively, to

$$\begin{pmatrix}\gamma_m+\gamma_l & 0\\ 0 & \gamma_n+\gamma_l\end{pmatrix}\mathbf{G}',\quad \begin{pmatrix}\gamma_m+\gamma_j & 0\\ 0 & \gamma_n+\gamma_j\end{pmatrix}\mathbf{G}'. \qquad (1.13)$$

In the general case, the form of $\hat{\mathbf{S}}'(\mathbf{G}')$ is the same as for the off-diagonal elements of the density matrix $\rho_{l\mathrm{m}}$, $\rho_{l\mathrm{n}}$ or ρ_{jm}, ρ_{jn}.

If the solutions of (1.12) and (1.10) are known, then the spontaneous emission in the transitions m → l and n → j can be calculated from the formulas

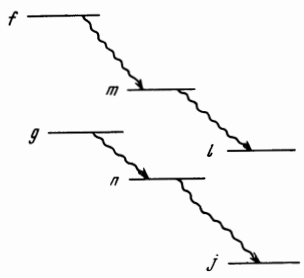
$$w(\Omega_\mu)=\frac{\gamma_{ml}}{2\pi^2}\mathrm{Re}\int d\mathbf{v}\,d\mathbf{v}_1\,d\mathbf{v}_0\int_{t_0}^{\infty}dt\int_{t_0}^{t}dt_1\exp\{-i\Omega_\mu(t-t_1)\}$$
$$\times\{G_{11}'(\mathbf{v},t|\mathbf{v}_1,t_1)[G_{11}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_m(\mathbf{v}_0)+G_{12}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_n(\mathbf{v}_0)]$$
$$+G_{12}'(\mathbf{v},t|\mathbf{v}_1,t_1)[G_{41}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_m(\mathbf{v}_0)+G_{42}(\mathbf{v}_1,t_1|\mathbf{v}_0\ t_0)q_n(\mathbf{v}_0)]\}, \qquad (1.14)$$

$$w(\Omega_\mu)=\frac{\gamma_{nj}}{2\pi^2}\mathrm{Re}\int d\mathbf{v}\,d\mathbf{v}_1\,d\mathbf{v}_0\int_{t_0}^{\infty}dt\int_{t_0}^{t}dt_1\exp\{-i\Omega_\mu(t-t_1)\}$$
$$\times\{G_{22}'(\mathbf{v},t|\mathbf{v}_1,t_1)[G_{21}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_m(\mathbf{v}_0)+G_{22}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_n(\mathbf{v}_0)]$$
$$+G_{21}'(\mathbf{v},t|\mathbf{v}_1,t_1)[G_{31}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_m(\mathbf{v}_0)+G_{32}(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_n(\mathbf{v}_0)]\}. \qquad (1.15)$$

The general structure of expressions (1.14) and (1.15) does not differ greatly from (1.11): one term is proportional to the probability of finding the atom at the upper level (the second lines), and the other is the interference term (the third lines of (1.14) and (1.15). The main difference lies in the appearance of $\mathbf{G}'(\mathbf{v},t|\mathbf{v}_1,t_1)$ in lieu of $\mathbf{G}(\mathbf{v},t|\mathbf{v}_1,t_1)$, which is perfectly understandable, since it is precisely G_{11}' and G_{22}' which determine the line shape in the transitions m → l and n → j in the absence of nonlinear effects.

For the transitions f → m, g → n, where the upper levels are not perturbed by the external field, the situation is much simpler. First, the populations of the levels f and g do not depend on the field and are determined only by the processes exciting these states. To find these populations it is sufficient, obviously, to solve the equation

$$i\hbar\left\{\frac{\partial}{\partial t}\mathbf{G}_i-\hat{\mathbf{S}}(\mathbf{G}_i)\right\}$$
$$=\mathbf{E}\delta(t-t_0)\delta(\mathbf{v}-\mathbf{v}_0),\quad i=f,g, \qquad (1.16)$$



and to specify the excitation rates $q_f(\mathbf{v}_0)$ and $q_g(\mathbf{v}_0)$. If we know also the solution of Eq. (1.12) with collision integrals characteristic of ρ_{mf}, ρ_{nf} and ρ_{mg}, ρ_{ng}, then the probability of spontaneous emission for the transitions f → m and g → n can be obtained from the formulas

$$w(\Omega_\mu)=\frac{\gamma_{fm}}{2\pi^2}\mathrm{Re}\int d\mathbf{v}\,d\mathbf{v}_1\,d\mathbf{v}_0\int_{t_0}^{\infty}dt\int_{t_0}^{t}dt_1\exp\{-i\Omega_\mu(t-t_1)\}$$
$$\times G_{11}'(\mathbf{v},t|\mathbf{v}_1,t_1)G_f(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_f(\mathbf{v}_0), \qquad (1.17)$$

$$w(\Omega_\mu)=\frac{\gamma_{gn}}{2\pi^2}\mathrm{Re}\int d\mathbf{v}\,d\mathbf{v}_1\,d\mathbf{v}_0\int_{t_0}^{\infty}dt\int_{t_0}^{t}dt_1\exp\{-i\Omega_\mu(t-t_1)\}$$
$$\times G_{22'}(\mathbf{v}_1t|\mathbf{v}_1,t_1)G_g(\mathbf{v}_1,t_1|\mathbf{v}_0,t_0)q_g(\mathbf{v}_0). \qquad (1.18)$$

Besides the singularity already noted above, attention must be called to the absence of "interference" terms in (1.17) and (1.18). This circumstance is obviously due to the fact that the upper level is not perturbed by the external field.

In concluding this section, let us dwell on some methodological questions. We used above the quasiclassical approximation for the description of the external field. This is not a fundamental limitation, for in analogy with the previously developed method[6], it is possible to construct a theory also for a quantized field. Since, however, nonlinear effects are noticeable at relatively large numbers of photons, the quasiclassical description is sufficient in practice.

In the derivation of (1.11) we started from formula (1.1), employed under the condition $\gamma_{\mathrm{mn}} \ll \gamma_{\mathrm{m}} + \gamma_{\mathrm{n}}$[6]. In the density-matrix formalism it is easy to take into account phenomena occurring when this condition is violated. It can be shown that in order to attain this purpose it is sufficient to introduce the arrival term $2\gamma_{\mathrm{mn}}\rho_{\mathrm{mm}}$ in the equation for the population ρ_{nn} of the lower level n.

The kinetic equations are usually written in the laboratory frame, and the left-hand side contains then the convective term $\mathbf{v}\nabla\mathbf{G}$. However, in the physical applications of interest to us, the collision integral does not contain operations on the atom coordinates $\mathbf{r}$. Therefore the change of variable $\mathbf{r}' = \mathbf{r} - \mathbf{v}t$ leads to the equations employed above, where $\mathbf{r}'$ enters as a parameter in $\mathbf{G}$ and $\mathbf{V}$.

2. COLLISION MODEL

We shall analyze the simplest model ("the model of three relaxation constants"), when the collision integral in the kinetic equation (1.10) is of the form

$$\hat{S}(G) = -\Gamma G, \qquad \Gamma = \begin{pmatrix} \Gamma_m & 0 & 0 & 0 \\ 0 & \Gamma_n & 0 & 0 \\ 0 & 0 & \Gamma + i\Delta & 0 \\ 0 & 0 & 0 & \Gamma - i\Delta \end{pmatrix}. \tag{2.1}$$

Unlike the purely spontaneous decay (formula (1.7)), the relaxation constants Γ_j and Γ in (2.1) are connected only by the inequality

$$2\Gamma \geqslant \Gamma_m + \Gamma_n. \tag{2.2}$$

The inequality in (2.2) becomes more strongly manifest in the case of the Weisskopf broadening mechanism (phase shift of the atomic oscillator). Here Γ_m and Γ_n are determined only by the rates of spontaneous damping γ_m and γ_n, and the line width contains also the impact term

$$\Gamma_m = 2\gamma_m, \quad \Gamma_n = 2\gamma_n, \quad \Gamma = \gamma_m + \gamma_n + \gamma_{Imp}. \tag{2.3}$$

In many cases even the strong inequality

$$\gamma_{Imp} \gg \gamma_m + \gamma_n, \quad 2\Gamma \gg \Gamma_m + \Gamma_n \tag{2.4}$$

may also be realized.

The collision integral (2.1) occurs in broadening by electrons, when the change of the velocity of the atom upon collision can be neglected. However, in the case of atom-atom collisions, which lead to diffusion of the atoms in velocity space, it is possible to use under certain limitations $\hat{S}(G)$ in the form (2.1). For example, in the strong-collision model[8,9] we have

$$\hat{S}(G) = -\nu G + \tilde{\nu} W_M(v) \int G dv',$$
$$W_M(v) = \frac{1}{(\sqrt{\pi}\,\bar{v})^3} \exp\left\{-\frac{v^2}{\bar{v}^2}\right\},$$
$$\nu = \begin{pmatrix} \nu_m & 0 & 0 & 0 \\ 0 & \nu_n & 0 & 0 \\ 0 & 0 & \nu & 0 \\ 0 & 0 & 0 & \nu \end{pmatrix}, \qquad \tilde{\nu} = \begin{pmatrix} \tilde{\nu}_m & 0 & 0 & 0 \\ 0 & \tilde{\nu}_n & 0 & 0 \\ 0 & 0 & \tilde{\nu} & 0 \\ 0 & 0 & 0 & \tilde{\nu}^* \end{pmatrix}. \tag{2.5}$$

An analysis of nonlinear effects with a collision integral (2.5) has shown[9-12] that the arrival term in (25), $\tilde{\nu} W \int G dv'$, can be discarded if the following condition is satisfied

$$\frac{\tilde{\nu}_j}{\Gamma_j + \nu_j - \tilde{\nu}_j} \frac{kv + \nu}{k\bar{v}} \ll 1, \quad j = m, n, \tag{2.6}$$

where $k\bar{v}$ is the Doppler line width. If $\Gamma + \nu \ll kv$ (as is frequently the case), then the inequality in (2.6) takes place even at relatively large pressures, when

$$(\Gamma_j + \nu_j - \tilde{\nu}_j) \frac{k\bar{v}}{\Gamma + \nu} \gg \tilde{\nu}_j \gtrsim \Gamma_j + \nu_j - \tilde{\nu}_j. \tag{2.7}$$

In this case, consequently, we also arrive at the model of "three relaxation constants," where, with allowance for spontaneous damping, we get

$$\Gamma_m = 2\gamma_m + \nu_m, \quad \Gamma_n = 2\gamma_n + \nu_n, \quad \Gamma = \gamma_m + \gamma_n + \nu. \tag{2.8}$$

If the departure frequencies ν_j and ν satisfy the equation $2\nu = \nu_m + \nu_n$, then relation (2.2) is an equality also for the constants Γ_j and Γ.

Thus, the collision integral (2.1) can describe a great variety of physical situations. We shall consider below spontaneous emission in precisely such a collision model.

Within the framework of the assumed model, the collision integral in (1.12) is given by

$$\begin{pmatrix} \Gamma_{ml} + i\Delta_{ml} & 0 \\ 0 & \Gamma_{nl} + i\Delta_{nl} \end{pmatrix} G', \quad \begin{pmatrix} \Gamma_{mj} + i\Delta_{mj} & 0 \\ 0 & \Gamma_{nj} + i\Delta_{nj} \end{pmatrix} G',$$
$$\begin{pmatrix} \Gamma_{fm} + i\Delta_{fm} & 0 \\ 0 & \Gamma_{fn} + i\Delta_{fn} \end{pmatrix} G', \quad \begin{pmatrix} \Gamma_{gm} + i\Delta_{gm} & 0 \\ 0 & \Gamma_{gn} + i\Delta_{gn} \end{pmatrix} G' \tag{2.9}$$

respectively for the transitions $m \to l$, $n \to j$, $j \to m$, and $g \to n$ (see the figure). The introduced constants Γ_{pq} and Δ_{pq} are the shock widths and the line shifts in the transition $p \to q$. In (1.16), the collision integral is

$$-\Gamma_i G_i, \quad i = f, g, \tag{2.10}$$

where Γ_i is the damping constant of the level i. All the remarks made above in connection with (2.1) remain in force also with respect to (2.9) and (2.10).

We note that in the model (2.1) the Green's matrices are proportional to $\delta(v - v')$, inasmuch as a constant velocity has been posulated. Therefore only one of the three integrations with respect to the velocities remains in the formulas for $w(\Omega_\mu)$. In particular, expression (1.11) for $w(\Omega_\mu)$ assumes for the $m \to n$ transition formally the same form as in (1.8).

3. LINE CONTOUR IN NEIGHBORING TRANSITIONS

In this section we shall pay attention to the so-called neighboring transitions ($m \to l$, $n \to j$, $f \to m$, $g \to n$, see the figure), which include only one of the two levels that are perturbed by the external field. The choice of these transitions is due to two causes. First, neighboring transitions will apparently be more convenient for the experimental study, since they will make it possible to avoid relatively simply the parasitic scattering of the external radiation. Second, the perturbation of only one of the combining levels greatly simplifies the line contour and makes the interpretation of the phenomena more lucid.

We assume further that the external field is a plane traveling monochromatic wave with frequency ω and wave vector $\mathbf{k}$. Then the matrix element H_{mn} equals

$$H_{mn} = \hbar G \exp\{-i(\Omega - kv)t\};$$
$$\Omega = \omega - \omega_{mn}, \quad G = d_{mn}E/2\hbar, \tag{3.1}$$

where E is the field amplitude, d_{mn} is the matrix element for the dipole moment in the transition $m \to n$.

We assume, finally, that the atoms have an equilibrium velocity distribution at the instant of excitation, i.e.,

$$q_m(v) = Q_m W_M(v), \quad q_n(v) = Q_n W_M(v). \tag{3.2}$$

In the case (3.1) it is natural to introduce the functions

$$G_{2i} \exp\{-i(\Omega - kv)t\},$$
$$G_{3i} \exp\{-i(\Omega - kv)t\}, \quad G' \exp\{-i(\Omega - kv)t\},$$

after which (1.10) reduces to an equation with constant coefficients, which can be readily solved by standard methods. The same pertains also to Eqs. (1.12) and (1.16). We therefore leave out all the intermediate steps and present the final result of the calculation of $w(\Omega_\mu)$.

We consider first the simpler case, when the levels perturbed by the external field are the lower levels. For the $g \to n$ transition (see the figure) we can obtain

$$w(\Omega_\mu)=\frac{W_{gn}}{\pi}\mathrm{Re}\left\langle\left[\Gamma_{gn}-i(\Omega_\mu-\Delta_{gn}-\mathbf{k}_\mu\mathbf{v})+\frac{G^2}{\Gamma_{gm}-i[\Omega_\mu-\Delta_{gm}-\Omega+\Delta_{mn}-\mathbf{v}(\mathbf{k}_\mu-\mathbf{k})]}\right]^{-1}\right\rangle. \quad (3.3)$$

The angle brackets denote here averaging over the velocities with a Maxwellian weight, and the quantity W_{gn} is the integral probability of the spontaneous emission:

$$W_{gn}=\int_{-\infty}^{\infty}w(\Omega_\mu)\,d\Omega_\mu=\frac{1}{2\pi}\frac{\gamma_{gn}}{\Gamma_g}. \quad (3.4)$$

The formula for $w(\Omega_\mu)$ in the f → m transition is obtained from (3.3) and (3.4) by interchanging the indices g → f and m → n, and in addition by replacing $\Omega-\Delta_{mn}-\mathbf{k}\cdot\mathbf{v}$ by $-[\Omega-\Delta_{mn}-\mathbf{k}\cdot\mathbf{v}]$.

Expression (3.3) differs from that obtained in[3] for the case of purely spontaneous relaxation in two respects: the radiative widths $\gamma_g+\gamma_m$ and $\gamma_g+\gamma_n$ are replaced by the impact widths Γ_{gm} and Γ_{gn}, and the line shifts Δ_{gn} and Δ_{gm} appear. Therefore there are no qualitatively new phenomena in (3.3). Inasmuch as a detailed analysis of a similar formula was made in[3], we confine ourselves to the foregoing statement and proceed to investigate the transitions m → l and m → j.

The formula for $w(\Omega_\mu)$ in the m → l transition is

$$w(\Omega_\mu)=\frac{W_{ml}}{\pi}\mathrm{Re}\left\langle\frac{p_{nl}+i(\mathbf{k}_\mu-\mathbf{k})\mathbf{v}}{[p_{ml}+i\mathbf{k}_\mu\mathbf{v}][p_{nl}+i(\mathbf{k}_\mu-\mathbf{k})\mathbf{v}]+G^2}\times\left\{1-\frac{NG^2}{|p_{mn}-i\mathbf{k}\mathbf{v}|^2+\Gamma^2\varkappa}\left[\frac{2\Gamma}{\Gamma_m}+\frac{p_{mn}^*+i\mathbf{k}\mathbf{v}}{p_{ln}+i(\mathbf{k}_\mu-\mathbf{k})\mathbf{v}}\right]\right\}\right\rangle. \quad (3.5)$$

Here

$$p_{mn}=\Gamma+i(\Omega-\Delta),\quad p_{ml}=\Gamma_{ml}-i(\Omega_\mu-\Delta_{ml}),$$
$$p_{nl}=\Gamma_{nl}-i(\Omega_\mu-\Delta_{nl}-\Omega),$$
$$\varkappa=\frac{2G^2}{\Gamma}\left(\frac{1}{\Gamma_m}+\frac{1}{\Gamma_n}\right),\quad N=\left(\frac{Q_m}{\Gamma_m}-\frac{Q_n}{\Gamma_n}\right)\Big/\frac{Q_m}{\Gamma_m};\quad W_{ml}=\frac{\gamma_{ml}}{2\pi\Gamma_m}. \quad (3.6)$$

The quantity W_{ml}, which is analogous to W_{gn} in (3.3), determines the integral probability of the spontaneous emission for the isolated atom. The factor N is none other than the relative population difference of the levels m and n in the absence of an external field. The factor

$$\frac{NG^2}{|p_{mn}-i\mathbf{k}\mathbf{v}|^2+\Gamma^2\varkappa}\frac{2\Gamma}{\Gamma_m}$$

specifies the relative change of the population[1] of the upper level m, due to the induced transitions:

$$\int w(\Omega_\mu)\,d\Omega_\mu=W_{ml}\left\langle1-\frac{NG^2}{|p_{mn}-i\mathbf{k}\mathbf{v}|^2+\Gamma^2\varkappa}\frac{2\Gamma}{\Gamma_m}\right\rangle. \quad (3.7)$$

The second term in the square brackets in (3.5) makes no contribution at all to the integral emission probability, i.e., in the terminology of Sec. 1, it is an interference term (see the discussion of (1.14) and (1.15)). Nonetheless, it may greatly influence the line shape.

To clarify this question, let us consider in greater detail the case of large Doppler broadening and relatively small amplitudes of the external field:

$$k_\mu\bar v,\ k\bar v\gg\Gamma,\ \Gamma_{ml},\ \Gamma_{nl};\quad \varkappa\ll1. \quad (3.8)$$

It is seen from (3.5) that the result of the averaging over the velocities depends on the mutual orientation of the vectors $\mathbf{k}_\mu$ and $\mathbf{k}$, i.e., on the angle between the directions of observation and the direction of propagation of the wave of the external field. The most interesting interference effects arise when $\mathbf{k}_\mu/k_\mu=\pm\mathbf{k}/k$, and we shall consider precisely these directions.

When $\varkappa\ll1$ we can disregard the terms G^2 and $\Gamma^2\varkappa$ in the resonant denominators of (3.5). Approximate integration with respect to v yields then

$$w(\Omega_\mu)=\frac{W_{ml}}{\sqrt{\pi}k_\mu\bar v}\exp\left\{-\left(\frac{\Omega_\mu-\Delta_{ml}}{k_\mu\bar v}\right)^2\right\}\left\{1-2\frac{k_\mu}{k}NG^2\times\mathrm{Re}\left[\frac{1}{\Gamma_{ml}+k_\mu\Gamma/k+i(\Omega_\mu-k_\mu\Omega/k-\delta_1^-)}\times\left(\frac{1}{\Gamma_m}+\frac{1}{\Gamma_{nl}+\Delta k\Gamma/k+i(\Omega_\mu-k_\mu\Omega/k-\delta_2)}\right)\right]\right\} \quad (3.9)$$

$$\delta_1^{\pm}=\Delta_{ml}\pm k_\mu\Delta/k,\quad \delta_2=\Delta_{nl}-\Delta k\Delta/k,\quad \Delta k=k_\mu-k,$$
$$\mathbf{k}_\mu\mathbf{k}>0,\quad k_\mu>k,$$
$$w(\Omega_\mu)=\frac{W_{ml}}{\sqrt{\pi}\,k_\mu\bar v}\exp\left\{-\left(\frac{\Omega_\mu-\Delta_{ml}}{k_\mu\bar v}\right)^2\right\}\left\{1-2\frac{k_\mu}{k}NG^2\times\mathrm{Re}\left[\frac{1/\Gamma_m}{\Gamma_{ml}+k_\mu\Gamma/k+i(\Omega_\mu+k_\mu\Omega/k-\delta_1^+)}\right]\right\},\quad (\mathbf{k}_\mu\mathbf{k}<0). \quad (3.10)$$

The integral probability is the same in both cases:

$$\int_{-\infty}^{\infty}w(\Omega_\mu)\,d\Omega_\mu=W_{ml}\left\{1-\frac{\sqrt{\pi}\,2}{\Gamma_m k\bar v}\frac{NG^2}{\sqrt{1+\varkappa}}\right\}. \quad (3.11)$$

Formulas (3.9) and (3.10) determine the contours of a line with a total width $k_\mu\bar v$ and with a relatively sharp "dip," which is described by the term with $2NG^2$ in the curly brackets[2]. The center of the dip is obviously located near the frequencies $\Omega_\mu=\pm k_\mu/k\Omega$, and its width (in view of (3.8)) is much smaller than the total line width $k_\mu\bar v$.

In observations along the direction opposite to k, the interference term turns out to be insignificant under the conditions (3.8) and does not affect the line shape. Accordingly, the dip has a simple dispersion form, and its width is made up of the line width Γ_{ml} of the m → l transition and the width of the "Bennett hole" (the dip in the velocity distribution), recalculated for the Doppler shift near the frequency ω_{ml} (the term $k_\mu\Gamma/k$).

If the observation is in the direction of k, then the shape of the dip is made more complicated by the interference term. We emphasize, first, that in this case the dip is always deeper, as can be readily verified by putting $\delta_1=\delta_2=0$ and $\Omega_\mu=\pm k_\mu/k\Omega$. At these points the expressions in the curly brackets of (3.9) and (3.10) are equal to

$$1-\frac{2NG^2}{\Gamma_{ml}+k_\mu\Gamma/k}\left(\frac{1}{\Gamma_m}+\frac{1}{\Gamma_{nl}+\Delta k\Gamma/k}\right);\quad 1-\frac{2NG^2}{\Gamma_{ml}+k_\mu\Gamma/k}\frac{1}{\Gamma_m}. \quad (3.12)$$

We recall that the change of the integral probability does not depend on the direction of observation (see (3.11)). This means that the areas of the dips are the same in

[1] More accurately, we are speaking of the number of atoms at the level m in a unit velocity interval.

[2] The decrease of the intensity due to this term occurs when N > O. On the other hand, if the population of the upper level is smaller (N < O), then the line has not a "dip" but a "peak".

the compared cases. But then it follows from (3.12) that in observation along $\mathbf{k}$ the width of the dip is always smaller than in observation along $-\mathbf{k}$. The relative narrowing of the dip is determined obviously by the ratio

$$\Gamma_m \Big/ \left(\Gamma_{nl} + \frac{k_\mu - k}{k}\Gamma\right), \qquad (3.13)$$

which, other conditions being equal, is the largest at $k_\mu - k \ll k$.

The form of the dip in the case of (3.9) depends on certain singularities of the broadening processes. If, for example,

$$\Gamma_m + \Gamma_{nl} + \frac{\Delta k}{k}\Gamma = \Gamma_{ml} + \frac{k_\mu}{k}\Gamma, \quad \delta_1 = \delta_2, \qquad (3.14)$$

then the dip, as can be readily seen from (3.9), will have a simple dispersion form and the width $\Gamma_{nl} + \Delta k\Gamma/k$. On the other hand, the condition imposed on the widths in (3.14) is equivalent to the following condition:

$$[\Gamma_{nl} - (\Gamma_n + \Gamma_l)/2] - [\Gamma - (\Gamma_m + \Gamma_n)/2] - [\Gamma_{ml} - (\Gamma_m + \Gamma_l)/2] = 0. \qquad (3.15)$$

For purely spontaneous relaxation, all three differences in the square brackets vanish identically, i.e., (3.15) is satisfied. This case was considered in[3]. In the strong-collision model, as was emphasized in Sec. 2, condition (3.15) can also be satisfied. On the other hand, as a rule, condition (3.15) is not satisfied in the Lorentz-Weisskopf broadening mechanism. Indeed, according to the well known formula for the impact widths and for the shift[13],

$$\Gamma_{\alpha\beta} + i\Delta_{\alpha\beta} = \langle\langle 1 - \exp\{-i(\delta_\alpha - \delta_\beta^*)\}\rangle\rangle; \quad \Gamma_{\alpha\alpha} = \Gamma_\alpha; \ \alpha, \beta = m, n, l, \qquad (3.16)$$

where δ_α and δ_β are the complex phase shifts of the atomic oscillator in collisions, and the double angle brackets denote averaging over all the collision parameters. Using (3.16), we can show that condition (3.15) denotes

$$\langle\langle (e^{-i\delta_m} - e^{-i\delta_l})(e^{i\delta_m^*} - e^{i\delta_n^*})\rangle\rangle = 0. \qquad (3.17)$$

Thus, to satisfy (3.15) it suffices to have the phase shift at the level m coincide with the phase shift at the level l or n. Of course, such cases are possible but are apparently quite rare.

Assume now that the condition (3.15) is not satisfied. Then, obviously, the dip will not have a simple dispersion form, and in particular, if $\mathbf{k}_\mu = \mathbf{k}$ and $\Gamma_{ml} + \Gamma = \Gamma_{nl} \approx \Gamma_m$, then the shape of the dip in (3.9) is described by the square of the dispersion function.

The line contour in the $n \to j$ transition can be obtained from (3.5) by replacing $\Gamma_m \to \Gamma_n$, $\Gamma_{ml} \to \Gamma_{nl}$ and $\Omega - \mathbf{k}\cdot\mathbf{v} \to -\Omega + \mathbf{k}\cdot\mathbf{v}$. Therefore all the physical conclusions drawn above remain in force also for the $n \to j$ transition. Here, however, observations along $\mathbf{k}$ and $-\mathbf{k}$ change places, namely, the interference effects are observed when $\mathbf{k}_\mu/k = -\mathbf{k}/k$.

4. CONCLUSION

Both the general analysis (Sec. 1) and the investigation of the concrete collision model (Secs. 2 and 3) demonstrate the noticeable role played by nonlinear interference phenomena in spontaneous emission. In the case when the Doppler broadening is large $k\bar{v} \gg \Gamma$, the change of the velocity distribution of the atoms, due to the induced transitions, is very important. If the external field does not disturb the velocity distribution at the upper level (N = 0, transitions $f \to m$ and $g \to n$), then noticeable deformations of the line contour occur only when $\kappa k\bar{v}/\Gamma \sim 1$. In the opposite case, the nonlinear effects are determined only by the value of the parameter κ.

On the other hand, the change of the velocity distribution does not determine the change of the line contour uniquely. The interference effects lead to an angular dependence of the emission spectrum, and the characteristic parameters of the line (depth, width of the "dip") may change by a factor of several times.

The physical cause of these effects is analogous to a certain degree to that which leads to the known singularities of resonance fluorescence. In both cases, the external field "mixes up" the states of the isolated atom and produced coherence of radiation in two coupled transitions. In resonance fluorescence we are dealing with transitions from the ground state to the excited one and vice versa. In our case, on the other hand, the coupling is between the induced $m \to n$ transition and the spontaneous emission in the neighboring transition. The distinction from fluorescence, which limits the analogy, consists in the fact that the initial and the final states do not coincide and have a finite level width. Nonetheless, both phenomena have obviously a common physical basis.

The sensitivity of the spontaneous-emission spectrum in the collisions gives grounds for hoping that the phenomena under consideration may become an interesting method for studying the processes of elastic and inelastic scattering of the atoms. Worthy of particular attention is the possibility of determining the relaxation characteristics for optically forbidden transitions (for example, the constant Γ_{nl} in the case $n \to l$). We must bear in mind, however, the relative complexity of the phenomenon. The situation becomes even worse if it is necessary not only to determine the numerical values of the parameters from the experimental data, but also to choose the collision model. One might think that an effective way out of the situation is to combine investigations of the spontaneous emission with those of other nonlinear phenomena (for example, the competition of two types of oscillations, the lamb "dip" etc.).

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