KINETICS OF THE RELAXATION INDUCED BY A SUDDEN POTENTIAL CHANGE

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A method is proposed for correct averaging of the density matrix of a system subjected to a random continuous perturbation of the Markov type. The equations obtained describe the relaxation of the system without any restrictions. The transformation of the Doppler spectral line contour due to pressure change and the broadening and splitting of the line due to powerful Lorentz emission are considered as illustrations.

INTRODUCTION

IN physical-kinetics problems pertaining to the discrete spectrum one deals as a rule with a continuously acting light or thermal perturbations, which either cause transitions between stationary states of the atom (molecule) or at least upset the phase correlation between them. We have considered recently [1] the population relaxation induced in a two-level system by monochromatic radiation $\hat{V} = \hat{F} \exp [i(\omega t + \alpha)]$, in which from time to time the phase α strays suddenly in an uncorrelated fashion. Radiation of this type is a concrete example of the broad class of perturbations $\hat{V}(\alpha)$ considered in the present article. The jumplike change in $\alpha(t)$ imparts to the time variation of $\hat{V}(t)$ a special Markoffian character, which distinctly differentiates it from the smoother normal process or from the loose sequence of short-duration perturbation bursts (separated by the collision mean free path), which is characteristic of a gas. The random parameter $\alpha(t)$ (Fig. 1) need not necessarily be the phase, and can also be the amplitude or the frequency of the perturbation or the energy of the stationary states [2]. Instantaneous changes of the Hamiltonian can be due not only to the field but also to the jumplike transitions of the atom from one position to another, jumps which are characteristic of condensed phases and which modulate its interaction with the medium.

The problem always consist of investigating the response of the system to a perturbation of the considered type, i.e., of describing the relaxation of the populations and the phases which the perturbation can cause. An estimate of the transition frequency makes it possible to judge the level of light absorption, the rate of energy transmission, or the rate of chemical transformation. The kinetics of

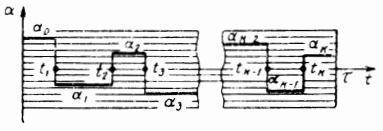

FIG. 1. Change in random variable in one of the realizations.

the phase relaxation contains information on the width and shape of the spectral lines.

The most general method of solving such problems is perturbation theory, first used by Dirac to calculate the transition probabilities [3], and leading —in a more refined form—to different modifications [2,4] of kinetic equations for the density matrix ρ. This method is universal: no matter what the random process $\hat{V}(t)$ perturbing the system may be, the process leads to unique results—to stochastic equations with probabilities expressed in terms of the dispersion $\overline{\hat{V}^2}$ and the spectral density of the perturbation. It is applicable only in the case when the perturbation becomes strong, i.e., it effects appreciable changes in the system within the scale of the correlation times [4] τ_0. This essential limitation cannot be eliminated by taking into account higher approximations, since its origin is not dynamic but static [2,5]. The perturbation becomes "strong" when τ_0 turns out to be too long and independent averaging of the quantities $\rho(t')$ and $\hat{V}(t)\hat{V}(t')$ in the Schrödinger equation ("decoupling") ceases to be correct. Our aim in the present paper, in choosing the special type of the process $\hat{V}(t)$, is to average the density matrix in rigorous fashion over all its realization regardless whether the perturbation is "weak" or "strong," i.e., without resorting to "decoupling."

This program has been realized only in some cases [6-8] and only for strictly adiabatic perturbations: $[\hat{H}_0\hat{V}] = 0$, $\hat{H} = \hat{H}_0 + \hat{V}$. Both the averaging method itself and its results, beyond the limits of

applicability of perturbation theory, are determined essentially by the type of random process (normal [6], Markoffian [7], collisions [8]) which perturbs the system. The diagonality (adiabaticity) of the perturbation simplifies matters greatly, since the possibility of expressing $\rho(t)$ in quadratures in terms of $\hat{V}(t)$ makes it possible to use the averaging methods developed in the theory of random processes [9]. However, if the problem is narrowed down to this extent, one can consider only phase relaxation; the level populations remain unchanged under adiabatic perturbations.

The special type of perturbation which we consider in the present article is apparently unique and admits of an averaging which is not restricted at all in the general case, for both adiabatic and the nonadiabatic perturbation. The possibility of considering the kinetics of transitions in the traditional Dirac formulation of the problem, but with arbitrarily strong perturbation, afforded by this approach, has already been used by us earlier [1]. This has made it possible to obtain solutions that are real both within the limits of applicability of perturbation theory and in the region where the very concept of "transition probability" becomes meaningless. At the same time, the previously employed [1] averaging of the state populations has restricted the problem and has called for the use of special initial conditions even in a two-level system. The matrix formulation of the problem developed in the present article makes it possible not only to get rid of these unjustified limitations, but also to consider, along with the population relaxation (for an arbitrary number of levels), the relaxation of the phases both for adiabatic and nonadiabatic perturbation.

Inasmuch as the relaxation of the populations has already been analyzed in detail [1], we illustrate the expanding possibilities of the method by considering only phase relaxation. As always in the solution of problems in all of the volume, two limiting situations are observed. In the case of short τ_0 (weak perturbation), the phase relaxation is exponential and the decay parameter, which determines the width of the corresponding Lorentz-shape spectral line, is simply double the probability of the transition in the Dirac definition. To the contrary, in the case of strong perturbation (long τ_0), the decay is not exponential, and the line shape is more complicated. In the adiabatic case, when the perturbed frequencies have a Gaussian distribution, the spectrum is also Gaussian. In the nonadiabatic case, when the transitions are induced by powerful light radiation with intermittent phase, the line is split into three components in a 1:2:1 ratio, with the magnitude of the splitting proportional to the amplitude of the radiation and the width of the components proportional to the width of the radiation spectrum. Reasonable results are obtained not only for the limiting situations but also for the intermediate ones, and reflect all the details of the line contour (for example, the transition from a Gaussian center to Lorentzian wings in case of an adiabatic perturbation).

1. METHOD

Let the operator $\hat{V}$ depend parametrically on α, viz., let the element of randomness be introduced in the time dependence of the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}(\alpha)$ only by a change of $\alpha(t)$. Assume, further, that the changes in $\alpha(t)$ occur instantaneously, jumpwise, and are separated by time intervals of the order of τ_0, in which $\alpha = \text{const}$, with the distribution

$$dW(\tau) = e^{-\tau/\tau_0} d\tau / \tau_0$$

specifying the probable duration of each such interval. Assume also that the values of α in the neighboring intervals are not correlated, i.e., in any section of the process, at any instant of time, the probability of finding a given α remains the same and equal to $dW(\alpha)$. No limitations are imposed on the form of this distribution.

The averaging of the density matrix is a purely statistical problem and therefore, proceeding to solve it, we assume that we know beforehand the unitary transformation $\hat{S}(t, t')$ which determines the dynamic change of the system between two successive changes of α:

$$\rho(t) = \hat{S}(\alpha;\ t,\ t')\,\rho(t')\,\hat{S}^{-1}(\alpha;\ t,\ t'). \qquad (1.1)$$

The unitary operator $\hat{S}(\alpha)$ is determined by the Schrödinger equation

$$i\hbar \frac{d\hat{S}}{dt} = \hat{H}(\alpha)\,\hat{S}$$

and therefore depends parametrically on α, and also on the times t' and t—the start of the interval and the current time. At the end of each (i-th) interval (Fig. 1) we find the density matrix $\rho(t)$, which is the initial condition for the next one, so that if in the interval (0, t) there were k changes of α, then

$$\rho(t, t_k) = \hat{S}(\alpha_k;\ t,\ t_k) \ldots \hat{S}(\alpha_1;\ t_2,\ t_1)\,\hat{S}(\alpha_0;\ t_1,\ 0)$$
$$\times \rho(0)\,\hat{S}^{-1}(\alpha_0;\ t_1,\ 0)\,\hat{S}^{-1}(\alpha_1;\ t_2,\ t_1) \ldots \hat{S}^{-1}(\alpha_k;\ t,\ t_k). \qquad (1.2)$$

The multiplicative nature of this expression makes

it possible to average it by the method already employed by us earlier. [1]

The probability that in the interval (0, t) k changes of α have actually occurred at successive instants $t_1, t_2, \ldots, t_k$, and that a certain sequence $\alpha_0, \alpha_1, \ldots, \alpha_k$ was realized between them is obviously equal to

$$dW(t_1, t_2, \ldots, t_k;\ \alpha_0, \alpha_1, \ldots, \alpha_k;\ t) = e^{-t/\tau_0} \prod_{i=1}^{k} \frac{dt_i}{\tau_0} \prod_{i=0}^{k} dW(\alpha_i). \tag{1.3}$$

Recognizing that k can assume all values from 0 to ∞, we must, multiplying (1.2) by (1.3), not only integrate over all α_i and over all t_i, which follow in chronological order, but also to sum with respect to k. The density matrix averaged in this fashion over all possible realizations of the process is represented in the form of the series

$$\bar{\rho}(t)\, e^{t/\tau_0} = \sum_{k=0}^{\infty} \frac{1}{\tau_0^k} \int_0^t dt_k \int_0^{t_k} dt_{k-1} \ldots \int_0^{t_2} dt_1 \times \int dW(\alpha_k) \int dW(\alpha_{k-1}) \ldots \int dW(\alpha_0)\, \rho(t, t_k), \tag{1.4}$$

and the term with k = 0 (when α does not change at all in the interval (0, t)) does not contain integrals with respect to the time, and is equal simply to $\int dW(\alpha_0)\rho(t, 0)$.

Using the recurrence formula (1.1), we can multiply both sides of (1.4) from the right and from the left respectively by $\hat{S}(\alpha;\ \tau, t)$ and $\hat{S}^{-1}(\alpha;\ \tau, t)$ and also by $dW(\alpha)dt/\tau_0$, and verify that integration with respect to t from 0 to τ, yields an equation whose right side again contains the same series as in (1.4), but of a different argument (τ) and without the first term. Adding (and subtracting) the missing term, we can eliminate this entire series with the aid of (1.4), after which we obtain

$$\bar{\rho}(\tau)\, e^{\tau/\tau_0} = \int_\alpha \hat{S}(\alpha;\ \tau, 0)\, \rho(0)\, \hat{S}^{-1}(\alpha;\ \tau, 0)\, dW(\alpha) + \frac{1}{\tau_0} \int_0^\tau e^{t/\tau_0} \int_\alpha \hat{S}(\alpha;\ \tau, t)\, \bar{\rho}(t)\, \hat{S}^{-1}(\alpha;\ \tau, t)\, dW(\alpha)\, dt. \tag{1.5}$$

If we set in correspondence with each element of the density matrix ρ_{im} a certain operator $\hat{R}^{im}(\tau, t)$, such that

$$R_{lk}^{im} = \int_\alpha \hat{S}_{ik}(\alpha;\ \tau, t)\, \hat{S}_{lm}^{-1}(\alpha;\ \tau, t)\, dW(\alpha), \qquad R_{lk}^{im} = (R_{kl}^{mi})^*, \tag{1.6}$$

then Eq. (1.4) can be rewritten in the form [1)]

$$\rho_{im}(\tau) = e^{-\tau/\tau_0} \mathrm{Sp}\,[\hat{R}^{im}(\tau, 0)\, \rho(0)] + \frac{1}{\tau_0} \int_0^\tau dt \exp\left[-\frac{\tau - t}{\tau_0}\right] \mathrm{Sp}\,[\hat{R}^{im}(\tau, t)\, \rho(t)]. \tag{1.7}$$

This equation is the end result of the statistical calculation, since the randomness element has been completely eliminated from it (unlike the Schrödinger equation with Hamiltonian $\hat{H}(\alpha)$). The solution of the dynamic problem (the determination of $\hat{R}$) still remains the necessary preliminary stage, but now we are dealing not with a long-time random behavior of the system, but only with an interval in which α = const and the change in ρ is perfectly regular. Knowing $\hat{R}$, we can solve Eq. (1.5) not only in principle, but also in fact, and by the same token find the averaged variation of the system, unbounded with respect to time, during the relaxation process. We shall consider below by way of illustration two most interesting particular cases.

2. ADIABATIC PERTURBATION

If the perturbation operator $\hat{V}$ is diagonal in the representation which is proper for $\hat{H}_0$, then

$$S_{ik} = \exp\left[-\frac{i}{\hbar} E_i(\tau - t) - \frac{i}{\hbar} \int_t^\tau V_{ii}(t)\, dt\right] \delta_{ik}, \tag{2.1}$$

$$R_{lk}^{im} = \int_\alpha \exp\left[i\omega_{mi}(\tau - t) + i \int_t^\tau \Delta\omega_{mi}(\alpha, t)\, dt\right] \times \delta_{ik}\delta_{lm}\, dW(\alpha), \tag{2.2}$$

where

$$\omega_{mi} = (E_m - E_i)/\hbar, \qquad \Delta\omega_{mi} = (V_{mm} - V_{ii})/\hbar.$$

Substituting this result in (1.7), we obtain

$$\rho_{ii}(t) = \rho_{ii}(0), \tag{2.3a}$$

$$\rho_{im}(\tau) \exp\left[\left(\frac{1}{\tau_0} - i\omega_{mi}\right)\tau\right] = \rho_{im}(0) \int_\alpha \exp\left[i \int_0^\tau \Delta\omega_{mi}(\alpha, t)\, dt\right] dW(\alpha) + \frac{1}{\tau_0} \int_0^\tau dt \exp\left[\left(\frac{1}{\tau_0} - i\omega_{mi}\right) t\right] \rho_{im}(t) \times \int_\alpha \exp\left[i \int_t \Delta\omega(\alpha, t')\, dt'\right] dW(\alpha). \tag{2.3b}$$

The invariance of the diagonal elements could be predicted, since the adiabatic perturbation only changes the energies of the states, without mixing them. For the same reason, the equations for the nondiagonal elements, describing the phase relaxa-

[1)] Here and throughout we leave out the averaging symbol over ρ.

tion, are independent and an examination of any one of them is sufficient.

Introducing for this purpose more convenient variables $\sigma_{im} = \rho_{im} \exp(i\omega_{mi}t)$ (i.e., going over to the interaction representation), and leaving out the indices, we obtain

$$X(\tau) = e^{-\tau/\tau_0} R(\tau, 0) + \frac{1}{\tau_0} \int_0^\tau dt\, R(\tau, t) \exp\left[-\frac{\tau - t}{\tau_0}\right] X(t)\, dt, \tag{2.4}$$

where $X(\tau) = \sigma_{im}(\tau)/\sigma_{im}(0)$ is the normalized relaxation function, and

$$R(\tau, t) = \int_\alpha \exp\left[i \int_t^\tau \Delta\omega(\alpha, t')\, dt'\right] dW(\alpha). \tag{2.5}$$

The entire remainder of the exposition depends on the concrete form of the kernel $R(\tau, t)$.

We note that Eq. (2.4) can be obtained also in a different manner, viz., by averaging, with the aid of the procedure developed above, the quantity

$$\exp\left(i \int_0^\tau \Delta\omega\, dt'\right),$$

which characterizes the relaxation of the phases in the wave emitted by the atom. Therefore the Fourier transform $X(\tau)$ is the normalized contour of the emitted spectral line. We can fit into the framework of this latter interpretation, in particular, the Doppler broadening of the spectrum of the gas, which we shall now consider by way of an example. This broadening is a result of the dispersion of the velocities in the emission direction. Assuming the velocity distribution to be equilibrium (one-dimensional Maxwellian), we must put

$$\Delta\omega = \omega_0 v / c, \quad dW(v) = \sqrt{a/\pi}\; e^{-av^2} dv, \tag{2.6}$$

where ω_0 is the unperturbed line frequency, c the velocity of light, and $a = m/2kT$. The linear velocity v of the molecules in the emission direction plays in these formulas the role of the parameter α over which we average in (2.5). Therefore, substituting (2.6) in (2.5), we obtain

$$R(\tau, t) = \exp[-\beta^2(\tau - t)^2/2], \quad \beta = \omega_0/c\sqrt{2a}. \tag{2.7}$$

Substituting this kernel in (2.4), we have

$$X(\tau)\exp\left(\frac{\tau}{\tau_0}\right) - \exp\left(-\frac{\beta^2\tau^2}{2}\right) = \frac{1}{\tau_0} \int_0^\tau dt \exp\left[-\frac{\beta^2(\tau - t)^2}{2} + \frac{t}{\tau_0}\right] X(t). \tag{2.8}$$

In such a form, this equation is valid for any normally-distributed frequency shift linear in α, (only the magnitude of the parameter α can change).

Equation (2.8) can be reduced by successive differentiation to a differential equation. Indeed, differentiating with respect to τ and then integrating the integral obtained in the right side by parts, we obtain

$$\dot{X}\exp\left(\frac{\tau}{\tau_0}\right) + \tau\beta^2 \exp\left(\frac{\beta^2\tau^2}{2}\right) = -\frac{\beta^2}{\tau_0} \int_0^\tau dt \int_0^t \exp\left[-\frac{\beta^2(t - t')^2}{2} + \frac{t'}{\tau_0}\right] X(t')\, dt'. \tag{2.9}$$

Differentiating once more and eliminating the right side with the aid of (2.8), we obtain ultimately

$$\ddot{X} + \frac{1}{\tau_0}\dot{X} + \beta^2 X = \beta^4\tau^2 \exp\left[-\frac{\beta^2\tau^2}{2} - \frac{\tau}{\tau_0}\right]. \tag{2.10}$$

This equation should be solved in conjunction with the initial conditions

$$X(0) = 1, \qquad \dot{X}(0) = 0, \tag{2.11}$$

the first of which follows from the definition of X, and the second from (2.9) with $\tau = 0$.

Equation (2.10) can be easily integrated in quadratures, and therefore, introducing the natural dimensionless variable $t = \tau/\tau_0$ and performing all the necessary manipulations, we obtain

$$X(t) = \exp\left[-\frac{\gamma^2 t^2}{2} - t\right] + \frac{1}{2}\left[1 + \frac{1}{(1 - 4\gamma^2)^{1/2}}\right] \times \exp\left\{r_1 t \int_0^t \exp\left(-\frac{1}{2}\gamma^2 z^2 + r_2 z\right) dz\right\} + \frac{1}{2}\left[1 - \frac{1}{(1 - 4\gamma^2)^{1/2}}\right] \times \exp\left\{r_2 t \int_0^t \exp\left(-\frac{1}{2}\gamma^2 z^2 + r_1 z\right) dz\right\}, \tag{2.12}$$

where

$$r_{1,2} = -1/2 \pm (1/4 - \gamma^2)^{1/2}, \tag{2.13}$$

and a single universal dimensionless parameter

$$\gamma = \beta\tau_0 = \frac{\omega_0\tau_0}{c\sqrt{2a}} = \frac{\omega_0(\overline{v^2})^{1/2}}{c}\tau_0 = 2\pi\frac{l}{\lambda} = \frac{2\pi}{\lambda\sigma}\frac{1}{n}. \tag{2.14}$$

$\overline{v^2}$ is the mean square of one velocity component, equal, as is well known, to 1/2a; $l = \tau_0(v^2)^{1/2}$ is the mean free path; λ is the wavelength of the observed radiation, σ the effective collision cross section, and n the gas density.

In the general solution (2.12) we can easily differentiate between two limiting situations: $2\gamma \gg 1$ and $2\gamma \ll 1$. In the former we have

$$X = \exp\left[-\frac{1}{2}\gamma^2 t^2 - t\right] + e^{-t/2}\left\{\frac{\cos\gamma t}{t} \int_0^{\gamma t} e^{-x^2/2}\cos x\, dx + \frac{\sin\gamma t}{\gamma} \int_0^{\gamma t} e^{-x^2/2}\sin x\, dx\right\} \approx \exp\left[-\frac{1}{2}\gamma^2 t^2 - t\right], \tag{2.15}$$

and in the latter

$$X = e^{-\gamma^2 t} + e^{-t}[1 - e^{-\gamma^2 t}] \approx e^{-\gamma^2 t}. \qquad (2.16)$$

The first situation corresponds to a "strong" perturbation of the particles and the second to a "weak" one, which is subject to calculation with the aid of perturbation theory. Indeed, turning to the initial variables, we can note that result (2.16) is none other than exp (– 2W_ft), where

$$W_f = \frac{1}{2}\gamma^2\tau_0^{-1} = \frac{1}{2}\frac{\omega_0^2\overline{v^2}}{c^2}\tau_0 = \frac{1}{2}\overline{\Delta\omega^2}\,\tau_0$$

$$= \frac{\pi}{2\hbar^2}\overline{(V_{11} - V_{22})^2}\,g(0) \qquad (2.17)$$

is the phase transition probability[5] expressed in the usual fashion (by perturbation theory) in terms of the dispersion of the perturbation (noise) and its spectral density at the carrier frequency ω:

$$g(\omega) = \frac{1}{\pi}\int_0^\infty K(\tau)\,e^{i\omega\tau}\,d\tau.$$

Since the interchange of the emitted frequencies is quite random, the carrier frequency is equal to zero, and the correlation function is $K(\tau) = \exp(-\tau/\tau_0)$, so that $g(0) = \tau_0$. It is easy to verify that the condition under which the exponential relaxation with probability (2.7) takes place, $2\gamma \ll 1$, reduces with accuracy to a numerical factor to the known inequality that limits the application of perturbation theory: $W_f\tau_0 \ll 1$. As soon as this inequality reverses sign, the relaxation ceases to be exponential and displays, as can be seen from (2.15), traces of a dynamic process—oscillation with frequency $(\overline{\Delta\omega^2})^{1/2}$. The concept of transition probability and the statistical description of relaxation are not applicable in this region.

Formulas (2.15) and (2.16) are of interest also from the point of view of the transformation of the Doppler contour of the line with increasing gas pressure. When the collisions that cause the alternation of the radiated frequency are relatively rare ($W_f \gg 1/\tau_0$), the line contour is essentially Gaussian, but only up to frequencies lower than W_f. In the more remote regions of the spectrum ($\Delta\nu \gg W_f$), the contour becomes more closely Lorentzian (Fig. 2). This is connected with the fact that no matter how rarely the line shift changes, the frequency drift produced by it is perfectly sufficient to broaden each of these components. The frequency perturbation under such conditions is "strong," i.e., the phase difference between two succeeding collisions

$$\int \Delta\omega dt' \sim (\overline{\Delta\omega^2})^{1/2}\tau_0$$

greatly exceeds unity, the neighboring radiation

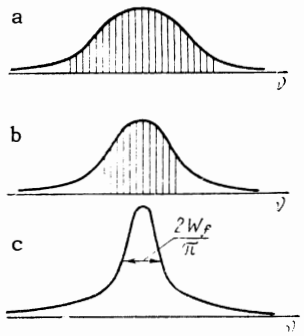

FIG. 2. Change in the contour of a Doppler line by pressure: a – $2\gamma \gg 1$, b – $2\gamma \ll 1$, c – $2\gamma \sim 1$ (the Gaussian part of the spectrum is shaded.)

trains are uncorrelated, and the broadening of each of them, according to Lorentz, is equal to $1/\tau_0$. Therefore, although the distribution of the components in the spectrum is Gaussian, the Lorentz shape of each of the components is manifest in slowly vanishing wings, which move out from under the Doppler contour. With increasing n, the width $1/\tau_0$ of the components increases, and the Lorentz wings move towards the center. When this width becomes comparable with the width of the Gaussian contour ($\omega_0\overline{v}/c$) and the entire spectrum becomes Lorentzian, general narrowing of the line begins, since subsequently its half-width is

$$W_f = \frac{\pi}{\lambda\sigma}\left(\frac{kT}{m}\right)^{1/2}\frac{1}{n}.$$

The narrowing by pressure is possible only in the case when, as assumed from the very beginning, the phase does not collapse during the instant of collision, i.e., the perturbation by the collision itself is weak[10] (high temperatures, magnetic spectroscopy).

3. NONADIABATIC PERTURBATION

We now consider the effect of a perturbation capable of inducing transitions between stationary states. In order for the solution to be possible in rigorous form, it is necessary to simplify the problem. We confine ourselves to only two states of the discrete spectrum of the system—the only ones essentially perturbed by radiation which is in close resonance with them. Transition between these states lead to irreversible equalization of the populations only if the effective radiation is a random process. To be able to use the method developed above, we assume that the element of randomness is introduced only instantaneously and is not correlated with the varying phase of the light wave, so that

$$\hat{V} = \hat{F}\exp[i\omega t + \alpha(t)];$$

$$F_{11} = F_{22} = 0, \quad F_{12} = F_{21} > 0.$$

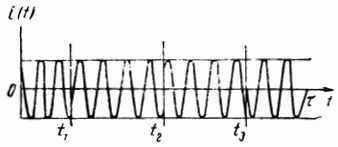

FIG. 3. Wave with random phase (Lorentz radiation).

Radiation of this type is emitted by the molecules of a gas under conditions when impact broadening (in the Lorentz approximation) prevails over natural and Doppler broadening. Monochromatic trains of radiation of the same frequency ω, emitted during free travel, turned out to be broken up in phase by abrupt and strong collisions (Fig. 3). In the intervals between them, the effect of the light on the two-level system is fully determined and can be rigorously described by means of the well known dynamic solution [11]. We obtain with its aid without difficulty the corresponding unitary transformation

$$\hat{S} = \begin{vmatrix} a\varepsilon_- + b\varepsilon_+ & \gamma(\alpha)[\varepsilon_- - \varepsilon_+] \\ \gamma^*(\alpha)[\varepsilon_+^{-1} - \varepsilon_-^{-1}] & a\varepsilon_-^{-1} + b\varepsilon_+^{-1} \end{vmatrix}, \quad (3.1)$$

where

$$\varepsilon_- = \exp[{}^1/_2 i(\omega - \Omega)t], \quad \varepsilon_+ = \exp[{}^1/_2 i(\omega + \Omega)t],$$
$$a = \frac{1}{2}\left(1 + \frac{\Delta\omega}{\Omega}\right), \quad b = \frac{1}{2}\left(1 - \frac{\Delta\omega}{\Omega}\right),$$
$$\gamma(\alpha) = \frac{1}{2}\frac{\omega_1}{\Omega} e^{i\alpha}, \quad (3.2)$$

with $\Delta\omega$ representing the frequency deviation $\omega_0 - \omega$ ($\omega_0 = (E_2 - E_1)/\hbar$), $\omega_1 = 2F_{12}/\hbar$ is the characteristic frequency of interaction, and $\Omega = (\Delta\omega^2 + \omega_1^2)^{1/2}$ is the so-called nutation frequency.

Since the dependence on α enters only in γ and γ^*, the only elements actually averaged in the calculation of R^{im}_{lk} from (1.6) are those containing these coefficients or their squares. Inasmuch as the phases of the trains remain equally probable, i.e.,

$$dW(\alpha) = d\alpha/2\pi, \quad (3.3)$$

all such terms vanish after averaging. The few remaining nonvanishing elements of the matrix R^{im}_{lk} will have the following form

$$R_{11}{}^{11} = R_{22}{}^{22} = 1 - P_{12}(\tau - t), \quad R_{22}{}^{11} = R_{11}{}^{22} = P_{12}(\tau - t),$$
$$R_{21}{}^{12} = R_{12}{}^{21\,*} = \Big[P_{12}(\tau - t) + \cos\Omega(\tau - t) + i\frac{\Delta\omega}{\Omega}\sin\Omega(\tau - t)\Big] e^{i\omega(\tau - t)}, \quad (3.4)$$

where

$$P_{12}(\tau - t) = \frac{\omega_1^2}{\Omega^2}\sin^2\frac{\Omega(\tau - t)}{2} \quad (3.5)$$

has the usual meaning of the probability of finding the system at the instant τ in the second state, if it was completely located in the first at the start of the train (at the instant t).

There is no need for writing out Eq. (1.7) immediately for all the components of the density matrix of the two-level system. Inasmuch as $\rho_{22} = 1 - \rho_{11}$ and $\rho_{12} = \rho_{21}^*$, it is perfectly sufficient to have only two, ρ_{11} and ρ_{12}. In the first case we have

$$\hat{R}^{11} = \begin{vmatrix} 1 - P_{12} & 0 \\ 0 & P_{12} \end{vmatrix}$$

and, using this operator in (1.7), we obtain

$$\rho_{11}e^{\tau/\tau_0} = \rho_{11}(0) + [\rho_{22}(0) - \rho_{11}(0)]P_{12}(\tau) + \frac{1}{\tau_0}\int_0^\tau e^{t/\tau_0}\{\rho_{11}(t) + [\rho_{22}(t) - \rho_{11}(t)]P_{12}(\tau - t)\}dt. \quad (3.6)$$

Going over to the more natural variable $n = \rho_{11} - \rho_{22}$, we obtain

$$n(\tau)e^{\tau/\tau_0} = n(0)[1 - 2P_{12}(\tau)] + \frac{1}{\tau_0}\int_0 [1 - 2P_{12}(\tau - t)]n(t)e^{t/\tau_0}dt. \quad (3.7)$$

This integral equation, which describes the relaxation of the populations and which is the end result of the statistical calculation, coincides exactly with the equation which we have obtained earlier [1]. Therefore, following the already known procedure of differentiation, we can obtain from it

$$\dddot{n} + \frac{2}{\tau_0}\ddot{n} + \left(\frac{1}{\tau_0^2} + \Omega^2\right)\dot{n} + \frac{\omega_1^2}{\tau_0}n = 0, \quad (3.8)$$

where the sought solution must satisfy the initial conditions

$$\dot{n}(0) = 0, \quad \ddot{n}(0) = -\omega_1^2 n(0). \quad (3.8a)$$

Inasmuch as this solution itself as well as all of its corollaries have already been considered in detail in [1] we confine ourselves here only to an indication of the methodological advantage of the deduction presented above. The derivation of (3.7) in [1] entailed the need of having at the start of the process a diagonal density matrix $\rho_{12}(0) = 0$, which by virtue of the phase disorder of the radiation continued to remain so subsequently. The method developed here is free of this limitation, and since it nevertheless leads again to Eqs. (3.7)—(3.8), this means that the relaxation of the populations cannot depend in any manner on the phase state of the system.

The foregoing advantage of the method employed here is manifest especially convincingly in the possibility of describing, along with the relaxation of the populations, also the phase relaxation; the corresponding information is contained in the equation

for $\rho_{12}(\tau)$, which describes the vanishing of the phase correlation of the atom, if such a correlation existed at the beginning ($\rho_{12}(0) \neq 0$). Indeed, using the operator

$$\hat{R}^{12} = \begin{vmatrix} 0 & 0 \\ R_{21}{}^{12} & 0 \end{vmatrix},$$

we obtain from (1.7)

$$\rho_{12}(\tau)\exp\left[\left(\frac{1}{\tau_0} - i\omega\right)\tau\right]$$
$$= \left[\cos\omega\tau + i\frac{\Delta\omega}{\Omega}\sin\Omega\tau + P_{12}(\tau)\right]\rho_{12}(0)$$
$$+ \frac{1}{\tau_0}\int_0^\tau \left[\cos\omega(\tau - t) + i\frac{\Delta\omega}{\Omega}\sin\Omega(\tau - t)\right.$$
$$\left. + P_{12}(\tau - t)\right]\rho_{12}(t)\exp\left(\frac{1}{\tau_0} - i\omega\right)t\,dt. \qquad (3.9)$$

A triple successive differentiation likewise transforms this equation into a differential equation

$$\dddot{\sigma}_{12} + \frac{2}{\tau_0}\ddot{\sigma}_{12} + \left(\Omega^2 + \frac{1}{\tau_0{}^2} - i\frac{\Delta\omega}{\tau_0}\right)\dot{\sigma}_{12}$$
$$- \left(i\frac{\Delta\omega}{\tau_0{}^2} - \frac{\Delta\omega^2}{\tau_0} - \frac{\omega_1{}^2}{2\tau_0}\right)\sigma_{12} = 0, \qquad (3.10)$$

where $\sigma_{12} = \rho_{12}\exp(-i\omega t)$ is the component of the density matrix in the reference frame that rotates with frequency ω. Like all the preceding equations, this equation is linear, homogeneous, and has constant coefficients. However, by virtue of the nonremovable complexity of the coefficients, its order is actually equal to six. If we go over to more convenient variables—the components of the energy spin [5]

$$l = 2\mathrm{Re}\,\sigma_{12}, \quad m = -2\mathrm{Im}\,\sigma_{12},$$

then we obtain the system

$$\dddot{l} + \frac{2}{\tau_0}\ddot{l} + \left(\frac{1}{\tau_0{}^2} + \Omega^2\right)\dot{l} + \left(\frac{\Delta\omega^2}{\tau_0} + \frac{\omega_1{}^2}{2\tau_0}\right)l$$
$$= \frac{\Delta\omega}{\tau_0}\dot{m} + \frac{\Delta\omega}{\tau_0{}^2}m,$$
$$\dddot{m} + \frac{2}{\tau_0}\ddot{m} + \left(\frac{1}{\tau_0{}^2} + \Omega^2\right)\dot{m} + \left(\frac{\Delta\omega^2}{\tau_0} + \frac{\omega_1{}^2}{2\tau_0}\right)m$$
$$= -\frac{\Delta\omega}{\tau_0}\dot{l} - \frac{\Delta\omega}{\tau_0{}^2}l. \qquad (3.11)$$

The initial conditions

$$\dot{\rho}_{12}(0) = i\Delta\omega\rho_{12}(0), \quad \ddot{\rho}_{12}(0) = (1/2\omega_1{}^2 - \Omega^2)\rho_{12}(0)$$

take the form

$$\dot{m} = \Delta\omega l, \quad \dot{l} = \Delta\omega m, \quad \ddot{m} = (1/2\omega_1{}^2 - \Omega^2)m,$$
$$\ddot{l} = (1/2\omega_1{}^2 - \Omega^2)l \qquad (3.12)$$

for arbitrary $l(0)$ and m(0). Thus, the phase relaxation proceeds independently of the population relaxation (n), but the change in the equatorial components of the energy spin (transverse projections of the magnetic moment—for spin systems) is in general mutually correlated.

The phase memory vanishes in simplest fashion under conditions of exact resonance ($\Delta\omega = 0$). In this particular case, the relaxation of the two components takes place independently and is described by the same equation, which in natural variables

$$t = \tau/\tau_0, \quad X = l(t)/l(0) = m(t)/m(0) \qquad (3.13)$$

has the form

$$\dddot{X} + 2\ddot{X} + (1 + \gamma^2)\dot{X} + \frac{1}{2}\gamma^2 X = 0, \quad \gamma = \omega_1\tau_0$$

with

$$X(0) = 1, \quad \dot{X}(0) = 0, \quad \ddot{X}(0) = -\gamma^2/2.$$

(3.13) differs from (3.8) only in the coefficient of the last term, but it is precisely because of this term that the corresponding characteristic equation

$$z(z+1)^2 + (z + 1/2)\gamma^2 = 0 \qquad (3.14)$$

cannot be reduced to quadratic, in spite of the rigorous resonance.

The exact solution of (3.13) takes the form

$$X = \frac{z_3z_2 - \gamma^2/2}{(z_3 - z_1)(z_2 - z_1)}e^{z_1t} - \frac{z_3z_1 - \gamma^2/2}{(z_3 - z_2)(z_2 - z_1)}e^{z_2t}$$
$$+ \frac{z_2z_1 - \gamma^2/2}{(z_3 - z_2)(z_3 - z_1)}e^{z_3t}, \qquad (3.15)$$

where z_1, z_2, and z_3 are the roots of Eq. (3.14). As always, two limiting cases are possible: $\gamma \gg 1$—strong perturbation, and $\gamma \ll 1$—weak perturbation. For each of them we can find all the z_i by iteration. To a satisfactory approximation, they are equal to

$$z_1 = -1/2, \quad z_{2,3} = -3/4 \pm i\gamma \quad \text{for } \gamma \gg 1, \qquad (3.16)$$

$$z_1 = 1/2\gamma^2, \quad z_{2,3} = -1 \pm i\gamma/\sqrt{2} \quad \text{for } \gamma \ll 1. \qquad (3.17)$$

Using these estimates in (3.15) and returning to the initial variable, we have accordingly

$$X(\tau) = 1/2e^{-\tau/\tau_0} + 1/2e^{-3\tau/4\tau_0}\cos\omega_1\tau \qquad (3.18)$$

for $\gamma \gg 1$ and

$$X(\tau) = (1 + \gamma^2/2)e^{-W_1\tau} - 1/2\gamma^2e^{-\tau/\tau_0}\cos\frac{\omega_1}{\sqrt{2}}\tau \qquad (3.19)$$

for $\gamma \ll 1$. The quantity

$$W_1 = \frac{\omega_1{}^2\tau_0}{2} = \frac{2|F_{12}|^2\pi}{\hbar^2}g(\omega_0) = \frac{2|F_{12}|^2}{\hbar^2}\int_0^\infty K(\tau)e^{i\omega_0\tau}\,d\tau \qquad (3.20)$$

in (3.19) is none other than the probability per unit

time of transitions between stationary states under conditions of exact resonance ($K(\tau) = \exp[-i\omega_0\tau - \tau/\tau_0]$). Inasmuch as the oscillating term in (3.19) is small compared with the exponential term, this limiting situation is described satisfactorily by a statistical transition scheme: $X(\tau) = \exp[-2W_2\tau)$, with

$$W_2 = W_1/2 \tag{3.21}$$

being the probability of a total phase reversal (through π) in a unit time interval.

Equation (3.21) is a particular form of the general relation [5,7] and expresses the fact that any nonadiabatic perturbation gives rise, besides population relaxation, also to phase relaxation, but with half the efficiency. The condition $\omega_1\tau_0 \ll 1$ for the applicability of (3.20) can, if desired, be represented in the form $W_2\tau_0 \ll 1/4$, in perfect analogy with the standard representation. Violation of this inequality leads us to the opposite situation, namely (3.18), in which the probabilistic description is invalid even asymptotically. As frequently under strong-interaction conditions [1], the relaxation function contains oscillating terms which are in no manner smaller in magnitude than the aperiodic terms.

Regardless of the cause of the phase relaxation —adiabatic or nonadiabatic perturbation—the relaxation always leads to deformation of the contour of the line which can be absorbed (or radiated) by the relaxing atom. This is a very valuable aspect of the problem, since it makes possible the use of a stationary spectroscopic experiment as a criterion for the correctness of results pertaining to the kinetics of fast processes that do not easily lend themselves to direct measurement. In this case it is necessary to use for this purpose an additional weak source of light, which makes it possible to plot the spectrum without distorting in practice the relaxation caused by strong radiation of a type under consideration. The frequency dependence of the spectrum, as always, is the Fourier transform of the relaxation function, specified in the laboratory system: a function of ρ_{12} but not of σ_{12}. Under resonance conditions ($\omega = \omega_0$), which we have just considered in detail, the contour of this spectrum

$$g(\nu) = \int_{-\infty}^{+\infty} X(\tau)\exp[i\omega_0\tau - i2\pi\nu\tau]\,d\tau = \int_{-\infty}^{+\infty} X(\tau)\exp[i2\pi(\nu-\nu_0)\tau]\,d\tau \tag{3.22}$$

represents, in the form (3.15), a superposition of three Lorentz lines.

Under weak-interaction conditions

$$g(\nu) = 1 + \frac{\gamma^2}{2}\frac{\Gamma_0}{\pi[(\nu-\nu_0)^2+\Gamma_0^2]} - \frac{\gamma^2}{4}\frac{\Gamma}{\pi[(\nu-\nu_0+\delta)^2+\Gamma^2]} - \frac{\gamma^2}{4}\frac{\Gamma}{\pi[(\nu-\nu_0-\delta)^2+\Gamma^2]}, \tag{3.23}$$

the main peak with half-width $\Gamma_0 = W_1/2\pi$ is only slightly deformed by small dips, spaced by a distance $\delta = \omega_1/2\pi\sqrt{2}$, which are too broad to become noticeable ($\Gamma = 1/2\pi\tau_0 \gg \delta \gg \Gamma_0$). To the contrary, in the case of sufficiently strong supply

$$g(\nu) = \frac{\Gamma_0}{2\pi[(\nu-\nu_0)^2+\Gamma_0^2]} + \frac{\Gamma_1}{4\pi[(\nu-\nu_0+\Delta)^2+\Gamma_1^2]} + \frac{\Gamma_1}{4\pi[(\nu-\nu_0-\Delta)^2+\Gamma_1^2]}, \tag{3.24}$$

the spectrum breaks up into three components with intensity ratio 1:2:1 the half-width of which, $\Gamma_0 = 1/4\pi\tau_0$ or $\Gamma_1 = 3\Gamma_0/2$, is much smaller than the splitting Δ, which is equal to $\omega_1/2\pi$ (Fig. 4).

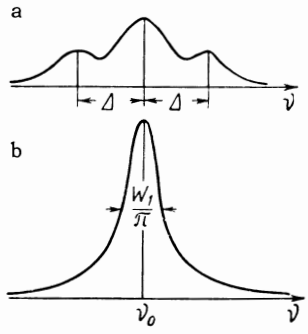

FIG. 4. Spectra under conditions of strong (a) and weak (b) interaction ($\gamma \gtrless 1$).

It is useful to call attention also to the variation of the spectrum with increasing width $1/\tau_0$ of the effective radiation. So long as this width is sufficiently small compared with the intensity (strong perturbation), its increase leads to a broadening of all three components of the resolved spectrum in the same proportion, $\sim 1/\tau_0$. At the instant when the components broaden to such an extent that the structure becomes smeared out, the interaction becomes weak and further broadening of the effective radiation will lead to a narrowing of the spectrum, as should also be the case by virtue of (3.21).

The condition for observing the anomalous effects connected with the strong interaction ($\omega_1\tau_0 \gg 1$) impose requirements of different stringency on the radiation intensity as a function of the specific nature of the two-level system (atom, molecule, spin). The energy density in the radiation flux should satisfy the inequality

$$P = \frac{cE_0^2}{8\pi} \gg \frac{c\hbar^2}{8\pi\mu_{12}^2\tau_0^2} = \frac{c}{8\pi}\left(\frac{\hbar}{\mu_{12}\tau_0}\right)^2 = P_0, \tag{3.25}$$

where μ_{12} is the dipole moment of the system

($F_{12} = \mu_{12}E_0/2$, since account is taken of only the resonant components of the actual radiation field $E(t) = E_0 \cos(\omega t + \alpha)$). When $\tau_0 = 10^{-9}$ sec, the critical value $P_0 \sim 10^{29}$ quanta/cm^2 sec for atomic spectroscopy and $\sim 10^{25}$ quanta/cm^2 sec for molecular spectroscopy. Larger values unavoidably cause deviations from normal (exponential) kinetics, provided the other relaxation mechanisms do not turn out to be more effective than the field mechanism. However, even in the latter case the region of strong interactions does not vanish completely, and only shifts towards larger intensities, in accordance with the effective reduction of τ_0.

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