

# Kinetic approach to the theory of electromagnetic wave propagation in disordered atomic substances

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We propose a new kinetic approach to the problem of the interaction of light with disordered atomic substances. Starting from the equation for the density matrix we derive kinetic equations for the components of the polarization vector  $\mathcal{P}(t)$ ; together with the Maxwell-Lorentz equations these form a closed system. In obtaining the kinetic equations we take into account the contributions to the rate of change of  $\mathcal{P}(t)$  from the classical precession of the dipoles in the local fields produced by the neighboring atomic dipoles and the quantum fluctuations of the dipole motion in the form of sequences of virtual transitions induced by the light field. The multilevel effects caused by these sequences of nonresonant transitions leading to small-amplitude, high-frequency scintillations of the dipole trajectories are taken into account through canonical transformations which in the Hamiltonian replace the infinite set of rapidly oscillating atomic interactions with the light by time-averaged effective interactions with one another. We obtain from the canonically transformed equation for the density matrix a kinetic equation for  $\mathcal{P}(t)$  which enables us to analyze the slow resonant motions of the dipoles. This kinetic equation describes both the dephasing of the dipoles and the mechanism which produces coherent oscillations of the optical dipole motion leading to superradiance effects and the spectral condensation of the radiation which is observed in interresonance laser spectroscopy. The approach suggested here makes it possible to consider consistently various linear and nonlinear optical effects which have been observed in disordered substances. © 1995 American Institute of Physics.

## 1. INTRODUCTION

To describe the propagation of electromagnetic waves in disordered dielectric substances we must supplement the Maxwell-Lorentz equations<sup>1</sup> with a kinetic equation for the density of the optical dipoles, which together constitute a closed system.

Such kinetic equations must be derived from the fundamental equation for the density matrix (the quantum Liouville equation<sup>2</sup>) of the system of optical dipoles, which are coupled through dipole-dipole interactions, and which take part in the thermal motion together with the atoms which carry them, exactly as the Boltzmann kinetic equation<sup>3</sup> for interacting molecules in a gas is derived from the classical Liouville equation. Bloch kinetic equations were derived in this way back in the 50s<sup>4,5</sup> for the density of quantum magnetic dipoles; these equations have the same form as the Bloch equations derived from phenomenological considerations.<sup>6</sup>

After the appearance of lasers in the sixties these kinetic equations were taken over with great success in resonance optics.<sup>7</sup> The success of the Bloch equations in optics and for describing magnetic resonance<sup>7,8</sup> was reflected in the profound unity of the laws of motion of optical and quantum dipoles. The analysis carried out using these equations for the decay of the free polarization, for echo effects, for saturation, and so on<sup>7,8</sup> and also the successful molecular dynamic calculations<sup>9</sup> of the oscillating decay of the free polarization, observed<sup>10</sup> in crystalline nuclear paramagnetics,

showed clearly that the unity of the laws of motion of optical and quantum dipoles stems from the unity of the elementary dynamic process, i.e., the precession of dipoles in external and local electric or magnetic fields.

However, the approximations made in Refs. 4 and 5 in the Bloch kinetic equations meant that one could describe only the dephasing but not the collective oscillations of the dipoles which were observed<sup>11-13</sup> in optically strongly excited gases and the decay of the free polarization of paramagnetic crystals.<sup>10</sup> The collective motions together with the dephasing were successfully described for crystal paramagnetics<sup>14-16</sup> using kinetic equations for the partial densities of magnetic dipoles,  $\sigma_\alpha(h, t)$ ,  $\alpha = x, y, z$  (the layer polarizations for short) which characterize the density of the dipoles in a longitudinal local dipole field  $h$  parallel to the quantization axis of the dipoles (in optics and when describing magnetic resonances one chooses the quantization axis of the dipoles in the direction of light propagation or parallel to the strong constant magnetic field).

The aim of the present paper is the generalization of the kinetic equations for the layer polarization<sup>14</sup> to the case of optical dipoles. In the next section we start by using the method proposed in Refs. 17 to 21 to obtain the Hamiltonian of the atomic substance in an "optical" representation which is convenient for the description of optical effects; after this in sections 3 to 5 we shall use this Hamiltonian to derive the kinetic equation for the optical layer polarizations from the equation for the density matrix and to apply it to analyze optical effects.

## 2. THE HAMILTONIAN OF THE OPTICAL SUBSTANCE IN THE OPTICAL REPRESENTATION

It is important when generalizing the kinetic equations for the polarizations of layers of magnetic dipoles<sup>14</sup> to the case of optical dipoles to take into account both the similarity and the essential difference between the Zeeman Hamiltonians of quantum magnetic dipoles interacting with a constant magnetic field and with atomic Hamiltonians. The similarity manifests itself in the fact that the precessions of optical and magnetic dipoles in the electric or magnetic fields acting upon them are the same. The difference, on the other hand, is caused by the fact that the Hamiltonian of an atom in the atomic representation determines an infinite number of levels and allowed transitions, whereas the Zeeman Hamiltonian of a magnetic dipole is characterized by only a few levels and transitions.

The method which helps us to overcome this difference will be given in Sec. 3 where the effect on the motion of the polarization of all dipoles of nonresonant allowed transitions will be taken into account by means of an original canonical transformation<sup>17-21</sup> which leaves the form of the equation for the density matrix unchanged but significantly changes its Hamiltonian through the addition to the resonance interactions of time-averaged rapidly oscillating interactions of the nonresonant dipoles with the field  $\mathbf{E}$  and the local fields, also called effective interactions. We must emphasize that the optical representation of the Hamiltonian was applied long ago to describe optical effects in atomic substances<sup>7</sup> in the approximation in which in the atomic spectrum only two levels of a transition, in resonance with respect to the field  $\mathbf{E}$ , and the interaction of the atomic dipole with the field  $\mathbf{E}$  were taken into account but the interatomic dipole-dipole interactions were neglected in the calculations.

The generalization of this Hamiltonian to the case of multilevel atoms which are coupled through dipole-dipole interactions was carried out by one of the present authors,<sup>20,21</sup> in those papers the Hamiltonian of the atomic substance was obtained (in frequency units) in the form

$$H = H_0 + H_1 + H_d, \quad (1)$$

where

$$H_0 = \sum_{n,i} \frac{1}{\hbar} E_n^{(i)} \hat{P}_{nn}^{(i)}, \quad (2)$$

$$H_1 = - \sum_{n' < n} \frac{1}{\hbar} \mathbf{E}(\mathbf{d}_{nn'}^{(i)} \hat{P}_{nn'}^{(i)} + \mathbf{d}_{n'n}^{(i)} \hat{P}_{n'n}^{(i)}), \quad (3)$$

$$H_d = H_d^0 + H_d^{+2} + H_d^{-2}, \quad (4)$$

$$H_d^0 = \sum_{\substack{i < k, n' < n, \\ m' < m}} \frac{3 \cos^2 \theta_{ik} - 1}{2\hbar r_{ik}^3} (\mathbf{d}_{nn'}^{(i)} \hat{P}_{nn'}^{(i)} \mathbf{d}_{m'm}^{(k)} \hat{P}_{m'm}^{(k)} + \mathbf{d}_{n'n}^{(i)} \hat{P}_{n'n}^{(i)} \mathbf{d}_{mm'}^{(k)} \hat{P}_{mm'}^{(k)}), \quad (5)$$

$$H_d^{+2} = - \frac{3}{4} \sum_{\substack{i < k, n' < n, \\ m' < m}} \frac{\sin^2 \theta_{ik}}{\hbar r_{ik}^3} e^{-2i\varphi_{ik}} \mathbf{d}_{nn'}^{(i)} \hat{P}_{nn'}^{(i)} \mathbf{d}_{mm'}^{(k)} \hat{P}_{mm'}^{(k)}, \quad (6)$$

$$H_d^{-2} = - \frac{3}{4} \sum_{\substack{i < k, n' < n, \\ m' < m}} \frac{\sin^2 \theta_{ik}}{\hbar r_{ik}^3} e^{2i\varphi_{ik}} \mathbf{d}_{n'n}^{(i)} \hat{P}_{n'n}^{(i)} \mathbf{d}_{m'm}^{(k)} \hat{P}_{m'm}^{(k)}. \quad (7)$$

Here  $H_0$  is the Hamiltonian of the unperturbed stationary atoms,  $H_1$  is the Hamiltonian of the interaction between the atoms and the external field in the dipole approximation,  $H_d$  is the Hamiltonian of the dipole-dipole interaction of the atoms,  $H_d^0$  is its secular part, and  $H_d^{+2}$  and  $H_d^{-2}$  are its nonsecular parts,<sup>8</sup>  $r_i E_n^{(i)}$  and  $\mathbf{d}_{nn'}^{(i)}$ , are the energy levels and the matrix elements of the dipole moments of the allowed transitions of the  $i$ th atom,  $\theta_{ik}$  is the angle between the quantization axis ( $z$ -axis) and the vector  $\mathbf{r}_{ik} = \mathbf{r}_i - \mathbf{r}_k$ . It is clear from Eq. (9) that the projection operators

$$\hat{P}_{nn}^{(i)} = \begin{vmatrix} 0 & 0 \\ 0 & 1 \end{vmatrix}, \quad \hat{P}_{n'n'}^{(i)} = \begin{vmatrix} 1 & 0 \\ 0 & 0 \end{vmatrix},$$

$$\hat{P}_{nn'}^{(i)} = \begin{vmatrix} 0 & 1 \\ 0 & 0 \end{vmatrix}, \quad \hat{P}_{n'n}^{(i)} = \begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix}, \quad (8)$$

which are defined by the equation<sup>20</sup>

$$\hat{P}_{nn'}^{(i)} \Psi_l^{(i)} = \delta_{n'l} \Psi_n^{(i)}, \quad (9)$$

have nonvanishing matrix elements only for allowed transitions between the states  $\Psi_n^{(i)}$  and  $\Psi_{n'}^{(i)}$ .

In the Hamiltonian (1) we have neglected the interactions between the atoms and the field of the electromagnetic vacuum, and the atoms are assumed to be stationary. One can easily include the contributions from this and other factors to the motion of  $\mathcal{P}(t)$  directly in the kinetic equation for the optical layer polarization; this will be done in what follows.

The profound similarity between the Hamiltonian of the atomic substance and the Hamiltonian of a spin system<sup>8,14</sup> shows up in the fact that the projection operators  $\hat{P}_{nn'}$  which occur in it are the same as the Pauli matrices for spin 1/2. It is clear that the commutation relations for the projection operators will also be the same as for the spins, which reflects the fact that the elementary dynamic processes (the precession of electric dipoles or spins in fields) are the same as those mentioned earlier.

We now use the method of canonical transformations developed in Refs. 17 to 21 to calculate how the virtual transitions between the levels of the atomic spectrum due to the external field  $\mathbf{E}$  contribute to the kinetics of the optical dipoles and to reduce the number of energy levels of the separate atoms which actually occur in the "optical" representation of the Hamiltonian of the atomic substance. After the canonical transformations the effective Hamiltonian which we obtain has only a small number of levels the population of which actually changes under the action of the resonant electromagnetic field.

### 3. TRANSITION TO THE EFFECTIVE HAMILTONIAN

In order to carry out the canonical transformations we must separate the interactions into those which are rapidly oscillating and those which depend weakly on the time. To

do this we must go over to the interaction representation for  $H_0$  in the equation for the density matrix after which that equation takes the form

$$\frac{\partial \rho'}{\partial t} = -i[H_1' + H_d', \rho'], \quad (10)$$

where

$$\begin{aligned} \rho' &= \exp(iH_0 t) \rho \exp(-iH_0 t), \\ H_1' &= \exp(iH_0 t) H_1 \exp(-iH_0 t), \\ H_d' &= \exp(iH_0 t) H_d \exp(-iH_0 t). \end{aligned} \quad (11)$$

In what follows we use the eigenfunctions of the Hamiltonian  $H_i$  of a free fixed atom for the basic wavefunctions. We can now write the Hamiltonian in Eq. (10) in the form

$$H'(t) = H_1' + H_d', \quad (12)$$

$$\begin{aligned} H_1'(t) &= -\frac{1}{2} \sum_j \sum_{n, n'} \frac{1}{\hbar} \mathbf{d}_{nn'}^{(j)} \mathbf{E} \{ \exp[i(\omega_{nn'}^{(j)} + \omega)t] \\ &+ \exp[i(\omega_{nn'}^{(j)} - \omega)t] \} \hat{P}_{nn'}^{(j)}, \end{aligned} \quad (13)$$

$$\begin{aligned} H_d'(t) &= \frac{1}{2} \sum_{i \neq j} \sum_{m, m'} \langle nm | H_{ij}^d | n' m' \rangle \exp[i(\omega_{nn'}^{(i)} \\ &+ \omega_{mm'}^{(j)})t] \hat{P}_{nn'}^{(i)} \hat{P}_{mm'}^{(j)}, \end{aligned} \quad (14)$$

where  $\omega_{nn'}^{(i)}$  is the frequency of the  $n \rightarrow n'$  transition of the  $i$ th atom.

Those terms in the Hamiltonians (13) and (14) for which the conditions

$$|\omega_{nn'}^{(j)} \pm \omega| \leq \left| \frac{1}{\hbar} \mathbf{d}_{nn'}^{(j)} \mathbf{E} \right| \quad (15)$$

and

$$|\omega_{nn'}^{(i)} + \omega_{mm'}^{(j)}| \leq |\langle nm | H_{ij}^d | n' m' \rangle|, \quad (16)$$

are satisfied oscillate slowly. The slowly varying parts of the Hamiltonian (13) describe single-photon transitions and the other terms oscillate rapidly. The terms in the Hamiltonian (14) with a frequency which satisfies condition (16) oscillate slowly while the others oscillate rapidly. We can write the slow part of the Hamiltonian (14) in the form

$$H_d' = \frac{1}{2} \sum_{i \neq j} \sum_{m, m'} \langle nm | H_{ij}^d | n' m' \rangle \hat{P}_{nn'}^{(i)} \hat{P}_{mm'}^{(j)}. \quad (17)$$

This interaction describes the resonance transfer of energy between atoms and it corresponds to phase relaxation and collisional broadening of the spectral lines in gases.<sup>22</sup>

The general Hamiltonian  $H'(t)$  of the atomic substance thus consists of a part  $\tilde{H}'(t)$  which changes slowly in time and a rapidly-oscillating part  $\tilde{H}'(t)$ :

$$H_1'(t) = \tilde{H}_1'(t) + \tilde{H}'_1(t), \quad H_d'(t) = \tilde{H}_d'(t) + \tilde{H}'_d(t). \quad (18)$$

The rapidly oscillating interactions have a significant effect on the atoms through the averaged effective interactions. Firstly, the rapidly oscillating part  $\tilde{H}'_1$  leads to high-

frequency shifts of the energy levels and  $n$ -photon transitions. Secondly, the fast part of the Hamiltonian  $\tilde{H}'_d$  leads to high-order corrections in the Hamiltonian  $\tilde{H}'_d$  (for instance, van der Waals interactions between the atoms arise, and so on) and, finally, when  $\tilde{H}'_1$  and  $\tilde{H}'_d$  act simultaneously effective interactions appear which describe radiative collision processes.<sup>23</sup>

From this it is clear that the rapidly oscillating interactions cannot be omitted as is usually done in the resonance approximation. In what follows we take them into account through the effective interactions, which we obtain by using a canonical transformation

$$\rho_A = \exp[i\tilde{A}(t)] \rho' \exp[-i\tilde{A}(t)], \quad (19)$$

which does not alter the form of the equation for the density matrix but which significantly changes its Hamiltonian through the addition of effective interactions when we go over to the new representation where there are no rapidly-oscillating interactions. After this Eq. (10) is transformed to<sup>20</sup>

$$\frac{\partial \rho_A}{\partial t} = -i[H_{\text{eff}}, \rho_A], \quad (20)$$

where

$$\begin{aligned} H_{\text{eff}} &= \exp(i\tilde{A}) [H_1'(t) + H_d'(t)] \exp(-i\tilde{A}) \\ &+ i \frac{d}{dt} [\exp(i\tilde{A})] \exp(-i\tilde{A}). \end{aligned} \quad (21)$$

To calculate the Hamiltonian  $H_{\text{eff}}$  we expand the operators  $\tilde{A}(t)$  and  $H_{\text{eff}}$  in the small parameter  $\varepsilon$ :

$$\begin{aligned} \tilde{A} &= \sum_{n=1}^{\infty} \tilde{A}_n, \quad H_{\text{eff}} = \sum_{n=0}^{\infty} H_{\text{eff}}^{(n)}, \quad \tilde{A}_n, H_{\text{eff}}^{(n)} \propto \varepsilon^n, \\ \varepsilon &\sim \frac{|\mathbf{d}_{nm}^{(i)} \mathbf{E}|}{\hbar |\omega_{nm}^{(i)} \pm \omega|}, \quad \left| \frac{\langle nm | H_{ij}^d | n' m' \rangle}{\omega_{nn'}^{(i)} + \omega_{mm'}^{(j)}} \right|, \end{aligned} \quad (22)$$

where the transition frequencies are those for which the Hamiltonians (13) and (14) are rapidly oscillating. Then substituting the series (22) into (21) and equating the coefficients of identical powers  $\varepsilon^n$  we get

$$H_{\text{eff}}^{(0)} = H_1'(t) + H_d'(t) - \frac{d\tilde{A}_1}{dt}, \quad (23)$$

$$H_{\text{eff}}^{(1)} = i[\tilde{A}_1, H_1'(t) + H_d'(t)] - \frac{i}{2} \left[ \tilde{A}_1, \frac{d\tilde{A}_1}{dt} \right] - \frac{d\tilde{A}_2}{dt}, \quad (24)$$

Equating in (23) the sum of the rapidly oscillating parts  $\tilde{H}'_1 + \tilde{H}'_d$  to the operator  $d\tilde{A}_1/dt$  we get

$$H_{\text{eff}}^{(0)} = \tilde{H}'_1(t) + \tilde{H}'_d(t), \quad (25)$$

$$\tilde{A}_1 = \tilde{A}_{1H_1} + \tilde{A}_{1H_d} = \int_0^{t^-} dt' \tilde{H}'_1(t') + \int_0^{t^-} dt' \tilde{H}'_d(t'), \quad (26)$$

where the tilde indicates the rapidly oscillating part of the integral. In (25)  $\tilde{H}'_1$  is the Hamiltonian which describes the single-photon transitions and  $\tilde{H}'_d$  describes the longitudinal

and transverse relaxation due to collisions in the gas. Substituting  $\tilde{A}_1$  in (24) and equating the rapidly oscillating part of the first two terms to the last term,  $d\tilde{A}_2(t)/dt$ , we get

$$\tilde{A}_2 = i \int_0^{t^-} dt' \left\{ [\tilde{A}_1(t'), \tilde{H}'(t')] - \frac{i}{2} \left[ \tilde{A}_1(t'), \frac{d\tilde{A}_1(t')}{dt} \right] \right\} \quad (27)$$

and the effective Hamiltonian in the next order is

$$H_{\text{eff}}^{(1)} = H_{H_1 H_1}^{(1)} + H_{H_d H_d}^{(1)} + H_{H_1 H_d}^{(1)}, \quad (28)$$

where

$$H_{\alpha\beta}^{(1)} = \frac{i}{4} \left\{ \left[ \tilde{A}_{1\alpha}, \frac{d\tilde{A}_{1\beta}}{dt} \right] + \left[ \tilde{A}_{1\beta}, \frac{d\tilde{A}_{1\alpha}}{dt} \right] \right\}, \quad (29)$$

$$\alpha, \beta = H_1, H_d.$$

From this it is clear that to first order in  $\varepsilon$  a number of terms appear in  $H_{\text{eff}}^{(1)}$  which describe effects which take place under the action of the coherent field and of collisions separately, as well as jointly.

We write down a few terms of  $H_{\text{eff}}^{(1)}$  and elucidate their meaning. One can find a more detailed discussion of this problem in Refs. 20 and 21.

The rapidly oscillating part of the coherent interaction  $\tilde{H}'_1(t)$  leads to the effective interactions<sup>20</sup>  $H_{H_1 H_1}^{(1)}$

$$H_{H_1 H_1}^{(1)} = H_{H_1 H_1}^{(1)d} + H_{H_1 H_1}^{(1)n}, \quad (30)$$

$$H_{H_1 H_1}^{(1)d} = \frac{1}{2} \sum_{m,n,i} \left| \frac{\mathbf{d}_{mn} \mathbf{E}}{\hbar} \right|^2 \frac{\omega_{mn}}{\omega_{mn}^2 - \omega^2} \hat{P}_{mm}^{(i)}, \quad (31)$$

$$H_{H_1 H_1}^{(1)n} = \frac{1}{8} \sum_{m,n,n',i} \left[ \frac{(\mathbf{d}_{mn'} \mathbf{E})(\mathbf{d}_{n'n} \mathbf{E})}{\hbar^2 (\omega_{mn'} - \omega)} + \frac{(\mathbf{d}_{mn'} \mathbf{E})(\mathbf{d}_{n'n} \mathbf{E})}{\hbar^2 (\omega_{mn} - \omega)} \right] \hat{P}_{mn}^{(i)} \exp[i(\Delta_{mn} t + \mathbf{k} \mathbf{r})] + \text{c.c.}, \quad (32)$$

where  $\Delta_{mn} = \omega_{mn} - 2\omega$  is the mismatch of the two-photon resonance,  $H_{H_1 H_1}^{(1)d}$  is the dynamic Stark shifts of the energy levels, and  $H_{H_1 H_1}^{(1)n}$  is the amplitude of the two-photon transition.

The term  $H_{H_d H_d}^{(1)}$  is split off from the rapidly oscillating part of the collisional Hamiltonian  $\tilde{H}'_d(t)$  and describes the interaction between the atoms:

$$H_{H_d H_d}^{(1)} = \frac{1}{4} \sum_{i \neq j} \sum_{m,n} \frac{\langle m\alpha | H_d^{+2} | n\beta \rangle \langle n\beta | H_d^{-2} | m\alpha \rangle}{\hbar^2 (\omega_{mn} + \omega_{\alpha\beta})} \times \hat{P}_{mm}^{(i)} \hat{P}_{\alpha\alpha}^{(j)}. \quad (33)$$

If  $(H_d)_{ij}$  has a dipole character this term describes van der Waals interactions proportional to  $1/r_{ij}^6$  ( $r_{ij}$  is the distance between the atoms  $i$  and  $j$ ). Similarly, one can calculate  $\tilde{A}_3$ ,  $H_{\text{eff}}^{(2)}$ ,  $\tilde{A}_4$ ,  $H_{\text{eff}}^{(3)}$ , and so on. In successive orders one obtains terms describing three-photon processes, dynamic Stark level shifts to third order in  $\varepsilon$  (to fourth order in the field), that is, hyperpolarization,<sup>24</sup> four-photon processes, and so on.

It is clear from the structure of  $H_{\text{eff}}$  that only a small number of such atomic energy levels (and of dipoles of allowed transitions corresponding to them), the populations of which actually change under the action of the resonance electromagnetic fields, are active. This means that having carried out the canonical transformations we have reduced the complicated problem of solving the equation for the density matrix of a system of multilevel atoms, coupled through dipole-dipole interactions, to the problem of a system of atoms with a small number of levels coupled through effective interactions.

One sees easily that the equation with  $H_{\text{eff}}$  for the slow motions is analogous to the equation which is usually applied in the resonance approximation. However, there is a significant difference: Eq. (20) has been obtained in the representation where there is no rapidly motions. Only by going over to the "laboratory system" using the canonical transformations inverse to (19) and the transformations inverse to (11) to the density matrix can we restore the information about the fast and interatomic motions, which becomes the complete solution of the initial equation. The value of this time-dependent solution is that we can use it to analyze not only stationary but also transient optical effects.

It has thus been possible for the first time<sup>17-21</sup> to find a general theoretical approach enabling us to take consistently into account all multilevel effects (caused by virtual transitions) such as dynamic Stark shifts and multiphoton transitions in the slow motions of atomic dipoles under the action of resonance fields. On the other hand, this approach makes it possible to analyze at the same time resonance processes as well as processes which are multilevel in nature and multiplication as well as combination of frequencies.<sup>25</sup>

A kinetic equation for the layer polarizations describing the motion of the magnetization of a substance, taking into account many-particle effects, had been obtained earlier<sup>14</sup> by using Eq. (20) for systems similar to the one considered here. The aim of the next section is to generalize the kinetic equation derived in Ref. 14 for the layer polarizations of magnetic dipoles to the case of optical dipoles.

Such a generalization is nontrivial because the degeneracy of the atomic levels, which does not occur in Zeeman spectra, has to be included. Writing down the kinetic equation for the optical layer polarizations we can find solutions averaged over quantum and many-particle fluctuations in a form similar to the one found in Refs. 14 to 16, and for the first time consistently describe on the basis of these solutions such effects as superradiance<sup>25-27</sup> and the spectral condensation of radiation.<sup>11,28,29</sup> These have as yet not been studied sufficiently in optics, and up to now the dipole-dipole interactions could not be taken properly into account.

#### 4. KINETIC EQUATION FOR THE POLARIZATION OF ATOMIC SUBSTANCES

We consider the simplest and often encountered case when a circularly polarized field of frequency  $\omega$  excites only a single line of the atomic spectrum which lies rather far from other lines. This line is characterized by several  $\kappa_0$

degenerate allowed transitions without common levels (we assign to each of them a number  $\kappa$ ); the Hamiltonian of the slow motions can then be written in the form

$$H = \sum_{\kappa, i} (\omega_{21} + \Delta_{21}^{\kappa}) \hat{\sigma}_{z\kappa}^{(i)} - \sum_{\kappa, i} \frac{d_{\kappa}}{\hbar} (E_x \hat{\sigma}_{x\kappa}^{(i)} + E_y \hat{\sigma}_{y\kappa}^{(i)}) + \sum_{i < k} \sum_{\kappa < \kappa'} \frac{b_{ik}}{\hbar} d_{\kappa} d_{\kappa'} (\hat{\sigma}_{x\kappa}^{(i)} \hat{\sigma}_{x\kappa'}^{(k)} - \hat{\sigma}_{y\kappa}^{(i)} \hat{\sigma}_{y\kappa'}^{(k)}) + \sum_n (H_n e^{in\omega t} + H^+ e^{-in\omega t}), \quad (34)$$

where we have  $\omega_{21} = (E_2 - E_1)/\hbar$ ,  $\Delta_{21}^{\kappa}$  is the Stark shift of the frequency of the  $\kappa$  transition, and we have  $b_{ik} = (3 \cos^2 \theta_{ik} - 1)/2r_{ik}^3$ . The projection operators  $\hat{P}_{nn}^{(i)}$ , [see Eqs. (31) to (33)] are here replaced by the Pauli matrices

$$\hat{\sigma}_{x\kappa}^{(i)} = \hat{P}_{12}^{(i)\kappa} + \hat{P}_{21}^{(i)\kappa}, \quad \hat{\sigma}_{y\kappa}^{(i)} = i(\hat{P}_{12}^{(i)\kappa} - \hat{P}_{21}^{(i)\kappa}), \\ \hat{\sigma}_{z\kappa}^{(i)} = \hat{P}_{22}^{(i)\kappa} - \hat{P}_{11}^{(i)\kappa}, \quad (35)$$

which are more convenient for an analysis of the precession of atomic dipoles in external and local fields because of their simple commutation relations. The amplitudes  $H_n$  of the  $n$ -photon transitions evaluated in a similar way as  $H_{H_1 H_1}$  reflect both the dynamic Stark shifts and the effect of all nonresonant transitions, which appear under experimental conditions, on the slow motions of  $\hat{\sigma}_{\alpha\kappa}$ .

The inclusion through the canonical transformation of the quantities  $\Delta_{21}^{\kappa}$  and  $H_n e^{in\omega t}$  in the effective Hamiltonian (34) makes it possible, firstly, to take consistently into account the effect of multi-level effects on the slow motions of the atomic dipoles. Secondly, it gives us the possibility of using the inverse canonical transformation to include in the polarization  $\mathcal{P}(t)$  which occurs in the Maxwell-Lorentz equations its high-frequency components which are the most difficult ones to take into account. We have in mind components proportional to the matrix elements of the density matrix which are small in magnitude but which under conditions of phase synchronism lead to such striking observable effects as high-harmonic generation, frequency mixing, and so on.<sup>25</sup> Hence it is clear that a consistent description of optical effects cannot proceed without the canonical transformations although in practice one will use them only in the case of sufficiently strong laser fields.

The Hamiltonian (34) is considerably more complicated than the Hamiltonian of a paramagnetic substance, since in the case of magnetic resonance all interacting magnetic dipoles are the same, whereas in optics  $\kappa_0$  different kinds of dipoles interact with one another.

We must now obtain kinetic equations for the density matrix with the Hamiltonian (34) from Eq. (20) for any macroscopic variables which describe the motion of the polarization  $\mathcal{P}(t)$  of the substance.

For these variables we choose the complex layer polarizations for each of the transitions excited by the field  $\mathbf{E}(t)$ :

$$F^{\kappa}(h, t) = \sigma_{x\kappa}(h, t) + i \sigma_{y\kappa}(h, t), \quad (36)$$

in which

$$h = h_1 + h_2 + \dots + h_{\kappa_0}, \quad (37)$$

where

$$h_{\kappa} = \sum_k d_{\kappa} b_{ik} \sigma_{z\kappa}^{(k)}, \quad h = \sum_{\kappa, k} d_{\kappa} b_{ik} \sigma_{z\kappa}^{(k)}. \quad (38)$$

Here  $h$  is the total local electric field acting on each dipole  $d_{\kappa}^{(i)}$  due to the presence of all other dipoles  $d_{\kappa'}^{(k)}$ ; this field is the same for all dipoles  $d_{\kappa}^{(i)}$  of one atom.

In the treatment of the contribution of the dipole-dipole interactions to the rate of change of the complex layer polarization  $F(h, t)$  it is convenient to write the dipole-dipole interactions in (34) in the equivalent form

$$H_d = \sum_{i < k} \sum_{\kappa < \kappa'} \frac{1}{\hbar} b_{ik} d_{\kappa} d_{\kappa'} (\hat{\sigma}_{x\kappa}^{(i)} \hat{\sigma}_{x\kappa'}^{(k)} + \hat{\sigma}_{y\kappa}^{(i)} \hat{\sigma}_{y\kappa'}^{(k)}) = H_{zz} + H_{is}, \quad (39)$$

where

$$H_{zz} = - \sum_{i < k} \sum_{\kappa < \kappa'} \frac{1}{\hbar} b_{ik} d_{\kappa} d_{\kappa'} \hat{\sigma}_{z\kappa}^{(i)} \hat{\sigma}_{z\kappa'}^{(k)}, \quad (40)$$

$$H_{is} = \sum_{i < k} \sum_{\kappa < \kappa'} \frac{1}{\hbar} b_{ik} d_{\kappa} d_{\kappa'} \hat{\sigma}_{\kappa}^{(i)} \hat{\sigma}_{\kappa'}^{(k)}. \quad (41)$$

Apart from an additional summation over  $\kappa$ ,  $H_{zz}$  and  $H_{is}$  are here exactly the same as the interactions considered in the analysis of the kinetics of magnetic dipoles in Refs. 14 to 16. Using this analogy we can write for the complex layer polarization of each transition in the case when we have  $H_k = H_k^+ = 0$

$$\frac{\partial F^{\kappa}(h, t)}{\partial t} = i \left( \omega_{21} + \Delta_{21}^{\kappa} \frac{\alpha d_{\kappa} h}{\hbar} \right) F^{\kappa}(h, t) + i \beta \frac{d_{\kappa}}{\hbar} \times \left( -h F^{\kappa}(h, t) + h \frac{F_0}{\kappa_0} + \frac{F_1}{\kappa_0} \right), \quad (42)$$

$$F_0 = \sum_{\kappa} F_0^{\kappa} = \sum_{\kappa} dhg(h) F^{\kappa}(h, t),$$

$$F_1 = \sum_{\kappa} F_1^{\kappa} = \sum_{\kappa} \int dh h g(h) F^{\kappa}(h, t), \quad (43)$$

where  $g(h)$  is the distribution function of the longitudinal fields<sup>8</sup> which has a shape close to that of Lorentzian and Gaussian functions, respectively, for small and large densities  $n_0$  of the atoms. In (42) we have taken into account the exchange between the polarizations of different transitions  $\kappa$ .

The terms on the right-hand side of (42) which are simultaneously proportional to  $F^{\kappa}(h, t)$  and to  $\omega_{21}$ ,  $\Delta_{21}^{\kappa}$  describe the precession of  $F^{\kappa}(h, t)$  around the quantization axis of the atoms which was chosen in the propagation direction of the electromagnetic field. On the other hand, the contributions on the right-hand side of (42) proportional to  $\alpha d_{\kappa} h$ ,  $\beta d_{\kappa} h$  and to  $F^{\kappa}(h, t)$  characterize the precession of the dipoles in the effective local longitudinal fields since the components of the electric dipole fields along the propagation direction of the light are equal to zero.

In order to determine the contribution of  $H_{is}$  to the rate of change of the layer polarizations it is important to note that one can consider this as the result of the precession of the dipoles in the isotropic local fields produced by the neighboring dipoles and as the result of the exchange of polarization between separate spin pairs which is the consequence of the conservation of the total spin of the two dipoles participating the exchange.

Consequently, we can now formulate five important properties of the contributions of  $H_{is}$  to the rate of change of the layer polarizations. Since this interaction describes the precession of the dipoles in local fields this contribution must, firstly, be linear in the field  $h$  and in the layer polarizations  $F^\kappa(h, t)$ ; secondly, include the rigorously determined contribution  $ihF^\kappa(h, t)$  of part of the isotropic interaction  $H_{zz}$ . Moreover, because  $H_{is}$  tends to equalize the polarizations  $F^\kappa(h, t)$  its contribution must be proportional to  $d_\kappa$  and, moreover, tend to zero when  $F^\kappa = \text{const}$ , and also when one integrates over all layers and sums over  $\kappa$ .

These properties determine the contribution of  $H_{is}$  to the rate of change of the layer polarizations represented in (42), apart from the constant  $\beta$ . We also emphasize that all the properties listed here are also satisfied by the analogous contribution of  $H_{is}$  which was calculated approximately in Ref. 14. One can also consider that this contribution was derived from Eq. (10) from which we obtain rigorously in the Appendix all characteristic properties listed above for an isotropic interaction. When evaluating this contribution we neglected the memory effects which are taken into account in the kinetic equation (A2) for the layer polarizations, on the grounds that the precession of the dipoles is determined by the vectors of the dipole and of the local magnetic field acting on it taken at one and the same time.

The constant  $\beta$  must be determined from additional considerations. For instance, when evaluating the oscillating decay of the free polarization in  $\text{CaF}_2$  crystals, the results of which turned out to be in good agreement with the experimental data, one is able to obtain the constant  $\beta$  using the exactly calculated second and fourth moments of the absorption line.<sup>14</sup>

It is interesting to note that an expression similar to (42) was successfully applied in Ref. 16 to take into account the contributions of isotropic interactions to the rate of change of the layer polarizations:

$$\left[ \frac{\partial F(h, h_{ex}, t)}{\partial t} \right]_{ex} = i \text{const} [h_{ex} F(h, h_{ex}, t) - h_{ex} F_0 - F_{1,ex}], \quad (44)$$

which made it possible to describe the decay of the free polarization, observed in  $^3\text{He}$  quantum crystals and in solutions of radicals, the magnetization, and the effect of exchange narrowing of the observed absorption lines in magnetic resonance spectra. In (44)  $h_{ex}$  is the longitudinal component of the local exchange field.

We now add to Eq. (42) the contributions to the rate of change of the layer polarizations which are connected with the change in the field  $h$ , which lead to transitions of the spins between the layers: the spectral diffusion contributions.

An important relation for the spectral diffusion contribution  $D(h, t)$  to the rate of change of the layer polarizations,

$$\int D(h, t) dh = 0 \quad (45)$$

is easily obtained from the kinetic equation (A2). The Markovian uncorrelated random process which describes the fluctuations of the local longitudinal fields connected with the thermal motion of the atoms satisfies this relation. If the changes in the field are determined by this process, the contributions to the rate of change of the layer polarizations can be written in the form<sup>8,14</sup>

$$\left. \frac{\partial F}{\partial t} \right|_{Sd}^c = \frac{F_0^\kappa - F^\kappa(h, t)}{\tau_c}, \quad \left. \frac{\partial F}{\partial t} \right|_{Sd}^0 = \frac{F_0/\kappa_0 - F^\kappa(h, t)}{\tau_0}, \quad (46)$$

where  $\tau_c$  and  $\tau_0$  are characteristic times of change of the atomic surroundings and, hence, also of the field  $h$ , and of the orientations of the atomic angular momenta.

These contributions differ from one another in their physical nature. In the first case the thermal motion causes a fast change in the distribution of the atoms closest to the one considered and, hence, also a fast change in the magnitude of  $h$ . In the second case, for instance, at a high gas density, at the same time as the change in the surroundings strong collisions are present which change the orientation of the atomic angular momentum and of  $\kappa$  at the same time.

Taking the contributions (46) and the action of the field  $E$  into account we obtain

$$\begin{aligned} \frac{\partial F^\kappa(h, t)}{\partial t} = & i \left( \omega_{21} + \Delta_{21}^\kappa + \frac{\alpha d_\kappa h}{\hbar} \right) F^\kappa(h, t) + i\beta \frac{d_\kappa}{\hbar} \\ & \times \left[ -h F^\kappa(h, t) + h \frac{F_0}{\kappa_0} + \frac{F_1}{\kappa_0} \right] \\ & + \left[ i \frac{d_\kappa}{\hbar} E_x \sigma_{z\kappa}(h, t) + E_y \sigma_{x\kappa}(h, t) \right] \\ & + \frac{\sigma_{z\kappa}^0 - \sigma_{z\kappa}(h, t)}{\tau_c} + \frac{\sigma_{0z} - \sigma_{z\kappa}(h, t)}{\tau_0} \\ & - \frac{F^\kappa(h, t)}{T_2'}, \end{aligned} \quad (47)$$

$$\begin{aligned} \frac{\partial \sigma_{z\kappa}(h, t)}{\partial t} = & \frac{d_\kappa}{\hbar} [E_x \sigma_{y\kappa}(h, t) - E_y \sigma_{x\kappa}(h, t)] \\ & + \frac{\sigma_{z\kappa}^0 - \sigma_{z\kappa}(h, t)}{\tau_c} + \frac{\sigma_{0z} - \sigma_{z\kappa}(h, t)}{\tau_0} \\ & - \frac{\sigma_z^0 - \sigma_{z\kappa}(h, t)}{T_1'}, \end{aligned} \quad (48)$$

where

$$\sigma_{z\kappa}^0 = \int dh g(h) \sigma_{z\kappa}(h, t), \quad \sigma_{0z} = \sum_{\kappa} \sigma_{z\kappa}^0 / \kappa_0,$$

$\sigma_z^0$  is the equilibrium value of  $\sigma_{z\kappa}(h, t)$ , and  $T_1'$  and  $T_2'$  are the longitudinal and transverse relaxation times which cause spontaneous transitions.

In (47) we divide  $F_0$  and  $F_1$  by  $\kappa_0$  so that spin exchange equalizes all polarizations  $F^\kappa(h, t)$  to a common average value. Since the field  $\mathbf{E}$  in electrodynamics is assumed to be spatially uniform at interatomic distances it turns dipoles in different local fields  $h$  in the same way, which is expressed in the  $h$ -independent coefficients with which the products proportional to  $E_x \sigma_{\alpha\kappa}$  and  $E_y \sigma_{\alpha\kappa}$  occur in the kinetic equations ( $\alpha = x, y, z$ ).

In the next section we apply the kinetic equations (47) and (48) which we have obtained here to describe various effects observed in the spectra of atomic gases.

## 5. KINETICS OF SYSTEMS OF INTERACTING DIPOLES IN ATOMIC GASES AND LIQUIDS

We shall show that the kinetic equations (47) and (48) can describe in optics and in magnetic resonance effects both dephasing and collective oscillatory motions of the interacting dipoles, and that they go over into the Bloch kinetic equation for  $\bar{d}^2 n_0 \tau_0 / \hbar \ll 1$ . (Here  $d$  and  $n_0$  are the middle dipole momentum of transition and the atoms concentration.)

Dephasing and collective oscillations of dipoles show up most strikingly in the decay of the free polarization and we start our discussion of the dipole kinetics with this effect. To obtain the kinetic equations for the decay of the free polarization we put  $E_x = E_y = 0$  in (47).

We consider the case when only dephasing occurs in the decay of the free polarization, which in (47) corresponds to  $\beta = 0$ ,  $\alpha = 1$ . It is then clear from (47) that the exchange of polarizations between the layers is included, and the equation for the layer polarizations takes the form

$$\frac{\partial F^\kappa}{\partial t} = i \left( \omega_{21} + \Delta_{21}^\kappa + \frac{d_\kappa h}{\hbar} \right) F^\kappa + \frac{F_0^\kappa F^\kappa}{\tau_c} + \frac{F_0 / \kappa_0 - F^\kappa}{\tau_0} - \frac{F^\kappa}{T_2'} \quad (49)$$

To begin with we consider the decay of the free polarization in gases in which  $1/\tau_c \gg 1/\tau_0$ . To calculate it we give the function  $g(h)$ . It was shown in Ref. 8 that in low-density gases  $g(h)$  is Lorentzian for  $\langle \sigma_z \rangle = 0$ :

$$g(h) = \frac{1}{\pi} \frac{\gamma}{(h - h_L)^2 + \gamma^2}, \quad \gamma = 3.8 n_0 \sqrt{\sum_\kappa |d_\kappa|^2} \approx 3.8 \bar{d} n_0. \quad (50)$$

For the weakly excited gas we are considering, where  $\langle \sigma_z \rangle \approx n_0$ , we can assume to a good approximation that the Lorentzian (50) with a shift  $h_L$  in the resonance field<sup>8,30</sup> is equal to the local Lorentz field

$$h_L = 4 \pi \bar{d} n_0 / 3, \quad (51)$$

which we shall use in what follows, putting  $\bar{d} = \sqrt{\sum_\kappa d_\kappa^2}$ .

Substituting into (49)

$$F^\kappa = \bar{F}^\kappa \exp \left[ i \left( \omega_{21} + \Delta_{21}^\kappa \right) - \frac{1}{T_2'} \right] t$$

and using a Laplace transformation to solve the equation obtained for  $F^{(\kappa)}$ , we get for  $\bar{F}_0^\kappa(0) = 1$

$$\bar{F}_0^\kappa(t) = \exp \left( - \frac{1}{T_2^{0\kappa}} + h_L \right) t, \quad (52)$$

where

$$\frac{1}{T_2^{0\kappa}} = \frac{d_\kappa \gamma}{\hbar}$$

determines the rate of dephasing of the dipoles caused by the precession of the dipoles in the local dipole fields. This expression differs in the  $\kappa$ -dependence of  $T_2^{0\kappa}$  from the result of the theory of collisional broadening of spectral lines<sup>22</sup> obtained for atoms coupled through dipole-dipole interactions. An interesting feature of the expression (52) which we have obtained for the decay of the free polarization is the way it depends on the time  $\tau_c$  and, hence, on the velocities of the atoms.

For a comparison with the actually observed decay of the free polarization we must multiply (52) by the function

$$G(t) = \exp \left( - \frac{\langle \delta^2 \rangle t^2}{2} \right),$$

where  $\langle \delta^2 \rangle$  is the mean square Doppler shift.

The exponential time dependence of  $\bar{F}_0^\kappa$  makes it possible to obtain at once the difficult to calculate contributions of the local dipole field to the rate of change of the polarization

$$\frac{\partial \mathcal{P}_{0\alpha}^\kappa}{\partial t} = - \frac{\mathcal{P}_{0\alpha}^\kappa}{T_2^{0\kappa}}, \quad \alpha = x, y. \quad (53)$$

We can now write the Bloch equation for  $\mathcal{S}_0^\kappa$  in the form

$$\begin{aligned} \frac{\partial \mathcal{S}_0^\kappa}{\partial t} = & \left[ \mathbf{k} \omega_{21} + \mathbf{i} \frac{d_\kappa}{\hbar} E_x + \mathbf{j} \frac{d_\kappa}{\hbar} E_y, \mathcal{S}_0^\kappa \right] - \mathbf{i} \frac{\mathcal{P}_{0x}^\kappa}{T_2} - \mathbf{j} \frac{\mathcal{P}_{0y}^\kappa}{T_2} \\ & + \mathbf{k} \frac{\mathcal{P}_0 - \mathcal{P}_{0z}^\kappa}{T_1}, \end{aligned} \quad (54)$$

where  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$  are the unit basis vectors of the coordinate system,  $1/T_2^\kappa = 1/T_2^{0\kappa} + 1/T_2'$ ,  $1/T_2'$  and  $1/T_1^\kappa$  characterize the contributions to the rate of change of the partial polarizations  $\mathcal{P}_{0\alpha}^\kappa$  from the spontaneous processes and the nonsecular part of the dipole-dipole interactions, and  $\mathcal{P}_0$  corresponds to the equilibrium value of the population difference of the levels of the resonance transition.

The principle underlying the kinetic equations (54) in the case of incoherent motions is simple: independent interactions produce independent increases in the vector  $\mathcal{S}_0^\kappa(t)$  and, hence, make independent contributions to the rate of change of the polarizations.

In liquids we have  $\bar{d}^2 n_0 / \hbar \gg \bar{\delta}$  and we can therefore neglect the Doppler broadening. Moreover, because of the strong interatomic interactions we have  $1/\tau_0 > 1/\tau_c$  so that we can write the kinetic equations (49) for the decay of the free polarization for liquids in the form

$$\frac{\partial F^\kappa}{\partial t} = i \left( \omega_{21} + \Delta_{21}^\kappa + \alpha \frac{d_\kappa}{\hbar} h \right) F^\kappa + \frac{F_0 / \kappa_0 - F^\kappa}{\tau_0} - \frac{F^\kappa}{T_2'}. \quad (55)$$

One can easily solve this equation if one bears in mind that in liquids the condition

$$\bar{d}^2 n_0 \tau_0 / \hbar \ll 1 \quad (56)$$

is well satisfied. Changing in (55) to

$$F^\kappa = \bar{F}^\kappa \exp \left[ i t \left( \omega_{21} + \Delta_{21}^\kappa - \frac{1}{T_2} \right) \right]$$

and multiplying both sides of Eq. (55) by  $g(h)$ , and afterwards by  $hg(h)$ , where<sup>8,14</sup>

$$g(h) = (2\pi \langle h^2 \rangle)^{-1/2} \exp(-h^2/2 \langle h^2 \rangle), \quad (57)$$

we get after summation at  $\kappa$  and integration over  $h$

$$\begin{aligned} \frac{\partial \bar{F}_0}{\partial t} &= i \frac{\bar{d}}{\hbar} \sum_{\kappa} \bar{F}_1^\kappa, \\ \frac{\partial \bar{F}_1}{\partial t} &= i \frac{\bar{d}^2}{\hbar^2} \sum_{\kappa} \int dh g(h) h^2 \bar{F}^\kappa(h, t) - \frac{\bar{F}_1}{\tau_0}. \end{aligned} \quad (58)$$

When condition (56) is satisfied we can put in (58)

$$h^2 \bar{F}^\kappa(h, t) \approx h^2 \bar{F}_0^\kappa$$

after which Eqs. (58) become closed and give

$$\frac{\partial \bar{F}_0}{\partial t} = -\frac{\bar{F}_0}{T_2^0}, \quad (59)$$

where

$$\frac{1}{T_2^0} = \frac{\bar{d}^2 \langle h^2 \rangle \tau_0}{\hbar^2}.$$

We now go over to considering collective coherent dipole oscillations. Such motions can arise only when the kinetic equations have isotropic interactions which are proportional to  $\beta$  and which operate actively, since only those interactions combine spins or pseudospins into a single entity and tend to equalize the polarizations of the layers and thereby facilitate the appearance of coherent collective dipole motions, which in optics<sup>25-27</sup> and in magnetic resonance phenomena<sup>31</sup> lead to superradiance effects.

Up to the present moment collective oscillatory motions of dipoles have been well studied experimentally<sup>10</sup> only in magnetic resonance phenomena where the oscillating decay of the free polarization has been observed in calcium fluorite crystals. Theoretically this decay was described in Ref. 14 by means of the kinetic equations for the partial density components of the magnetic dipoles in which the field  $h' = \hbar d / \hbar$  was expressed in frequency units:

$$\begin{aligned} \frac{\partial F(h', t)}{\partial t} &= i \alpha h' F(h', t) + i \beta [h' f(h', t) - h' F_0 - F_1] \\ &+ \frac{F_0 - F(h', t)}{\tau_c}. \end{aligned} \quad (60)$$

It is important to emphasize that this equation is the particular case  $\kappa=1$  of the kinetic equations (47) for the case when we have  $E_x = E_y = 0$ ,  $\tau_0 \rightarrow \infty$ . We see here the profound unity of the kinetics of magnetic and electric quantum dipoles. One should note that in Ref. 16 a contribution, similar

to the one in (60) which is proportional to  $\beta$ , from the isotropic exchange interactions to the rate of change of the layer polarizations was used to describe successfully the decay of the free polarization in solutions with arbitrary concentrations of radicals.

It is natural to assume, by virtue of the symmetry with which the magnetic and electric dipoles occur in the kinetics, that the key role in the appearance of collective oscillations of the optical and magnetic dipoles is played by the effects of the exchange of polarization between pseudospins proportional in magnitude to the quantum magnetic or optical dipoles.

Replacing in (49)  $F^\kappa$  by  $\bar{F}^\kappa$ , assuming that  $\tau_c, T_2' \rightarrow \infty$ , and adding the contribution from (47) which is proportional to  $\beta$  we get a kinetic equation for the layer polarizations in an optically strongly excited gas:

$$\begin{aligned} \frac{\partial \bar{F}^\kappa}{\partial t} &= i \frac{d_\kappa}{\hbar} \alpha h \bar{F}^\kappa + i \beta \frac{d_\kappa}{\hbar} \left( h \bar{F}^\kappa - h \frac{\bar{F}_0}{\kappa_0} + \frac{\bar{F}_1}{\kappa_0} \right) \\ &+ \frac{\bar{F}_0 / \kappa_0 - \bar{F}^\kappa}{\tau_0}. \end{aligned} \quad (61)$$

This equation is the same as (60), if we sum over  $\kappa_0$  and change to new local fields  $h' = \hbar d / \hbar$ , expressed in frequency units, and a new distribution function  $\bar{g}(h')$  of these fields, which characterizes the distribution of the real precession frequencies of the dipoles:

$$\begin{aligned} \frac{\partial \bar{F}(h', t)}{\partial t} &= i \alpha h' \bar{F}(h', t) + i \beta (h' \bar{F}(h', t) - h' F_0 - \bar{F}_1) \\ &+ \frac{\bar{F}_0 - \bar{F}(h', t)}{\tau_0}, \quad \bar{g}(h') = \frac{1}{\pi} \frac{\gamma \bar{d} / \hbar}{h'^2 + (\gamma \bar{d} / \hbar)^2}. \end{aligned} \quad (62)$$

The choice of  $\bar{g}(h')$  in the form (62), which is a convolution of the Lorentzian lines with all possible values of the Lorentz width  $\gamma \bar{d}_\kappa / \hbar$  is justified by the independence of the precession of the dipoles  $\mathbf{d}_\kappa$  in the fields  $h$  and their strong quantum fluctuations.

Equation (62) makes it possible to describe not only the dephasing of optical dipoles but also their coherent oscillations leading to superradiance effects<sup>25-27</sup> and the spectral condensation of the radiation.<sup>11,12</sup>

A last effect, observed in intraresonance laser spectroscopy, appears in the redistribution of the intensity in the spectrum of the radiation generated by a laser when the vessel with the resonant atomic gas moves inside the laser resonator. The intensity of the radiation at the resonance frequency and close to it is then reduced but at the frequencies

$$\omega'_{21} = \omega_{21} \pm \omega_{\text{osc}}, \quad \omega_{\text{osc}} = \sqrt{\frac{c \bar{d}^2 n_0 \omega_{21}}{\hbar}}, \quad c \sim 1, \quad (63)$$

it is increased.

We consider the eigenmodes of the polarization of the atoms of the gas in the vessel which are coupled through dipole-dipole interactions. We shall assume that the laser radiation acting on the atoms has a spiky structure. In the interval between the separate bunches of radiation passing

through the atomic gas the atomic dipoles carry out free oscillations, which for the case of the decay of the free polarization are described by the kinetic equation

$$\frac{d\bar{F}}{dt} = \frac{\bar{d}}{\hbar} (h\bar{F}_0 + \bar{F}_1) + \frac{(\bar{F}_0 - \bar{F}_1)}{\tau_0}, \quad (64)$$

which is obtained from Eq. (62) for  $\alpha = -1$ ,  $\beta = 1$ . This choice of  $\alpha$  and  $\beta$  is justified by the fact that in a strongly excited resonant atomic gas the amplitudes  $C_2$  and  $C_1$  of the upper and the lower states of the atom are approximately the same and, hence, the magnitude of the dipole moment of the resonance transition, which is proportional to  $C_1 C_2$ , has a maximum value. Hence the main role in the dipole kinetics is played not by the exchange of the polarization and the precession of the dipoles in the longitudinal effective fields but by the precession of the dipoles in the transverse local electric fields which actually act on the atoms.

Multiplying the kinetic equation (64) first by  $g(h)$  and afterwards by  $hg(h)$  and integrating the equations obtained over  $h$  we are led to an easily solved set of equations for  $\bar{F}_0$  and  $\bar{F}_1$ . The eigenmodes of this set have the form

$$\bar{F}_0^{1,2} \sim C_1 C_2 \exp\left[\pm i \sqrt{\frac{\bar{d}^2 \langle h^2 \rangle}{\hbar^2} - \frac{1}{\tau_0^2}} - \frac{1}{\tau_0}\right] t, \quad (65)$$

where (see Ref. 8)

$$\begin{aligned} \frac{\bar{d}^2}{\hbar^2} \langle h^2 \rangle &= \frac{\text{Tr}(b_{1k} \hat{\sigma}_z^{(k)})^2}{\text{Tr} 1} \\ &= 2\pi \frac{\bar{d}^4 n_0}{\hbar^2} \int_{2r_0}^{\infty} \frac{dr}{r^4} \int_{-1}^1 d \cos \theta (3 \cos^2 \theta - 1)^2 \\ &= \frac{3.25 \bar{d}^4 n_0}{(2r_0)^3 \hbar^2}, \end{aligned} \quad (66)$$

$b_{ik}$  is determined by (34),  $2r_0$  is the diameter of an atom,  $v$  is the thermal velocity, and we have

$$\omega_{\text{osc}} = \sqrt{\frac{\bar{d}^2 \langle h^2 \rangle}{\hbar^2} - \frac{1}{\tau_0^2}}. \quad (67)$$

It is important to emphasize that the oscillations occur only under the conditions  $\omega_{\text{osc}} > \sqrt{\langle \delta \rangle^2} \sim 10^9 \text{ s}^{-1}$ , which is satisfied when we have  $n_0 > 10^{12} \text{ cm}^{-3}$  and  $\omega_{\text{osc}} \gg 1/\tau_0$ . The appearance of damped periodic collective oscillations clearly indicates the occurrence of a coherent motion of the pseudospins and the large magnitude of  $\omega_{\text{osc}}$  indicates a high level of coherence of the increments of the polarization which are exchanged by the pseudospins under the influence of the isotropic interactions. The increment in the polarization of the  $i$ th spin (pseudospin) is proportional to  $b_{ik} \hat{\sigma}_\alpha^{(i)} \hat{\sigma}_\beta^{(k)}$  for  $\alpha \neq \beta$ . Hence it follows that the coherence of the increments of the polarization is connected with the correlator  $\langle \hat{\sigma}_\alpha^{(i)} \hat{\sigma}_\beta^{(k)} \rangle$  of the pseudospins. This correlation between near pseudospins can, of course, be established only due to the exchange of polarization since the dephasing destroys any coherence.

In  $\text{CaF}_2$ , for instance, the frequency of the oscillations<sup>14</sup> is  $\omega_{\text{osc}} = 1.6 M_2$  where  $M_2$  is the second moment of the observed absorption line which corresponds to such an orienta-

tion of the  $k$ th spin relative to the  $i$ th spin corresponding to the largest possible value of the quantities  $\langle \hat{\sigma}_\alpha^{(i)} \hat{\sigma}_\beta^{(k)} \rangle \approx 1$  when the  $k$ th spin is in the first coordinate sphere relative to the  $i$ th spin. The quantity  $2r_0$  in (66) therefore characterizes not only the smallest distance between the atoms but also the degree of their correlation. Its reduction, however, reflects the increase in the increments of the spin polarization under exchange, not as a result of a decrease of the actual distances between the spins but as the result of such a correlation between them that the rate of exchange of polarization and the frequency  $\omega_{\text{osc}}$  increases.

To determine the parameter  $2r_0$  in this problem we must compare (67) with the experimental formula

$$\omega_{\text{osc}}^2 = 2\pi \bar{d}_{12}^2 \omega_{12} n_0 / \hbar \quad (68)$$

for sodium vapor, which was obtained experimentally in Refs. 12 and 28; here  $d_{12}$  and  $\omega_{12}$  are the matrix element and the frequency of the resonance transition.

Taking into account that (see Ref. 28)

$$\bar{d}_{12}^2 = \hbar e^2 f_{12} / m \omega_{12},$$

where  $f_{12}$  are the oscillator strengths, which for the  $3P_{3/2} - 3S_{1/2}$  ( $\lambda = 589 \text{ nm}$ ) and  $3P_{1/2} - 3S_{1/2}$  ( $\lambda = 589.6 \text{ nm}$ ) transitions in the Na atom are, respectively, equal to 0.65 and 0.32, we find for those transitions that  $2r_0 = 1.6 \times 10^{-8}$  and  $1.1 \times 10^{-8} \text{ cm}$ .

The appearance of collective dipole oscillations therefore requires not just coherent motions of the dipole themselves but also an even more important coherence between the forces exerted on the separate dipoles by the moments which rotate them, which are proportional to<sup>14</sup>  $b_{ik} \hat{\sigma}_\alpha^{(i)} \hat{\sigma}_\beta^{(k)}$ . This coherence can, of course, be established only under the influence of the dipole-dipole interactions.

To explain the effect of the spectral condensation of the radiation we note now that in the intervals between the passage a small region of the gas of two bunches of radiation (we are dealing here with laser radiation having a spiky structure) the polarization will move like the eigenmodes of the decay of the free polarization. The electric field produced by such oscillations is

$$\mathbf{E} \propto \cos \omega_{\text{osc}} t \cos \omega_{12} t,$$

and hence the oscillating atomic dipoles will emit light energy at the frequencies  $\omega_{12} \pm \omega_{\text{osc}}$  which is, in fact, observed in the radiation condensation effect.

As to the superradiance effect, after a time approximately equal to the delay time of a spontaneous emission pulse following a  $\pi$ -pulse, a time is also reached when the amplitudes of the upper and the lower atomic states become equal in magnitude. Then any local polarization arising due to fluctuations in the orientations of the atomic dipoles will excite in the gas coherent eigenmodes of the dipoles with a frequency  $\omega_{\text{osc}}$ . It is now clear that just those collective oscillations trigger off Dicke's superradiance mechanism<sup>26</sup> leading to a burst of light emission with an intensity which becomes proportional to  $n_0^2$ .

The fluctuational nature of the appearance of  $\mathcal{S}_0$  was confirmed by experiments<sup>32</sup> in which a superradiant pulse was triggered by an additional pulse with a small cross-section  $\theta=10^{-4}$  rad for  $n_0=2\times 10^8$  cm<sup>-3</sup>.

In analyzing the appearance of coherent dipole oscillations and of the occurrence of a superradiant pulse it is convenient to use the simplest lumped Dicke model.<sup>26</sup> To do this we must add to Eq. (64) a contribution which is proportional to the number  $N$  of the dipoles considered<sup>26,27</sup> describing the precession of the dipoles in the radiation reaction field and take into account the change in  $\sigma_z$ :

$$\begin{aligned} \frac{dF}{dt} &= i(hF_0 + F_1) + \frac{N}{2T} F_0 \sigma_z, \\ \frac{d\sigma_z}{dt} &= -\frac{2N}{T} (\sigma_{x0}\sigma_x + \sigma_{y0}\sigma_y) \end{aligned} \quad (69)$$

(here  $T$  is the time for the spontaneous transition of a separate atom).

For small  $t$  we can put  $\sigma_z=1$  and solving Eq. (69) we easily get an expression describing the appearance of collective dipole oscillations and of the superradiant pulse for  $\langle h^2 \rangle \gg 1/\tau_c$ :

$$F_0 = \mathcal{S}_0 \exp\left(\frac{N}{2T} + i\sqrt{\langle h^2 \rangle}\right)t. \quad (70)$$

For large  $t$  the kinetic equations become non-linear. We shall consider the solutions of those equations in our next paper.

We now discuss briefly the problem of taking into account the effects of the propagation of electromagnetic waves under superradiance conditions. To take those into account we must analytically study or numerically find the solutions of the system consisting of the Maxwell equations and the common kinetic equations (47) and (48). Such studies were carried out in Refs. 33 and 34. However, in those papers the Maxwell equations were closed by the kinetic Bloch equations, which are applicable only in those cases when the motions of the dipoles show up only in the dephasing of the dipoles, rather than by Eqs. (47) and (48). Therefore, as was noted in Ref. 25, the results of the calculations of Ref. 34 could clearly only show a qualitative agreement with the experimental data.

We also note that in Refs. 12 and 28 phenomenological equations for the interresonator field  $\mathbf{E}(t)$  were successfully applied to describe the radiation condensation effect. It is interesting to note that the solutions of those equations turned out to be the same as the solutions of (65), apart from the physical nature of the damping rate. In Refs. 12 and 28 and in (65) these damping rates describe the rate of dephasing and the spectral diffusion. However, it is unclear why we have agreement since the kinetic equations in Refs. 12 and 28 describe the exchange of energy between the atoms and the electromagnetic field, whereas Eqs. (64) characterize the precession of the dipoles in the local fields.

In conclusion we must emphasize that on the whole we have carried out in the present paper a generalization of the well known two-level resonance approximation to the case of optical dipoles of real multilevel atoms coupled by dipole-dipole interactions.

In this generalization we took into account the effect of the enormous number of nonresonant atomic transitions which arise due to the quantum fluctuations of the dipoles, using an original canonical transformation which changes the rapidly-oscillating interactions of the nonresonant dipoles with the field  $\mathbf{E}$  and with other dipoles to effective interactions which are averaged over the fast oscillations and which determine the slow resonance motions of the dipoles just like the usual interactions.

Equation (20) contains terms which describe both single-quantum as well as various multi-quantum resonances. We can therefore obtain from this equation kinetic equations to describe not only the single-quantum resonance determined by the kinetic equations (47) and (48) but also any multi-quantum resonances. The single- and multi-quantum coherences calculated using such kinetic equations turn when the inverse canonical transformation is applied into various harmonics characterizing the various nonlinear susceptibilities which like the usual susceptibilities can be used for spectroscopic purposes. So far the cubic susceptibility has been successfully used for such purposes.<sup>35</sup>

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## APPENDIX

For a rigorous proof of the properties of  $H_{is}$  used in Sec. 4 to obtain the kinetic equations we use the standard kinetic equations obtained in Ref. 30 by the memory function method for variables which are given by an arbitrary set of orthogonal operators. We choose such operators in the form which is similar to the one proposed in Ref. 14:

$$\hat{\sigma}_{\alpha\kappa}(h) = \sum_{i,\kappa} \hat{\sigma}_{\alpha\kappa}^{(i)} \delta(h - b_{i\kappa} \hat{\sigma}_z^k). \quad (A1)$$

We now write down the standard kinetic equation for the layer polarizations  $\sigma_{\alpha\kappa}(h,t) = \text{Tr} \rho(t) \hat{\sigma}_{\alpha\kappa}(h)$  with the set of operators (A1):

$$\begin{aligned} \frac{\partial \sigma_{\alpha\kappa}(h,t)}{\partial t} &= i \sum_{\kappa',\alpha'} \int dh' \text{Tr} \rho_0 \hat{\sigma}_{\alpha\kappa}(h) [H_d^0, \hat{\sigma}_{\alpha'\kappa'}(h',t)] \\ &\quad \times \sigma_{\alpha'\kappa'}(h',t) \\ &\quad - \sum_{\kappa',\alpha'} \int dh' \int dt' \text{Tr} \rho_0 \{ [\hat{\sigma}_{\alpha\kappa}(h), H_d^0] \\ &\quad \times \exp\{i(1 - \hat{P})H_d^0(t-t')\} (1 - \hat{P}) \\ &\quad \times [H_d^0 \hat{\sigma}_{\alpha'\kappa'}(h')] \} \sigma_{\alpha'\kappa'}(h',t). \end{aligned} \quad (A2)$$

Here  $\hat{P}$  is a projection operator defined by the relation  $\hat{P}\rho(t) = \bar{\rho}(t)$  in which  $\bar{\rho}(t)$  contains only the selected orthogonal operators. We chose the operator

$$\rho_0 = \exp(-\alpha \hat{\sigma}_{0z}) / \text{Tr} \exp(-\alpha \hat{\sigma}_{0z})$$

to take into account the effect of the occupations of the resonance levels on the distribution  $g(h)$  which leads to a shift in the resonance frequency and an asymmetry in  $g(h)$ .

The linearity of Eq. (A2) in  $\sigma_{\alpha\kappa}(h,t)$  is obvious, whereas the linearity of (A2) in the fields  $h$  and  $h'$  as well as the presence of the contribution  $ihF^\kappa(h,t)$  in (A2) follows from the definition of the layer polarizations. Moreover, one sees easily from (A2) that after integration over  $h$  and summation over  $\kappa$  or when  $\sigma_{\alpha\kappa}(h,t)=\text{const}$  the interaction  $H_{is}$  on the right-hand side of (A1) commutes with the total layer polarization and drops out of the kinetic equation. We have thus proved all five properties and we may assume that the kinetic equation (42) is now obtained also from the equation for the density matrix. In conclusion we must emphasize that in systems of dipoles which precess in the local fields the dipole oscillations are series of echos. For a more exact calculation of  $\omega_{\text{osc}}$  we must therefore study how the exchange of polarization between the spins affects an echo.

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