PHYSICAL REVIEW A VOLUME 1, NUMBER 2 FEBRUARY 1970

Kinetic Equations for Optical Pumping*

Charles R. Willis
Boston University, Boston, Massachusetts 02215
(Received 10 June 1969)

We derive quantum-mechanical kinetic equations for the matter density ρ and radiation density matrix R, which describe optical pumping phenomena. The resultant kinetic equations are a set of coupled nonlinear equations for ρ and R. With appropriate linearizations, we can obtain the present theories of optical pumping. The nonlinear equations describe multiple scattering and line narrowing due to imprisonment of resonant radiation. We show that the coupled equations for ρ and R are equivalent to coupled equations for ρ and a generalized polarization matrix II, whose matrix elements are the second moments of R. The polarization matrix Π constitutes a complete description of linear phenomena in the same manner as present theories describe optical pumping phenomena by using the matter density matrix ρ alone. As a consequence of our nonphenomenological treatment of radiation, we can provide a completely microscopic treatment of the externally modulated light-beam experiment of Bell and Bloom. We show that the atom absorbs the modulation envelope directly from the external thermal light beam in the same way that the atom absorbs transverse polarization directly from the light beam in optical pumping experiments.

I. INTRODUCTION

The clearest presentation of the current theory of optical pumping occurs in the thesis of Cohen-Tannoudji.[1] In this paper, the optical radiation field is treated as a given quantum-mechanical external beam and the matter in the sample is treated as N noninteracting atoms described by a single-particle density matrix. The Cohen-Tannoudji theory is linear in the matter density matrix because the incident radiation is treated throughout as given by the external beam and all changes in the optical radiation are obtained as consequences of changes in the single-particle density matrix ρ. Recently, Cohen-Tannoudji and Laloë[2] studied the propagation of a classical light beam in an atomic vapor in which the atoms are described by a given single-particle density matrix. Consequently, their new results correspond to a linear theory for the classical light beam. In this paper, we derive the equations of motion for the single-particle density matrix ρ and the radiation density matrix R, starting from the quantum-mechanical Liouville equation for the combined system of N particles and the radiation. The resulting equations for ρ and R are coupled, nonlinear, and describe multiple scattering phenomena such as line narrowing due to imprisonment of resonant radiation. We next show that the coupled equations for ρ and R are equivalent to a set of coupled equations for the ground-state density matrix ρ_g and a generalized radiation polarization matrix Π, whose matrix elements are the second moments of R, $\mathrm{Tr} a_i^\dagger(\vec{k}) a_j(\vec{k}') R$, where the $a_i^\dagger(\vec{k})$ and $a_j(\vec{k}')$ are the usual creation and annihilation operators for photons of wave number $\vec{k}, \vec{k}'$, and polarization i,j. The reduction of the equations for ρ and R to equations for ρ_g and Π follows from the Gaussian or "thermal-like" statistics of the optical radiation which is completely determined by its second moments. When we linearize our equations by taking the radiation polarization matrix to be that of the external optical beam, we obtain the equations of motion for ρ which are equivalent to those of Ref. 1. When we linearize our equations by taking ρ as given, we obtain a linear equation for the radiation polarization matrix Π, which is a generalization of the results of Ref. 2. We also show that in the linear problem it is possible to obtain all the physics from the solution of the equations of motion for the radiation polarization matrix alone, just as it is also possible to obtain all results in the linear problem from the solution[1] for ρ alone.

We treat the radiation fully quantum-mechanically for the following reason: If we treated the radiation purely classically, then the induced absorption and the induced emission would be the same as in the quantum-mechanical treatment. In order to obtain spontaneous emission classically, it is absolutely necessary to introduce radiation-matter correlations such that the density matrix of radiation and matter cannot be written as a product $R\rho$. However, if we treat the radiation quantum-mechanically, we obtain spontaneous emission without the need for any radiation-matter correlations. Consequently, in the quantum-mechanical treatment, we can consider the radiation-matter density matrix to be a product $R\rho$ and still have spontaneous emission. Thus, even though we could treat the optical radiation in optical pumping completely classically, the large amount of extra work required to retain the requisite radiation-matter correlations

in order to include spontaneous emission classically is not worthwhile. The remarks in this paragraph do not imply that the quantum theory of radiation is equivalent to the classical theory of radiation, but only that the question of spontaneous emission, as it appears in optical pumping expressions for lineshapes, is not a quantum-versus-classical problem, but a statistical question of no correlations or correlations between radiation and matter variables.

One of the questions to ask of a theory of radiation in optical pumping is whether there are any linear phenomena which require a more detailed analysis of radiation than that obtained from the matter density matrix and an external optical beam of given intensity and polarization. We find that the experiments using a radio-frequency-modulated light beam of Bell and Bloom require detailed knowledge of the correlations between photons of different wave numbers. These correlations are contained in the radiation polarization matrix Π. One of the main results of the present paper is a completely nonphenomenological explanation of the Bell-Bloom[3] experiment. We find that the atom can absorb modulation directly from the light beam in the same manner that the atom absorbs transverse polarization from the light beam. Modulation of the light beam creates correlations between photons differing in frequency by the modulation frequency in the same way that a polarizer creates correlations between photons of different spin states. The coherence of the light modulator is transmitted by means of the correlations created between the photons of the thermal optical beam to the coherence of the atomic system. The result is essentially the same as the direct absorption of a coherent electromagnetic field whose frequency is the same as the frequency of modulation of the light beam.

Modulation of the optical beam in optical pumping is usually produced by the coherent dipole moment of the atomic system created by a resonant rf or microwave field. The method of derivation in this paper is valid for time-dependent rf fields. However, the extra transformation required to go to the rotating wave coordinate system so complicates the notation that the underlying physics is obscured. Consequently, we defer the treatment of the rf case to a separate publication.

In Sec. II, we obtain the kinetic equation for optical pumping by a heuristic argument. Section III contains a discussion and an analysis of the kinetic equations obtained heuristically in Sec. II. Those readers who are not interested in the foundations of kinetic equations can proceed from Sec. II directly to Sec. IV, where we work out the detailed form of the equations of motion for the single-particle density matrix and show that the linearized form of the equations of motion are equivalent to the equations for ρ derived in Ref. 1. We show in Sec. V that the coupled equations for ρ and R rigorously reduce to coupled equations for the ground-state density matrix ρ_g and the generalized polarization matrix Π, whose matrix elements are the second moments of R. The linearization of the equations of motion for Π and the neglect of emission terms yield the equations of motion of Ref. 2. In Sec. VI, we analyze the Bell-Bloom[3] experiment and provide a microscopic explanation of their results. Section VII describes spatial effects, and Sec. VIII contains the discussion.

II. KINETIC EQUATIONS FOR RADIATION AND MATTER

The Hamiltonian for our system of N atoms interacting with an optical electromagnetic field in the dipole approximation is

$$\begin{aligned} H &\equiv H_a(N) + H_{\mathrm{cm}} + H_f + \gamma V(N) \\ &\equiv H_0(N, \{k\}) + \gamma V(N) , \end{aligned} \tag{2.1}$$

where $H_a(N) \equiv \sum_{\alpha=1}^{N} h(\alpha)$;

$$H_f = \sum_{k,i} \Omega_k a_i^{\dagger}(k) a_i(k) .$$

We use units where $\hbar = c = 1$. For each value of $\vec{k}$ there are two values of i corresponding to any two linearly-independent states of polarization. For circular polarization, the index i takes on the two values $\pm$ corresponding to $\vec{\epsilon}\pm = 2^{-1/2}(\vec{\epsilon}_1 \pm i\vec{\epsilon}_2)$. The symbol $\{k\}$ represents the infinite number of modes of the cavity. Usually we will consider the eigenmodes of the cavity to be plane waves. The $a_i(\vec{k})$ and $a_j^{\dagger}(\vec{k})$ are the usual annihilation and creation operators which satisfy the following commutation relations:

$$\begin{aligned} &[a_i(\vec{k}),\ a_j^{\dagger}(\vec{k}')] = \delta_{ij}\,\delta(\vec{k} - \vec{k}') ; \\ &[a_i(\vec{k}),\ a_j(\vec{k}')] = [a_i^{\dagger}(\vec{k}),\ a_j^{\dagger}(\vec{k}')] = 0 . \end{aligned} \tag{2.2}$$

The term $H_a(N)$ represents the Hamiltonian of N noninteracting atoms in a static magnetic field in the z direction. The eigenfunctions and eigenvalues of a single atom are

$$h|\mu\rangle = E_{\mu}|\mu\rangle , \quad \text{and} \quad h|m\rangle = E_m|m\rangle , \tag{2.3}$$

where we use the convention that Greek indices represent ground-state levels and Latin indices represent excited-state levels. The Hamiltonian $H_{\mathrm{c.m.}}$ describes atomic c.m. motion including collisions. The c.m. variables are classical variables.

The interaction Hamiltonian $\gamma V(N)$ is

$$\begin{aligned} &\gamma V(N) \\ &\equiv \gamma \sum_{\alpha=1,\vec{k},i}^{N} [\Gamma_{\vec{k}}^{*}(X_\alpha) P_g^{\alpha} \vec{\epsilon}_i^{\dagger}(\vec{k}) \cdot \vec{D}^{\alpha} P_e^{\alpha} a_i^{\dagger}(\vec{k}) \end{aligned}$$

$$+\Gamma_{\vec{k}}(X_\alpha)P_e{}^\alpha \vec{\epsilon}_i(\vec{k})\cdot\vec{D}^\alpha P_g{}^\alpha a_i(\vec{k})] \quad , \qquad (2.4)$$

where the ground-state projection operator $P_g{}^\alpha$ and the excited-state projection operator $P_e{}^\alpha$ are defined as

$$P_g{}^\alpha \equiv \sum_\mu |\mu^\alpha\rangle\langle\mu^\alpha| \quad \text{and} \quad P_e{}^\alpha \equiv \sum |m^\alpha\rangle\langle m^\alpha| \ .$$

The definition of the interaction Hamiltonian is such that products $\gamma V(N)\gamma V(N)$ do not contain $a^\dagger a^\dagger$ and aa terms. In another context, this is called the rotating wave approximation. The $\Gamma_{\vec{k}}(X_\alpha)$'s are the eigenmodes of the cavity evaluated at the c.m. X_α of the αth atom. The operator $\vec{D}^\alpha \equiv (\vec{r}_\alpha/|r_\alpha|^{-1})$ is the dimensionless dipole moment of the αth atom, and the term $\vec{\epsilon}_i(\vec{k})\cdot\vec{D}^\alpha$ represents the angle between the electromagnetic polarization direction $\vec{\epsilon}_i(\vec{k})$ and the dimensionless dipole operator of the αth atom. The magnitude of the dipole matrix element appears in the constant

$$\gamma \equiv q\langle g|r|e\rangle(\Omega_0/2)^{1/2} \quad , \qquad (2.5)$$

where q is the charge on the electron, Ω_0 is the energy difference between the unperturbed ground state g and the unperturbed excited state e, and $\langle g|r|e\rangle$ is the matrix element of r between the radial parts of the ground and excited states. The expression for $\gamma V(N,\tau)$ in the interaction representation is

$$\gamma V(N,\tau) = e^{iH_0(N,\{k\})\tau}\gamma V(N)e^{-iH_0(N,\{k\})\tau}$$
$$= \gamma \sum_{k,\alpha,i} \Gamma^*_{\vec{k}}[X_\alpha(\tau)]\,|\mu^\alpha\rangle\langle\mu^\alpha|\vec{\epsilon}_i{}^\dagger(\vec{k})\cdot\vec{D}^\alpha|m_\alpha\rangle$$
$$\times\langle m_\alpha|a_i{}^\dagger(\vec{k})e^{i(\Omega_k-\Omega_{m\mu})\tau} + \text{h.c.}, \qquad (2.6)$$

where h.c. is the Hermitian conjugate, and $X_\alpha(\tau)$ is the position of the αth atom after τ seconds. If we neglect collisions, $X_\alpha(\tau)$ equals $X_\alpha(0) - V_\alpha\tau$. The frequency of the electromagnetic field is Ω_k and the frequency $\Omega_{m\mu}$ is $E_m - E_\mu$.

The quantum-mechanical Liouville equation for our system of N atoms interacting with the electromagnetic field is

$$\dot{F}_{N\{k\}} + i[H_0(N,\{k\}) + \gamma V(N), F_{N\{k\}}] = 0 \ , \qquad (2.7)$$

where the dot indicates differentiation with respect to time. The density matrix $F_{N\{k\}}$ is the density matrix for all N atoms and all the radiation modes of the cavity.

We want an approximate solution of Eq. (2.7) which is valid for the macroscopic times of measurement. In this section, we present a simple heuristic argument which gives us an equation of motion whose solution is the approximate solution of Eq. (2.7). The argument is not really a derivation because the range of validity is restricted to times which are too short. However, the result of the heuristic argument is correct for long times even though the argument is valid only for short times. We use the heuristic argument because its simplicity provides an insight into the much more lengthy and complex rigorous derivation we discuss in Sec. III.

We expand $F_{N\{k\}}$ in a power series in γ, substitute the expansion in Eq. (2.7), and obtain

$$\dot{F}^s_{N\{k\}} + i[H_0(N,\{k\}),\ F^s_{N\{k\}}]$$
$$= -i[V(N),\ F^{s-1}_{N\{k\}}] \ , \qquad (2.8)$$

where $F_{N\{k\}} = \sum_\gamma \gamma^\gamma F^\gamma_{N\{k\}}$ and $F^{-1}_{N\{k\}} = 0$.

The solution of Eq. (2.8) for $F^0_{N\{k\}}(t)$ is

$$F^0_{N\{k\}}(t) = \exp[-itH_0(N,\{k\})]F^0_{N\{k\}}(0)$$
$$\times\exp[itH_0(N,\{k\})] \ . \qquad (2.9)$$

The solution of Eq. (2.8) for $F^1_{N\{k\}}(t)$ is

$$F^1_{N\{k\}}(t) = -i\int_0^t [V(N,-\tau),\ F^0_{N\{k\}}(t)]\,d\tau \ . \qquad (2.10)$$

When we substitute Eq. (2.10) in Eq. (2.8) for $\dot{F}^2_{N\{k\}}$, we obtain

$$\dot{F}^2_{N\{k\}}(t) + i[H_0(N,\{k\}),\ F^2_{N\{k\}}(t)]$$
$$= -[V(N),\ \int_0^t [V(N,-\tau),\ F^0_{N\{k\}}(t)]]\,d\tau \ . \qquad (2.11)$$

The equation of motion for $F_{N\{k\}}(t)$ to order γ^2 is

$$\dot{F}_{N\{k\}}(t) + i[H_0(N,\{k\}),\ F_{N\{k\}}(t)] = -\gamma^2[V(N),$$
$$\int_0^t [V(N,-\tau),\ F_{N\{k\}}(t)]]\,d\tau \ , \qquad (2.12)$$

where we replace $F^0_{N\{k\}}(t)$ on the right-hand side of Eq. (2.11) by $F_{N\{k\}}(t)$, which is valid to order γ^4. We dropped the term linear in γ because terms linear in the electric field operators and linear in $\Gamma_k(X)$ do not survive subsequent averages over the incoherent light beam and over space. Equation (2.12) is rigorous for times short compared with the relaxation time.

Finally, we make two plausible but far-reaching assumptions. First that the time $t = 0$ in the

above derivation is not speciai, so Eq. (2.12) valid for all times t. This is the repeated random-phase assumption. The second assumption is that we can set the upper limit of the τ integration in Eq. (2.12) equal to infinity because $V(N, -\tau)$ varies more rapidly than $F_{N\{k\}}(t)$. As we show in Sec. III, the second assumption is true if the relaxation time τ_γ is larger than a suitably defined interaction time τ_i.

The final result for the kinetic equation for $F_{N\{k\}}$ to order γ^2, referred to as the first Born approximation master equation is

$$\dot{F}_{N\{k\}}(t) + i[H_0(N,\{k\}), F_{N\{k\}}(t)] = -\gamma^2\{V(N), \int_0^\infty [V(N,-\tau), F_{N\{k\}}(t)]\}d\tau . \tag{2.13}$$

Equation (2.13) is also valid when $H_0(N\{k\})$ depends explicitly on time if one replaces

$$\exp[-i\tau H_0(N,\{k\})]$$

by $$T\{\exp[-i\int_0^\tau H_0(N,\{k\}, t')dt']\} ,$$

where T denotes the time-ordered product.

We are interested in the behavior of the radiation density matrix R and the single-particle density matrix ρ, which we define in the following manner:

$$R(t) \equiv \mathrm{Tr}_{1,2,\ldots,N} F_{N\{k\}}(t) ,$$

and $$\rho(t) \equiv \mathrm{Tr}_{\{k\},2,\ldots,N} F_{N\{k\}}(t) .$$

When we trace Eq. (2.13) over all the matter variables, we obtain

$$\dot{R} + i[H_f, R] = -\gamma^2 \mathfrak{N}\, \mathrm{Tr}_1 [V, \int_0^\infty [V(-\tau), F_{1\{k\}}(t)]]\, d\tau, \tag{2.14}$$

where V without the N dependence is the single atom-radiation interaction, and $\mathfrak{N}$ is the number of atoms per unit volume. The trace of Eq. (2.13) over $(N-1)$ matter variables and all the radiation variables is

$$\dot{\rho}(t) + i[H_0(1), \rho(t)] = -\gamma^2 \mathrm{Tr}_{\{k\}}[V, \int_0^\infty [V(-\tau), F_{1\{k\}}(t)]]d\tau. \tag{2.15}$$

The $\mathfrak{N}$ in Eq. (2.14) results from the contribution of all $\mathfrak{N}$ atoms to the radiation while the absence of $\mathfrak{N}$ in Eq. (2.15) results from the interaction of the radiation with a single atom.

Equations (2.14) and (2.15) do not constitute a closed set of equations for R and ρ because they depend on $F_{1\{k\}}$, which depends on $F_{2\{k\}}$, and so on, until $F_{N\{k\}}$ is reached. The correlations[4] between radiation and matter are proportional to the ratio of the rate of induced emission to spontaneous emission, i.e., to the number of photons per mode which in the notation of Ref. 1 is $(\Gamma T_b)^{-1}$. The number of photons per mode in optical pumping is usually less than 10^{-4}. Consequently, when we replace $F_{1\{k\}}$ by $R\rho$ in Eqs. (2.14) and (2.15), we obtain the closed set of equations:

$$\dot{R} + i[H_f, R] = -\gamma^2 \mathfrak{N}\, \mathrm{Tr}_1 \times [V, \int_0^\infty [V(-\tau), R(t)\rho(t)]]d\tau , \tag{2.16}$$

$$\dot{\rho} + i[h(1), \rho] = -\gamma^2 \mathrm{Tr}_{\{k\}} \times [V, \int_0^\infty [V(-\tau), R(t)\rho(t)]]\, d\tau . \tag{2.17}$$

In a laser the difference between $F_{1\{k\}}$ and $R\rho$ is responsible[4] for the nonthermal statistics of the laser. The solution of Eq. (2.16) for R is uniquely determined by its second moments, which is another way of stating that R has "thermal-like" statistics. In Sec. V, we show that the neglect of radiation-matter correlations is responsible for the matter density matrix ρ being uniquely determined by no other property than the second moments of R.

The results for the arguments leading to Eqs. (2.16) and (2.17) carried out in the interaction representation are

$$\dot{\tilde{R}} = -\gamma^2 \mathfrak{N}\, \mathrm{Tr}_1 [V(t), \int_0^\infty [V(t-\tau), \tilde{R}(t)\tilde{\rho}(t)]]d\tau, \tag{2.18}$$

$$\dot{\tilde{\rho}} = -\gamma^2 \mathrm{Tr}_{\{k\}} [V(t), \int_0^\infty [V(t-\tau), \tilde{R}(t)\tilde{\rho}(t)]]d\tau , \tag{2.19}$$

where $$\tilde{R}(t) \equiv \exp[itH_f] R(t) \exp[-itH_f] ,$$

$$\rho(t) \equiv \exp[ith(1)]\rho(t)\exp[-ith(1)] .$$

The kinetic equations for R and ρ, Eqs. (2.16) and (2.17), constitute the fundamental description of the generalized theory of optical pumping which we develop in this paper. Section III is concerned with the justification of Eqs. (2.16) and (2.17). Those readers who are interested only in the consequences of Eqs. (2.16) and (2.17) can proceed to Sec. IV.

III. INVESTIGATION OF INTERACTION TIME τ_i

Though the results of Sec. II are correct, the derivation is deficient in two respects. First, the

derivation holds only for times short compared with a relaxation time. We discuss the removal of the short-time restriction at the end of this section.

Second, we did not justify the extension of the time integration from t to infinity in Eq. (2.12). This change of limits is closely related to the appearance of the δ function of the conservation of energy in Fermi's golden rule. The limit of t going to infinity in Eq. (2.12) means that there exists a t which is very large compared with an interaction times τ_i, but is small compared with the relaxation time τ_γ. In the present section, we find the three different τ_i's that play a role in optical pumping. In order to find the interaction times it is necessary to explicitly construct the kernels in the kinetic equations.

We iterate the Liouville equation in the interaction representation twice, trace over the radiation variables to get the equation for ρ, and trace over the matter variables to get the equation for R:

$$\tilde{\rho}(t)-\tilde{\rho}(0)\approx-\gamma^2\,\mathrm{Tr}_{\{k\}}\int_0^t\int^{t'}\times[V(t_1),\,[V(t_2),\,\tilde{R}(0)\tilde{\rho}(0)]]\,dt_1dt_2, \tag{3.1}$$

$$\tilde{R}(t)-\tilde{R}(0)\approx-\gamma^2\,\mathfrak{N}\,\mathrm{Tr}_1\int_0^t\int_0^{t'}\times[V(t_1),[V(t_2),\,\tilde{R}(0)\tilde{\rho}(0)]]\,dt_1dt_2\ , \tag{3.2}$$

where $\tilde{\rho}(0)$ and $\tilde{R}(0)$ are the initial values of $\tilde{\rho}(t)$ and $\tilde{R}(t)$, and we have dropped the term linear in γ because the average value of the electric field and the polarization is zero. We also assume $\tilde{F}_{1\{k\}}(0)$ is equal to $\tilde{R}(0)\tilde{\rho}(0)$, i.e., there are no radiation-matter correlations.

When we take the diagonal matrix elements of Eqs. (3.1) and (3.2), the right-hand sides take the form

$$\int d\alpha f(\alpha)\int_0^t dt_1\int_0^{t_1}dt_2\,e^{i\alpha(t_1-t_2)}\ , \tag{3.3}$$

where the integration over the continuous frequency variable α arises when we replace the traces over discrete variables by integrals over continuous variables. In the trace over matter variables, the continuous α is the variable $\vec{k}\cdot\vec{v}$, where $\vec{v}$ is the velocity of the atom. In the trace over radiation variables, the variable α is the mode frequency Ω_k of the radiation. The function $f(\alpha)$ is a function of the density of states and the interaction matrix elements. For t sufficiently large, Eq. (3.3) becomes

$$\int d\alpha f(\alpha)\int_0^t dt_1\int_0^{t_1}dt_2\,e^{i\alpha(t_1-t_2)}\approx t\int d\alpha f(\alpha)\pi\delta_+(\alpha)\ , \tag{3.4}$$

where $\delta_\pm(\alpha)=\delta(\alpha)\pm i\,\mathcal{P}\,(1/\alpha)\equiv\int_0^\infty d\tau e^{\pm i\alpha\tau}$,

and $\mathcal{P}$ is the principal part. A proof of Eq. (3.4) is given by Prigogine.[5] This section of our paper is based on Chap. 2 of Ref. 5. The condition that t be sufficiently large means that $t\gg(\delta\alpha)^{-1}\equiv\tau_i$, where $\delta\alpha$ is the width of the function $f(\alpha)$. This condition is equivalent to the condition for obtaining the energy conservation δ function in Fermi's golden rule.

We obtain a special case of Eqs. (2.18) and (2.19) by setting

$$t^{-1}[\tilde{\rho}(t)-\tilde{\rho}(0)]\approx\dot{\tilde{\rho}}(0)\ ,$$

and $\quad t^{-1}[\tilde{R}(t)-\tilde{R}(0)]\approx\dot{\tilde{R}}(0)\ ,$

and asserting that $t=0$ is not unique, so that $t=0$ is replaced by t in $\dot{\tilde{R}}(0)$, $\dot{\tilde{\rho}}(0)$, $\tilde{R}(0)$ and $\tilde{\rho}(0)$. We now see that the determination of the interaction time τ_i requires an explicit evaluation of the matrix elements on the right-hand side of Eqs. (3.1) and (3.2) in order to obtain $f(\alpha)$. For definiteness we calculate the equation of motion for the off-diagonal excited-state matrix element $\langle m|\tilde{\rho}|m'\rangle$.

When we insert the definition of V[Eq. (2.4)] in Eq. (3.1) and take the matrix elements between states m and m', we obtain

$$\langle m|\tilde{\rho}(t)|m'\rangle-\langle m|\tilde{\rho}(0)|m'\rangle=-\gamma^2\sum_{i=1}^{4}A_i, \tag{3.5}$$

where

$$A_1\equiv v^{-1}\sum_{\mu,m,\vec{k},\vec{k}',i,i'}[\mathrm{Tr}a_i(\vec{k})a_{i'}^{\dagger}(\vec{k}')R]e^{i(\vec{k}-\vec{k}')\cdot\vec{X}}\langle m|\vec{\epsilon}_i(\vec{k};\vec{D}|\mu\rangle\langle\mu|\vec{\epsilon}_j{}^{\dagger}(\vec{k}')\cdot\vec{D}|m\rangle\langle m|\tilde{\rho}|m'\rangle f_1(t); \tag{3.6a}$$

$$A_2\equiv v^{-1}\sum_{\mu,m,\vec{k},\vec{k}',i,i'}[\mathrm{Tr}a_i(\vec{k})a_{i'}^{\dagger}(\vec{k}')R]e^{i(\vec{k}-\vec{k}')\cdot\vec{X}}\langle m|\tilde{\rho}|\bar{m}\rangle\langle\bar{m}|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle\langle\mu|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|m'\rangle f_2(t); \tag{3.6b}$$

$$A_3\equiv v^{-1}\sum_{\mu,m,\vec{k},\vec{k}',i,i'}\mathrm{Tr}[a_i(\vec{k})a_{i'}{}^{\dagger}(\vec{k}')R]e^{i(\vec{k}-\vec{k}')\cdot\vec{X}}\langle m|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle\langle\mu|\tilde{\rho}|\nu\rangle\langle\nu|\vec{\epsilon}_{i'}{}^{\dagger}(\vec{k}')\cdot\vec{D}|m'\rangle f_3(t)\ ; \tag{3.6c}$$

$$A_4 \equiv v^{-1} \sum_{\mu,m,\vec{k},\vec{k}',i,i'} \mathrm{Tr}[a_{i'}^{\dagger}(\vec{k}')a_i(\vec{k})R]\, e^{i(\vec{k}-\vec{k}')\cdot\vec{X}} \langle m|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle\langle\mu|\tilde{\rho}|\nu\rangle\langle\nu|\vec{\epsilon}_{i'}^{\dagger}(\vec{k}')\cdot\vec{D}|m'\rangle f_4(t)\ ; \quad (3.6d)$$

and where $$f_l(t) = \int_0^t dt_1 \int_0^{t'} dt_2 e^{i(\alpha_l t_1 - \beta_l t_2)} \ . \quad (3.7)$$

The frequencies α_l and β_l are

$$\alpha_1 \equiv \Omega_{k'} + \vec{k}'\cdot\vec{v} - \Omega_{m'\mu} \quad \beta_1 \equiv \Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\mu}, \quad \alpha_2 \equiv -\Omega_k - \vec{k}\cdot\vec{v} + \Omega_{m\mu}, \quad \beta_2 \equiv -\Omega_{k'} - \vec{k}'\cdot\vec{v} + \Omega_{m'\mu},$$
$$\alpha_3 \equiv \Omega_{k'} + \vec{k}'\cdot\vec{v} - \Omega_{m'\nu}, \quad \beta_3 \equiv \Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\mu}, \quad \alpha_4 \equiv -\Omega_k - \vec{k}\cdot\vec{v} + \Omega_{m\mu}, \quad \beta_4 \equiv -\Omega_{k'} - \vec{k}'\cdot\vec{v} + \Omega_{m'\nu} \ . \quad (3.8)$$

Frequencies with two subscripts are defined as

$$\Omega_{m\nu} \equiv E_m - E_\nu \ . \quad (3.9)$$

We take the eigenfunctions of the cavity $\Gamma_{\vec{k}}(X)$ to be plane waves; $\Gamma_k(X) = v^{-1/2}\exp[i\vec{k}\cdot\vec{X}]$, where v is the volume of the system. If $k = k'$, the space dependence drops out. For $k \neq k'$, we have terms proportional to $\exp[i(\vec{k}-\vec{k}')\cdot\vec{X}]$. In most cases the wave numbers satisfy the inequality $|k-k'| \ll L^{-1}$, where L is the length of the sample and we may neglect the space dependence. For convenience we drop the space-dependent term $e^{i(k-k')\cdot X}$. We discuss spatial dependence in Sec. VII.

To determine τ_i we must convert the summations over $\vec{k}$ and $\vec{k}'$ into integrals over frequency by using the following relation:

$$v^{-1}\sum_{\vec{k}}(\cdots) \to (2\pi)^{-3}\int d\vec{k}\,(\cdots)$$
$$= (2\pi)^{-3}\int d\vec{\Omega}(\cdots) \ , \quad (3.10)$$

where the equality follows from our units with $c = 1$. In the remainder of the paper we use both the summation and integration symbols although it is understood that we have a continuous density of photon states.

For $\vec{k} = \vec{k}'$, the integral over k of $\langle a_j^{\dagger}(\vec{k})a_j(\vec{k})\rangle$ is the number of photons of polarization j, where $\langle(\cdots)\rangle$ is $\mathrm{Tr}(\cdots)R$. Consequently, the interaction time τ_i is the inverse linewidth of the photon distribution. For the terms $\langle a_j(\vec{k})a_j^{\dagger}(\vec{k})\rangle$, which represent spontaneous emission, the interaction time is given by the Wigner-Weisskopf treatment as approximately ω_0^{-1}, where ω_0 is the frequency difference between the ground and excited states.

The time integrals f_i in Eq. (3.7) do not, in general, approach $t\pi\delta_+(\beta_i)$, when α_i is not equal to β_i. However, for times t such that $(\alpha_i - \beta_i)t$ is much less than unity, the time integral f_i does approach $t\pi\delta_+(\beta_i)$. Since the maximum time involved in A_1 and A_2 is the lifetime of the excited state Γ_e^{-1}, our condition becomes $(\alpha_i - \beta_i) \ll \Gamma_e$ for A_1 and A_2. For A_3 and A_4, the maximum time involved is the lifetime of the ground state Γ_g^{-1}, so our condition for A_3 and A_4 is $(\alpha_i - \beta_i) \ll \Gamma_g$. We use the notation $\Delta_e(\alpha_i - \beta_i)$ for the condition $(\alpha_i - \beta_i) \ll \Gamma_e$, and $\Delta_g(\alpha_i - \beta_i)$ for the condition $(\alpha_i - \beta_i) \ll \Gamma_g$. The Δ condition is essentially equivalent to the secular approximation of Cohen-Tannoudji.[1] In Sec. IV, we show that we can drop the Δ condition completely. The exact theory of Sec. IV differs from the approximate theory of this section only in the fact that there is sometimes a small contribution from the region where $(\alpha_i - \beta_i) \sim \Gamma$ in the exact theory. (The importance of being able to drop the Δ conditions is not quantitative or qualitative, but is in the convenience of being able to ignore the conditions in the sum over states.)

The right-hand side of Eq. (3.5) with the Δ conditions imposed is proportional to t, and hence we have a kinetic equation for $\langle m|\tilde{\rho}|m'\rangle$. We first simplify the individual terms A_i. The terms A_1 and A_2 correspond to spontaneous emission, because $\mathrm{Tr}[a(\vec{k})a^{\dagger}(\vec{k}')R]$ is equal to $[1 - \langle a^{\dagger}(\vec{k})a(\vec{k})\rangle]$ for $\vec{k} = \vec{k}'$ and is equal to $\langle a^{\dagger}(\vec{k}')a(\vec{k})\rangle$ for $\vec{k} \neq \vec{k}'$. Since the number of photons per mode is very small compared with 1 and since $\langle a^{\dagger}(\vec{k}')a(\vec{k})\rangle$ is less than or equal to the number of photons per mode, the dominant contribution to the A_1 and A_2 terms comes from the one in the $\vec{k} = \vec{k}'$ term. This result is another way of stating that induced emission is negligible compared with spontaneous emission in optical pumping. When we set $\vec{k}$ equal to $\vec{k}'$ and perform the integrations over the wave vector $\vec{k}$, we obtain

$$\langle m|\tilde{\rho}(t)|m'\rangle - \langle m|\tilde{\rho}(0)|m'\rangle = -\gamma^2\sum A_i$$
$$= -\tfrac{1}{2}[\Gamma_e(m) + \Gamma_e(m')]t\langle m|\tilde{\rho}(0)|m'\rangle$$
$$-\gamma^2(A_3 + A_4) \ , \quad (3.11)$$

where $$\Gamma_e(m) \equiv (2\pi)^{-3}2\pi\gamma^2\sum_{\mu}\int|\langle m|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle|^2$$

$$\times \delta(\Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\mu})d\vec{k} \ .$$

When $\Omega_{mm'}$ is less than $\frac{1}{2}[\Gamma_e(m) + \Gamma_e(m')]$ we can drop the dependence of the lifetime on the excited state and replace $\frac{1}{2}[\Gamma_e(m) + \Gamma_e(m')]$ by Γ_e independent of m. We observe that the Δ condition does not appear in the spontaneous emission term. The terms A_3 and A_4 give the ground-state contribution to the excited-state density matrix $\langle m|\tilde{\rho}|m'\rangle$. When we substitute the limiting form of f_3 and f_4 in Eqs. (3.6c) and (3.6d), we obtain

$$\begin{aligned}
-\gamma^2(A_3 + A_4) &= \gamma^2 t\pi \sum_{\vec{k},\vec{k}',\mu,\nu} \langle a_{i'}^{\dagger}(\vec{k}')a_i(\vec{k})\rangle \\
&\times \langle m|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle\langle\mu|\tilde{\rho}|\nu\rangle\langle\nu|\vec{\epsilon}^{\dagger}(\vec{k}')\cdot\vec{D}|m'\rangle \\
&\times \delta_+(\Omega_{k'} + \vec{k}'\cdot\vec{v} - \Omega_{m'\nu}) + \delta_-(\Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\mu}) \\
&\times \Delta_g(\Omega_{k'} - \Omega_k + \Omega_{m\mu} - \Omega_{m'\nu} + \vec{k}'\cdot\vec{v} - \vec{k}\cdot\vec{v}) \\
&\approx 2\gamma^2\pi t \sum_{\vec{k},\vec{k}',\mu,\nu} \langle a_i^{\dagger}(\vec{k}')a_i(\vec{k})\rangle \ \langle m|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle \\
&\times \langle\mu|\tilde{\rho}|\nu\rangle\langle\nu|\vec{\epsilon}_{i'}^{\dagger}(\vec{k}')\cdot\vec{D}|m'\rangle\,\delta(\Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\mu}) \\
&\times \Delta_g(\Omega_{k'} - \Omega_k + \Omega_{m\mu} - \Omega_{m'\nu}). \qquad (3.12)
\end{aligned}$$

As a result of the Δ_g conditions the imaginary, principal part integrals cancel. For convenience we drop the usually negligible difference between $\vec{k}\cdot\vec{v}$ and $\vec{k}'\cdot\vec{v}$. To render Eq. (3.12) more transparent, we consider the case of no modulation, which corresponds to setting $\vec{k} = \vec{k}'$ in Eq. (3.12)

$$\begin{aligned}
-\gamma^2(A_3 + A_4) &= t\Gamma_g \sum_{\mu\nu} \langle i'|\Pi|i\rangle\langle m|\vec{\epsilon}_i\cdot\vec{D}|\mu\rangle\langle\mu|\rho|\nu\rangle \\
&\times \langle\nu|\vec{\epsilon}_{i'}^{\dagger}\cdot\vec{D}|m'\rangle\,\Delta_g(\Omega_{m\mu} - \Omega_{m'\nu}), \qquad (3.13)
\end{aligned}$$

where the ground-state inverse lifetime is

$$\Gamma_g \equiv \gamma^2 \int n(k)\delta(\Omega_k - \vec{k}\cdot\vec{v} - \Omega_{m\mu})d\vec{k} \ ,$$

and where

$$\langle i'|\Pi|i\rangle \equiv \langle a_{i'}^{\dagger}(\vec{k})a_i(\vec{k})\rangle\,[n(k)]^{-1}$$

is the polarization matrix of classical optics[6] normalized to one. The number of photons in mode k is $n(k)$. Equation (3.13) is equivalent to the contribution of the ground state to the excited state in the secular approximation of Ref. 1. The inverse lifetime Γ_g is equivalent to T_p^{-1} of Cohen-Tannoudji. Combining Eqs. (3.5), (3.11), and (3.13), we obtain for the no-modulation problem

$$\begin{aligned}
\langle m|\tilde{\rho}(0)|m'\rangle &\approx t^{-1}[\langle m|\tilde{\rho}(t)|m'\rangle - \langle m|\tilde{\rho}(0)|m'\rangle] \\
&= -\Gamma_e\langle m|\tilde{\rho}|m'\rangle + \Gamma_g \sum_{\mu\nu}{}' \langle i'|\Pi|i\rangle\langle m|\vec{\epsilon}_i\cdot\vec{D}|\mu\rangle \\
&\times \langle\mu|\tilde{\rho}|\nu\rangle\langle\nu|\vec{\epsilon}_{i'}^{\dagger}\cdot\vec{D}|m'\rangle \ , \qquad (3.14)
\end{aligned}$$

where the prime on the sum indicates the sum over states is subject to the Δ_g condition. Equation (3.14) is the equation for ρ in the secular approximation of Cohen-Tannoudji.

When we repeat the above arguments for the ground-state matrix elements $\langle\mu|\tilde{\rho}|\nu\rangle$, we again find the Cohen-Tannoudji equation in the secular approximation with the single-interaction time τ_i proportional to the inverse linewidth of the radiation. Thus, we find two interaction times for the matter density matrix. The requirement that $\tau_\gamma \gg \tau_i$ for spontaneous emission is identical to the Wigner-Weisskopf requirement that $\omega_0 \gg \Gamma_l$. The induced absorption and emission interaction time τ_i is the inverse linewidth δ^{-1} of the radiation and the condition $\tau_i \ll \tau_\gamma$ becomes $\delta \gg \Gamma_g$.

We obtain the interaction time for τ_i for the radiation density matrix R in the same manner used to obtain the interaction times τ_i for ρ. We can write the full operator equations for R without resorting to matrix elements of the radiation operators. The result for R is

$$\begin{aligned}
\dot{\tilde{R}}(0) \approx t^{-1}[\tilde{R}(t) - \tilde{R}(0)] &= \gamma^2 \pi\pi \sum_{\mu,\nu,m,m'} \sum_{\vec{k},\vec{k}',i,i'} \int d\vec{x}\,d\vec{v}\,\{a_{i'}(\vec{k}')Ra_i^{\dagger}(\vec{k})\Delta_g(\Omega_{k'} - \Omega_k + \Omega_{\mu\nu})\langle\mu|\tilde{\rho}|\nu\rangle \\
&\times \langle\nu|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|m\rangle\langle m|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|\mu\rangle\,[\delta_+(\Omega_{k'} + \vec{k}'\cdot\vec{v} - \Omega_{m\mu}) + \delta_-(\Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\nu})] - \langle\mu|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|m\rangle \\
&\times \langle m|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|\gamma\rangle\langle\gamma|\tilde{\rho}|\mu\rangle\,\Delta_g(\Omega_{k'} - \Omega_k + \Omega_{\gamma\mu})\,[a_i^{\dagger}(\vec{k})a_{i'}(\vec{k}')R\delta_-(\Omega_{k'} + \vec{k}'\cdot\vec{v} - \Omega_{m\gamma}) + Ra_i^{\dagger}(\vec{k})a_{i'}(\vec{k}')\delta_+ \\
&\times (\Omega_k + \vec{k}\cdot\vec{v} - \Omega_{m\mu})] + a_i^{\dagger}(\vec{k})Ra_{i'}(\vec{k}')\langle\mu|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|m\rangle\langle m|\tilde{\rho}|m'\rangle\langle m'|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|\mu\rangle
\end{aligned}$$

$$\times \Delta_e(\Omega_k - \Omega_{k'} - \Omega_{mm'})[\delta_-(\Omega_{k'} + \vec{k}' \cdot \vec{v} - \Omega_{m'\mu}) + \delta_+(\Omega_k + \vec{k} \cdot \vec{v} - \Omega_{m\mu})]$$

$$- \langle \mu | \vec{\epsilon}_i^{\dagger}(\vec{k}) \cdot \vec{D} | m \rangle \langle m | \tilde{\rho} | m' \rangle \langle m' | \vec{\epsilon}_{i'}(\vec{k}') \cdot \vec{D} | \mu \rangle \Delta_e(\Omega_k - \Omega_{k'} - \Omega_{mm'})$$

$$\times [a_{i'}(\vec{k}') a_i^{\dagger}(\vec{k}) R \delta_+(\Omega_{k'} + \vec{k}' \cdot \vec{v} - \Omega_{m'\mu}) + R a_{i'}(\vec{k}') a_i^{\dagger}(\vec{k}) \delta(\Omega_k + \vec{k} \cdot \vec{v} - \Omega_{m\mu})]\} , \tag{3.15}$$

where the first four terms are the contribution from the atomic excited states. The matter density matrix is a function of the c.m. position and velocity. The interaction time τ_i for the R equation is the shortest time associated with the matter variables. When collisions are negligible, then $\tau_i = \omega_d^{-1}$, where ω_d is the Doppler frequency. When collisions are more important than the Doppler motion, then $\tau_i = \tau_c$, where τ_c is the collision frequency.

We have written our equations so as to include correlations between c.m. variables and interval degrees of freedom, i.e., $\langle \mu | \rho(\vec{x}, \vec{v}, t) | \nu \rangle$. Such correlations are important, for example, when collision cross sections depend strongly on velocity and the state of excitation of the atom. In lasers, the c.m.–internal-degrees-of-freedom correlations are responsible for hole burning. When the c.m.–internal-degrees-of-freedom correlations are unimportant, we can replace $\rho(\vec{x}, \vec{v}, t)$ by $\rho(t)\mathcal{F}(\vec{x}, \vec{v}, t)$, where $\mathcal{F}(\vec{x}, \vec{v}, t)$ is the c.m. distribution function, which is usually Maxwellian. Alternatively, when spatial dependence is important and the velocity dependence is Maxwellian, we can replace $\rho(\vec{x}, \vec{v}, t)$ by $\rho(\vec{x}, t)\mathcal{F}(\vec{v})$, where $\mathcal{F}(\vec{v})$ is the velocity distribution. When c.m.–internal-degrees-of-freedom correlations are negligible, we can perform the c.m. integrations over the known c.m. distribution function and reduce the number of independent variables that ρ depends upon to just the time variable.

We conclude this section with a few remarks concerning the rigorous derivation of Eqs. (2.18) and (2.19). The rigorous derivation extends the range of validity of Eqs. (2.18) and (2.19) to all times and justifies dispensing with the Δ conditions of this section. Rigorous methods of deriving kinetic equations[5,7–9] obtain expressions for the solution of the Liouville equation for long times, and then they obtain a differential equation which the solution satisfies to some order in the expansion parameter. Equations (2.18) and (2.19) were obtained when the diagram technique of Ref. 5 was used and took the $\gamma^2 t$ limit. The $\gamma^2 t$ limit is the limit that $\gamma^2 \to 0$ and $t \to \infty$ such that $\gamma^2 t$ is finite. That $t \to \infty$ limit allows us to evaluate time integrals such as Eq. (3.4) asymptotically, and the limit $\gamma^2 \to 0$ picks out the lowest-order diagram in γ^2 for each power of t. Only one novel point arises in the derivation, namely, the order of taking the $\gamma^2 \to 0$ and $t \to \infty$ limits is important. If the $\gamma^2 \to 0$ limit is taken before the $t \to \infty$ limit, then the Δ conditions are not required. If the limits are taken in the reverse order, then the Δ conditions must be imposed. We can express the $\gamma^2 t$ limit in a more transparent fashion by requiring that there exists a t such that $\tau_i \ll t \ll \tau_\gamma \sim \gamma^{-2}$; thus the $\gamma^2 t$ limit is equivalent to the limit $(\tau_i/\tau_\gamma) \to 0$. In Sec. IV, we commence our study of the consequences of our fundamental equations.

IV. EQUATION FOR THE DENSITY MATRIX OF THE GROUND STATES

When we examine Eq. (2.17) for the off-diagonal matrix elements connecting the ground and excited states, i.e., $\langle \mu | \rho | m \rangle$, we find the equations of motion are linear and homogeneous in matrix elements of the form $\langle \bar{\mu} | \rho | \bar{m} \rangle$. Consequently, if the matrix elements connecting the ground and excited states are zero initially, they remain zero. If they are nonzero initially, they decay in times that are of the order of the lifetime of the excited state. Therefore, we can take the matrix elements of the form $\langle \mu | \rho | m \rangle$ equal to zero, and then the matter density matrix ρ reduces to the sum $\rho = \rho_g + \rho_e$, where ρ_g has matrix elements between ground states only, and ρ_e has matrix elements between excited states only. The reduction of ρ is possible when the pumping light is thermal, i.e., noncoherent. If the pumping light were coherent, there would be matrix elements of the form $\langle \mu | \rho | m \rangle$. However, more importantly, our Eqs. (2.16) and (2.17) would no longer be valid because the interaction time which is proportional to the inverse linewidth would no longer be small compared with a relaxation time, and it would be necessary to include radiation-matter correlations and higher-order terms.

When we take the matrix elements of Eq. (2.17) between ground states, we obtain the following equation of motion for the ground-state density matrix:

$$\langle \mu | \dot{\rho}_g | \nu \rangle + i\Omega_{\mu\nu} \langle \mu | \rho_g | \nu \rangle = \gamma^2 \pi \sum_{m, m', \vec{k}, \vec{k}', i, i'} \langle a_i^{\dagger}(\vec{k}) a_{i'}(\vec{k}') \rangle [\langle \mu | \vec{\epsilon}_i^{\dagger}(\vec{k}) \cdot \vec{D} | m \rangle \langle m | \vec{\epsilon}_{i'}(\vec{k}') \cdot \vec{D} | \mu' \rangle$$

$$\times\langle\mu'|\rho_g|\nu\rangle\,\delta_-(\Omega_{k'}+\vec{k}'\cdot\vec{v}-\Omega_{m\mu'})+\langle\mu|\rho_g|\mu'\rangle\langle\mu'|\vec{\epsilon}_i^{\,\dagger}(\vec{k})\cdot\vec{D}|m\rangle\langle m|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|\nu\rangle\,\delta_+(\Omega_k+\vec{k}\cdot\vec{v}-\Omega_{m\nu})]$$

$$-2\langle a_{i'}(k')a_i^{\dagger}(k)\rangle\langle\mu|\vec{\epsilon}_i^{\,\dagger}(\vec{k})\cdot\vec{D}|m\rangle\langle m|\rho_e|m'\rangle\langle m'|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|\nu\rangle\,\delta(\Omega_{k'}+\vec{k}'\cdot\vec{v}-\Omega_{m'\nu}) \quad . \tag{4.1}$$

When the linewidth of the radiation δ is large compared with the level spacing of the excited and ground states ω_e and ω_g, respectively, we can replace the various arguments of the δ functions $\delta_\pm$ by the same argument, namely, $\Omega_k-\omega_0-\vec{k}\cdot\vec{v}$, where ω_0 is the unperturbed frequency difference between atomic excited and ground states. The assumption, $\delta\gg\omega_e,\omega_g$, is not required for the existence of our kinetic Eqs. (2.16) and (2.17), but the assumption allows us to appreciably simplify Eq. (4.1):

$$\langle\mu|\dot{\rho}_g|\nu\rangle+i\Omega_{\mu\nu}\langle\mu|\rho_g|\nu\rangle+i\langle\mu|[\xi^I,\rho_g]|\nu\rangle$$

$$=-\langle\mu|[\xi^R,\rho_g]_+|\nu\rangle$$

$$+\sum_{m,m'}\mathfrak{L}_{\mu\nu}^{\,mm'}\langle m|\rho_e|m'\rangle \quad , \tag{4.2}$$

where $\xi\equiv\xi^R+i\xi^I$

$$=\gamma^2\sum_{\vec{k},\vec{k}',i,i'}\vec{\epsilon}_i^{\,\dagger}(\vec{k})\cdot\vec{D}P_e\vec{D}\cdot\vec{\epsilon}_{i'}(\vec{k}')$$

$$\times\langle a_i^{\dagger}(\vec{k})a_{i'}(\vec{k}')\rangle\,\pi\delta_+(\Omega_k-\omega_0-\vec{k}\cdot\vec{v}) \quad ,$$

and where the + subscript denotes the anticommutator. The superscripts R and I denote the real and imaginary parts, respectively. The operator $\mathfrak{L}_{\mu\nu}^{\,mm'}$ is

$$\mathfrak{L}_{\mu\nu}^{\,mm'}\equiv\Gamma_e\delta_{m-\mu,m'-\nu}\,c_{11}(F,m,m-\mu,\mu)$$

$$\times c_{11}(F,m',m'-\nu,\nu) \quad , \tag{4.3}$$

where the c_{11} are the appropriate Clebsch-Gordan coefficients for the problem . For definiteness we use the hyperfine coupling coefficients.

The atomic operator ξ is the trace over radiation variables of the product of the following two operators:

$$\xi\equiv\mathrm{Tr}_{k,i}K\Pi \quad , \tag{4.4}$$

where $\langle\vec{k}i\,|\,\Pi\,|i'\vec{k}\rangle\equiv\langle a_i^{\dagger}(\vec{k})a_{i'}(\vec{k}')\rangle$, (4.5)

and where

$$\langle\vec{k}'i'|K|i\vec{k}\rangle\equiv\gamma^2\Gamma_k^*(X)\vec{\epsilon}_i^{\,\dagger}(\vec{k})\cdot\vec{D}P_e\vec{D}\cdot\vec{\epsilon}_{i'}(\vec{k}')$$

$$\times\Gamma_{k'}(X)\pi\delta_+(\Omega_{k'}-\omega_0+\vec{k}'\cdot\vec{v})$$

$$=\int_0^\infty\mu_i^*(\vec{k},0)P_e\mu_{i'}(\vec{k}',-\tau)e^{-i\Omega_{k'}\tau}\,d\tau \quad . \tag{4.6}$$

The component of the atomic dipole moment in the direction of $\vec{\epsilon}_i^{\,\dagger}(\vec{k})$ is $\mu_i^*(k)\equiv\gamma\Gamma_k(X)\vec{\epsilon}_i^{\,\dagger}(\vec{k})\cdot\vec{D}$. The equality in Eq. (4.6) is a consequence of the integral representation of the δ_+ function. The matrix elements of Π are the generalized second moments of the radiation density matrix R. In Sec. V, we show that the coupled equations for ρ_g and R reduce without approximation to coupled equations for ρ_g and Π. For $\vec{k}=\vec{k}'$, the generalized polarization matrix $\langle\vec{k}i\,|\,\Pi\,|i'\vec{k}\rangle$ reduces to $n(k)\langle i\,|\,\Pi\,|i'\rangle$, where $\langle i\,|\,\Pi\,|\times i'\rangle$ is the polarization matrix of classical optics. The matrix elements $\langle\vec{k}i\,|\,\Pi\,|i'\vec{k}'\rangle$ depend on space and time through the original dependence of R on space and time.

The generalized susceptibility K is an operator in both the radiation and matter variables. The matrix elements $\langle\vec{k}'i'\,|K|i\vec{k}\rangle$ are the Laplace transforms of the dipole-dipole operator correlations. The matter operator ξ is the average of the generalized susceptibility K over the radiation density matrix.

Cohen-Tannoudji[1] showed that, for the case of an external beam without modulation, ρ_e in Eq. (4.2) could be simply expressed in terms of ρ_g because ρ_e followed ρ_g adiabatically as a consequence of the condition $(\Gamma T_p)\gg1$. This condition in our variables is $\Gamma_e\gg\Gamma_g$. We have already used this condition to eliminate radiation-matter correlations. The same condition is sufficient to eliminate ρ_e in our case of a generalized polarization matrix with modulation, and the derivation proceeds in an identical manner. The result of the adiabatic elimination of ρ_e is the following linear equation for ρ_g:

$$\dot{\rho}_g+i[h,\rho_g]+i[\xi^I,\rho_g]=-[\xi^R,\rho_g]_+-\mathfrak{G}\rho_g, \tag{4.7}$$

where $\langle\mu|\mathfrak{G}\rho_g|\mu'\rangle=\Gamma_e\Gamma_g\sum_{\mu'',\mu''',\vec{k}\vec{k}'}$

$$\times\frac{B_{\mu''\mu'''}^{\mu\mu'}\langle\mu''|\rho_g|\mu'''\rangle}{\Gamma_e+i[(\mu-\mu')\omega_e-(\mu''-\mu''')\omega_g]+i\Omega_{kk'}} \tag{4.8}$$

and where

$$\Gamma_e\Gamma_g B_{\mu''\mu'''}^{\mu\mu'}\equiv(2\pi\gamma^2)^2\sum_{m,m',i,i'}$$

$$\times\delta_{m-\mu,m'-\mu'}\langle\vec{k}'i'\,|\,\Pi\,|i\vec{k}\rangle\langle m\,|\vec{\epsilon}(\vec{k})\cdot\vec{D}\,|\mu''\rangle$$

$$\times\langle\mu'''\,|\vec{\epsilon}_{i'}{}^{\dagger}(\vec{k}')\cdot\vec{D}\,|m'\rangle\, c_{11}(F,m,m-\mu,\mu)$$

$$\times c_{11}(F,m',m'-\mu',\mu')\ . \qquad (4.9)$$

Equation (4.7) follows directly from the stationary solution of Eq. (2.17) for ρ_e:

$$\langle m\,|\rho_e\,|m'\rangle = \frac{C_{mm'}{}^{\mu''\mu'''}\langle\mu''\,|\rho_g\,|\mu'''\rangle\,\delta(\Omega_k-\omega_0-\vec{k}\cdot\vec{v})}{\Gamma_e+i(\Omega_{mm'}-\Omega_{\mu''\mu'''})+i\Omega_{kk'}}\ , \qquad (4.10)$$

where $C_{mm'}{}^{\mu''\mu'''}\equiv 2\pi\gamma^2\langle\vec{k}'i'\,|\,\Pi\,|i\vec{k}\rangle$

$$\times\langle m\,|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}\,|\mu''\rangle\langle\mu'''\,|\vec{\epsilon}_{i'}{}^{\dagger}(\vec{k}')\cdot\vec{D}\,|m'\rangle\ ,$$

and where we use Eq. (4.3).

Our Eq. (5.7) reduces to the fundamental equation (III D1) of Ref. 1, if we (i) assume that $\rho_g(\vec{x}\vec{v}t)$ is a product $\rho_g(\vec{x},t)\mathfrak{F}(\vec{v})$, where $\mathfrak{F}(\vec{v})$ is Maxwellian and integrate over $\vec{v}$; (ii) if we set $\langle\vec{k}'i'\,|\,\Pi\,|i\vec{k}\rangle = \delta_{\vec{k}\vec{k}'}\langle n(k)\rangle\langle i'\,|\,\Pi\,|i\rangle$; and (iii) if we take Π to be Π_p the polarization matrix of the external pumping beam. With the above approximations Eq. (4.7) becomes

$$\dot{\rho}_g+i[h,\rho_g]+i\Delta E'[A,\rho_g] = -(\tfrac{1}{2}T_p^{-1})[A,\rho_g]_+ + \mathfrak{C}\rho_g\ , \qquad (4.11)$$

where $A\equiv\sum_{i,\,i'}\langle i\,|\,\Pi_p\,|i'\rangle\langle i'\,|\,\mathfrak{a}\,|i\rangle\ , \qquad (4.12)$

$$\langle\mu i'\,|\mathfrak{a}\,|i\nu\rangle \equiv\sum\nolimits_m\langle\mu\,|\vec{\epsilon}_i{}^{\dagger}(\vec{k})\cdot\vec{D}\,|m\rangle\langle m\,|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}\,|\nu\rangle\ ,$$

$$\tfrac{1}{2}T_p^{-1}+i\Delta E' \equiv(2\pi)^{-3}\gamma^2(\tfrac{1}{2}\beta m)^{3/2}$$

$$\times\int d\vec{k}\,d\vec{v}\,\exp(-\tfrac{1}{2}\beta v^2)\langle n(k)\rangle_p\,[\pi\delta(\Omega_k-\omega_0-\vec{k}\cdot\vec{v}) +i\mathcal{P}(\Omega_k-\Omega_0-k\cdot v)]\ , \qquad (4.13)$$

where β is $(k_BT)^{-1}$ with k_B the Boltzmann constant and T the temperature. Equation (4.11) is Eq. (III D. 1) of Ref. 1. Our equation for ρ_g depends on R only through the second moments of R, namely, Π. In Sec. V, we obtain the equations of motion for Π.

V. EQUATION OF MOTION FOR Π

We have discussed the equation of motion for the radiation density matrix R without specifying the rate of change of R due to the pumping beam $(\delta R/\delta t)_{\text{pump}}$. The easiest way to specify the pumping beam while maintaining R as a density matrix and maintaining the commutation relations is to require R to satisfy the following equation in the absence of the radiation-matter interaction:

$$(\dot{R}-\dot{R}_p)+i[H_f,(R-R_p)]+\vec{n}\cdot\nabla\,(R-R_p) +\nu(R-R_p)=0, \qquad (5.1)$$

where $\vec{n}$ is the unit vector in the direction of propagation with magnitude 1 in our units but with magnitude c in ordinary units. The relaxation time ν depends on geometry, but it is of order L^{-1} where L is the dimension of the cavity and of magnitude cL^{-1} in ordinary units. The spatial dependence of R results ultimately from the spatial dependence of ρ_g. The density matrix of the pumping beam R_p is Hermitian, positive definite, and has trace unity. Equation (5.1) states that in absence of interaction with matter R approaches the radiation density matrix R_p of the pumping beam in ν^{-1} sec.

Equation (2.16) for R with $(\delta R/\delta t)_{\text{pump}}$ is given by Eq. (5.1) and assuming $\delta\gg\omega_e,\omega_g$ is

$$(\dot{R}-\dot{R}_p)+i[H_f,(R-R_p)]+\vec{n}\cdot\nabla(R-R_p)+\nu(R-R_p) = \sum_{\vec{k},\vec{k}'}-i[a_i{}^{\dagger}(\vec{k})a_{i'}(\vec{k}'),R]\chi_{i'i}{}^{I}(\vec{k}',\vec{k})$$

$$-([a_i{}^{\dagger}(\vec{k})a_{i'}(\vec{k}'),R]_+-2a_{i'}(\vec{k}')Ra_i{}^{\dagger}(\vec{k}))$$

$$\times\chi_{i'i}{}^{R}(\vec{k}',\vec{k})+2^{-1}[a_{i'}(\vec{k}')a_i{}^{\dagger}(\vec{k}),R]$$

$$\times S_{ii'}{}^{I}(\vec{k},\vec{k}')-2^{-1}([a_{i'}(\vec{k}')a_i{}^{\dagger}(\vec{k}),R]_+$$

$$-2a_i{}^{\dagger}(\vec{k})Ra_{i'}(\vec{k}'))\,S_{ii'}{}^{R}(\vec{k}\vec{k}')\ , \qquad (5.2)$$

where

$$S_{ii'}(\vec{k},\vec{k}')\equiv 2\gamma^2\mathfrak{N}\pi\sum_{\mu,m,m'}\int d\vec{v}\,\langle m'\,|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}\,|\mu\rangle$$

$$\times\langle\mu\,|\epsilon_i{}^{\dagger}(\vec{k})\cdot\vec{D}\,|m\rangle\,\langle m\,|\rho_e\,|m'\rangle\,\delta_+(\Omega_k-\omega_0+\vec{k}\cdot\vec{v}). \qquad (5.3)$$

is the source of radiation from excited atoms.

The operator χ is the electric susceptibility operator, whose definition is

$$\chi \equiv \mathfrak{N}\mathrm{Tr}_{\mathrm{matter}} K\rho_g, \tag{5.4}$$

where K is the same operator that appears in the definition of ξ and whose definition is given by Eq. (4.6). The matrix elements of χ are

$$\chi_{i'i}(\vec{k}',\vec{k}) \equiv \langle \vec{k}'i'|\chi|i\vec{k}\rangle = \gamma^2 \mathfrak{N}\pi\sum_{\mu} \times \int d\vec{v}\langle\mu|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}P_e\vec{D}\cdot\vec{\epsilon}_i(\vec{k}')\rho_g|\mu\rangle \times \delta_+(\Omega_K - \omega_0 + \vec{k}\cdot\vec{v}). \tag{5.5}$$

An alternative useful form of χ is

$$\langle \vec{k}'i'|\chi|i\vec{k}\rangle = \int_0^{\infty} \exp(-i\Omega_{\vec{k}'}\tau) \times [\mathrm{Tr}_{\mathrm{matter}}\mu_i^*(\vec{k},0)P_e\mu_{i'}(\vec{k}',-\tau)\rho_g]d\tau, \tag{5.6}$$

where the definition of $\mu_i(\vec{k},0)$ appears in Eq. (4.6). If the radiation were purely external and ρ_g were the equilibrium distribution of the matter, then Eq. (5.5) would be an example of Kubo's[10] fluctuation-dissipation theorem relating the susceptibility to equilibrium fluctuations. We can interpret both ξ and χ as generalized susceptibilities which are related to Laplace transforms of correlation functions; these susceptibilities may be time-dependent if Π and ρ_g are time-dependent.

We obtain the equation of motion for the polarization operator Π with matrix elements $\langle \vec{k}'j'|\Pi|j\vec{k}\rangle$ by multiplying Eq. (5.2) by $a_{j'}^{\dagger}(\vec{k}')a_j(\vec{k})$ and tracing over radiation variables. The resultant equation of motion for the matrix Π is

$$(\mathring{\Pi} - \mathring{\Pi}_p) + \vec{n}\cdot\nabla(\Pi - \Pi_p) + \nu(\Pi - \Pi_p) = -i[\Pi,\chi^I] - [\Pi,\chi^R]_+ + S^R. \tag{5.7}$$

In Eq. (5.7), the contribution from the commutator vanishes, and the imaginary part of the spontaneous-emission term vanishes, i.e., S^I vanishes, when we neglect $\langle a^{\dagger}(\vec{k})a(\vec{k})\rangle$ compared with 1.

It is worthwhile to see how the order of operators in Eq. (5.2) is responsible for spontaneous emission and also to illustrate how Eq. (5.7) follows from Eq. (5.2). The trace of the product $a_{j'}^{\dagger}(\vec{k}')a_j(\vec{k})$ with the last term of Eq. (5.2) is

$$\begin{aligned} &2^{-1}\sum S_{ii'}^R(\vec{k}\vec{k}')\,\mathrm{Tr}[a_{j'}^{\dagger}(\vec{k}')a_j(\vec{k})a_{i'}(\vec{k}')a_i^{\dagger}(\vec{k}) \\ &+ a_{i'}(\vec{k}')a_i^{\dagger}(\vec{k})a_{j'}^{\dagger}(\vec{k}')a_j(\vec{k}) - 2a_{i'}(\vec{k}')a_{j'}^{\dagger}(\vec{k}') \\ &\times a_j(\vec{k})a_i^{\dagger}(\vec{k})R] = 2^{-1}\sum S_{ii'}^R(\vec{k},\vec{k}')[\langle a_j(\vec{k})a_i^{\dagger}(\vec{k})\rangle \\ &\times \delta_{i',j'}\delta_{\vec{k}',\vec{k}'} + \langle a_{i'}(\vec{k}')a_{j'}^{\dagger}(\vec{k}')\rangle\delta_{ij}\delta_{\vec{k},\vec{k}}] \\ &\approx 2^{-1}\sum S_{ii'}^R(\vec{k},\vec{k}')[\delta_{i',j'}\delta_{\vec{k},\vec{k}'}\delta_{j,i}\delta_{\vec{k},\vec{k}} \\ &+ \delta_{ij}\delta_{\vec{k},\vec{k}}\delta_{i',j'}\delta_{k',k'}] = S_{ii'}^R(\vec{k},\vec{k}'). \end{aligned} \tag{5.8}$$

The approximate equality in Eq. (5.8) results from neglecting $\langle a^{\dagger}(\vec{k})a(\vec{k})\rangle$ with respect to 1. Consequently, we see the order of the noncommuting operations, $a^{\dagger}$ and a, is responsible for emission consisting of two pieces, induced emission and spontaneous emission. In optical pumping we can neglect induced emission relative to spontaneous emission because the number of photons per mode is much less than one. Equation (5.7) depends on ρ_g through χ and on ρ_e through S^R. We use Eq. (4.10) to eliminate ρ_e from S^R and thus we express S^R as a linear operator:

$$\langle i\vec{k}|L\Pi|i'\vec{k}'\rangle \equiv \langle \vec{k}i|S^R|i'\vec{k}'\rangle = 2\gamma^2\pi\mathfrak{N}\sum\langle\mu|\vec{\epsilon}_{i'}^{\dagger}(\vec{k}')\cdot\vec{D}|m\rangle\langle m|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu'\rangle\langle\mu'|\rho_g|\mu''\rangle\langle\mu''|\vec{\epsilon}_{i'}^{\dagger}(\vec{k}')\cdot\vec{D}|m'\rangle \times\langle m'|\vec{\epsilon}_i(\vec{k})\cdot\vec{D}|\mu\rangle\delta_+(\Omega_k - \omega_0 + \vec{k}\cdot\vec{v})(\Gamma + i\Omega_{mm'} - i\Omega_{\mu'\mu''} + i\Omega_{k,k'})^{-1}\langle\vec{k}i|\Pi|i'\vec{k}'\rangle. \tag{5.9}$$

When we substitute Eq. (5.9) in Eq. (5.7), we obtain

$$(\mathring{\Pi} - \mathring{\Pi}_p) + \vec{n}\cdot\nabla(\Pi - \Pi_p) + \nu(\Pi - \Pi_p) = -i[\Pi,\chi^I] - [\Pi,\chi^R]_+ + L\Pi. \tag{5.10}$$

Equation (5.10) together with Eq. (4.7),

$$\dot{\rho}_g + i[h,\rho_g] + i[\xi^I,\rho_g] = -[\xi^R,\rho_g]_+ + \mathfrak{G}\rho_g, \tag{4.7}$$

form a closed complete nonlinear set of equations for ρ_g and Π.

The surprising and important result is that Eq. (5.10) for Π depends on no higher moment of R than the second. If the equation for Π depended on higher moments, for example, the fourth mo-

ment $\langle a^\dagger a a^\dagger a\rangle$, then we would have been forced to find the full R and the equations for Π and ρ_g would not have been closed. The reason that the equation of motion for Π depends on no other moments of R than the second is that we assume radiation and matter are uncorrelated, i.e., $F_1 \approx R\rho$. If we did not assume that F_1 was a product $R\rho$, then the equation for Π would have depended on all the moments of R. The assumption that justifies the product ansatz $\Gamma_e \gg \Gamma_g$ is that induced emission is negligible compared with spontaneous emission. This is just the inverse of the requirement for laser action.

In Sec. IV, we showed that the linearization of Eq. (4.7) by taking Π to be Π_p leads to the fundamental equations of Cohen-Tannoudji for the matter density matrix. When we (i) linearized Eq. (5.10) by taking ρ_g as given, (ii) set $L\Pi$ equal to zero, (iii) set $(\dot{\Pi} - \dot{\Pi}_p)$ equal to zero, (iv) replace Π by Π_p on the right-hand side of Eq. (5.10), and (v) average over space, we obtain

$$\Pi(t) - \Pi_p = -\mathfrak{N}(2T_p)^{-1}[B(t), \Pi_p]_+ - i\mathfrak{N}\Delta E'[B(t), \Pi_p]\ , \qquad (5.11)$$

where $B(t) \equiv \mathrm{Tr}\rho_g \mathfrak{A}$, where $\mathfrak{A}$, T_p^{-1}, and Δ' are defined in Eqs. (4.12) and (4.13). The Eq. (5.11) is Eq. (III.5) of Ref. 2 averaged over space. Consequently, the appropriate linearizations and reductions of our nonlinear equations yield the present theories of optical pumping. In Sec. VI, we show that, even in the linearized theory for Π, off-diagonal matrix elements $\langle \vec{k}i|\,\Pi\,|i'\vec{k}'\rangle$ contain information not contained in present linear theories which treat radiation as off-diagonal only in the polarization variables.

VI. LIGHT MODULATION AND THE BELL-BLOOM EXPERIMENT

We now illustrate the microscopic role played by modulation in the polarization matrix by providing a nonphenomenological explanation of the Bell-Bloom[3] experiment. These authors modulated the pumping beam at frequencies close to the Larmor frequency and observed a spin polarization induced by the modulated light. Their experiment was the first time an rf resonance effect was produced by means that did not involve variation of a field directly coupling the rf separated energy levels. The Bell-Bloom experiment consists of a static field in the z direction and a circularly polarized optical beam traveling in the x direction. The circularly polarized beam in the x direction is modulated at a frequency ω which is approximately equal to the ground-state Zeeman frequency ω_g. Bell-Bloom gave a phenomenological explanation of their experiment by adding a modulation term to the transverse relaxation time T_2 and to the pumping term in a Bloch equation for the spin polarization. We find a different explanation by solving the equation for ρ_g to first order in γ^2. We also show that the Bell-Bloom experiment like most linear phenomena in optical pumping can be explained by solving the equations of motion for Π, directly.

For definiteness, we assume our atom has two Zeeman levels in the ground state, which we label + and −, where the plus represents $\mu = (\frac{1}{2})$ and the minus represents $\mu = -(\frac{1}{2})$. We first solve Eq. (4.7) to lowest order in γ^2 by replacing Π by Π_p. The polarization matrix of the pumping beam consists of modulated and unmodulated parts as follows:

$$\langle \vec{k}i\,|\,\Pi_p\,|i'\vec{k}'\rangle = \delta_{\vec{k},\vec{k}'}\langle n(k)\rangle\langle i\,|\,\Pi_p\,|i'\rangle + \delta_{\vec{k}',\vec{k}+\vec{\kappa}} \times \langle \vec{k}i\,|\,\Pi_p(\omega)\,|i'\vec{k}+\vec{\kappa}\rangle\ \exp(-i\omega t), \qquad (6.1)$$

where $\omega = \kappa$ is the modulation frequency and the wave number of the modulation. We assume the modulated beam has the same polarization as the unmodulated beam. When we substitute Eq. (6.1) in Eq. (4.7) for ρ_g we obtain the following equation for $\langle + |\rho_g| - \rangle$:

$$\langle + |\dot{\rho}_g| - \rangle + i(\omega_g + \epsilon)\langle + |\rho_g| - \rangle + T_2^{-1}\langle + |\rho_g| - \rangle = -i\langle + |[\xi^I(\omega), \rho_g]\,| - \rangle - \langle + |[\xi^R(\omega), \rho_g]_+\,| - \rangle + \langle + |\mathfrak{B}(\omega)\rho_g| - \rangle . \qquad (6.2)$$

The terms on the left-hand side of Eq. (6.2) arise from the unmodulated part of Π_p, while the terms on the right-hand side are linear and homogeneous in the modulated part of Π_p. The left-hand side of Eq. (6.2) is linear and homogeneous in $\langle + |\rho_g| - \rangle$ because $\omega_g \gg \Gamma_g$. Unmodulated terms connecting off-diagonal and diagonal matrix elements ρ_g are of order (Γ_g/ω_g) and thus are negligible. The inequality $\omega_g \gg \Gamma_g$ is the secular approximation of Cohen-Tannoudji. In the absence of modulation the right-hand side of Eq. (6.2) vanishes and the off-diagonal matrix elements of ρ_g, which are proportional to the spin polarization, decay to zero with time constant T_2.

The expression for ϵ and T_2 which come from the unmodulated part of Π_p are identical to Eq. (III D. 9a) and (III D. 9b) of Ref. 1, which are

$$\epsilon \equiv \Delta E_g[\langle + |A| + \rangle - \langle - |A| - \rangle] + \Gamma_g B_{+-}^{+-}\Gamma_e \times (\omega_e - \omega_g)[\Gamma_e^2 + (\omega_e - \omega_g)^2]^{-1}, \qquad (6.3a)$$

$$T_2^{-1} \equiv \Gamma_g[\,2^{-1}(\langle +|A|+\rangle + \langle -|A|-\rangle) - B_{+-}^{+-}\Gamma_e^{2}[\Gamma_e^{2} + (\omega_e - \omega_g)^2]^{-1}, \quad (6.3b)$$

where ω_e and ω_g are the energy-level separations of ground and excited states, respectively. The A and B coefficients are defined in Sec. V and are identical to those of Ref. 1. When we substitute the definition of ξ [Eq. (6.2)] and the definition of $\mathfrak{G}$ [Eq. (4.8)] in Eq. (6.2), we obtain

$$\langle +|\dot{\rho}_g|-\rangle + [T_2^{-1} + i(\omega_g + \epsilon)]\langle +|\rho_g|-\rangle = \langle +|\rho|+\rangle[\mathfrak{G}_{++}^{+-}(\omega) - \langle +|\xi^*(\omega)|-\rangle] + \langle -|\rho|-\rangle[\mathfrak{G}_{--}^{+-}(\omega) - \langle +|\xi(\omega)|-\rangle], \quad (6.4)$$

where

$$\langle +|\xi(\omega)|-\rangle = \gamma^2 \sum_{\vec{k},m,i,i'} \langle +|\vec{\epsilon}^{\dagger}(\vec{k})\cdot\vec{D}|m\rangle \times \langle m|\vec{\epsilon}_{i'}(\vec{k}')\cdot\vec{D}|-\rangle \langle \vec{k}+\vec{k}i'|\Pi_p(\omega)|i\vec{k}\rangle \times \exp(-i\omega t)\int d\vec{v}\,\delta_+(\Omega_k - \omega_0 + \vec{k}\cdot\vec{v}), \quad (6.5)$$

and where

$$\mathfrak{G}_{++}^{+-}(\omega) \equiv \Gamma_e\Gamma_g B_{++}^{+-}[\Gamma_e + i(\omega_e + \omega)]^{-1}. \quad (6.6)$$

The definitions of B_{++}^{+-} and B_{--}^{+-} appear in Eq. (4.9). The result of modulating the beam is to replace $\langle \vec{k}+\vec{k}i'|\Pi_p(\omega)|i\vec{k}\rangle$ by $d\langle \vec{k}i'|\Pi_p|i\vec{k}\rangle$, where d is the depth of the modulation. When we substitute the expression $d\langle \vec{k}i'|\Pi_p|i\vec{k}\rangle$ in Eq. (6.5), we obtain

$$\langle +|\xi(\omega)|-\rangle = d[(\tfrac{1}{2}\Gamma_g) + i\Delta E_g] \sum_{m,i,i'} \times \langle +|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|m\rangle\langle m|\vec{\epsilon}_{i'}(\vec{k})\cdot\vec{D}|-\rangle, = d[(\tfrac{1}{2}\Gamma_g) + i\Delta E_g]\langle +|A|-\rangle \exp(-i\omega t). \quad (6.7)$$

In the steady state $\langle +|\rho|-\rangle$ and $\langle -|\rho|-\rangle$ are constants which for convenience we take to be $\frac{1}{2}$. The solution of Eq. (6.4) is

$$\langle +|\rho_g(t)|-\rangle = \langle +|\rho_g(\omega)|-\rangle \exp(-i\omega t), \quad \langle +|\rho_g(\omega)|-\rangle = C[T_2^{-1} + i(\omega_g - \omega + \epsilon)]^{-1}, \quad (6.8)$$

where

$$C \equiv 2^{-1}\Gamma_e\Gamma_g(B_{++}^{+-} + B_{--}^{+-}) - \langle +|\xi^R(\omega)|-\rangle = -2^{-1}\Gamma_g d \sum_{m,i,i'} \langle i'|\Pi_p|i\rangle \{\langle +|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|m\rangle \times \langle m|\vec{\epsilon}_{i'}(\vec{k})\cdot\vec{D}|-\rangle - \Gamma_e[\Gamma_e + i(\omega+\omega_e)]^{-1}c_{11} \times (m, m-\tfrac{1}{2}, \tfrac{1}{2})c_{11}(m-1, m-\tfrac{1}{2}, -\tfrac{1}{2})(\langle m|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|\tfrac{1}{2}\rangle \times \langle \tfrac{1}{2}|\vec{\epsilon}_{i'}(\vec{k})\cdot\vec{D}|m-1\rangle + \langle m|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|-\tfrac{1}{2}\rangle \times \langle -\tfrac{1}{2}|\vec{\epsilon}_{i'}(\vec{k})\cdot\vec{D}|m-1\rangle)\}. \quad (6.9)$$

We make the expression for the constant C more transparent by considering the special case where the excited states m take on only the two values $m = \pm(\frac{1}{2})$. The result for C when $m = \pm(\frac{1}{2})$ is

$$C = -2^{-1}\Gamma_g d \sum_{i,i'} \langle i'|\Pi_p|i\rangle [\langle \tfrac{1}{2}|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|1/2\rangle\langle 1/2|\vec{\epsilon}_{i'}(\vec{k})\cdot\vec{D}|-\tfrac{1}{2}\rangle + \langle 1/2|\vec{\epsilon}_i^{\dagger}(\vec{k})\cdot\vec{D}|-\tfrac{1}{2}\rangle\langle -\tfrac{1}{2}|\vec{\epsilon}_{i'}(\vec{k})\cdot\vec{D}|-\tfrac{1}{2}\rangle] \times [1 - \Gamma_e\{\Gamma_e + i(\omega+\omega_e)\}^{-1}]c_{11}(\tfrac{1}{2}, 0, \tfrac{1}{2})\,c_{11}(-\tfrac{1}{2}, 0, -\tfrac{1}{2}). \quad (6.10)$$

The general expression for the constant C indicates that as a result of the optical modulation there are two contributions to the spin modulation. The first contribution to $\langle +|\rho_g|-\rangle$ comes from $\langle +|\xi|-\rangle$ during the process of optical absorption. The second contribution which is proportional to $(B_{++}^{+-} + B_{--}^{+-})$ arises as a result of optical absorption followed by emission and in many cases tends to cancel the spin polarization created by the direct absorption. The second contribution is smaller than the first contribution and is negligible compared with the direct absorption if ω_e or ω is much greater than Γ_e. The spin-polarization term produced by absorption alone, the $\langle +|\xi^R|-\rangle$ term, behaves as though the atom absorbs the "modulation photon" directly or, more precisely, the correlation between optical photons transfers the coherence of the optical modulator at frequency ω directly to the atom. This process is very similar to the way in which polarization correlations $\langle a_i^{\dagger}(k)a_{i'}(k)\rangle$

are transferred to the atom on absorption.

It is wortnwhile to look at the Bell-Bloom experiment from the point of view of the polarization matrix Π. To zeroth order ρ_g is diagonal and Π is given by the external pump polarization matrix Π_p. Earlier in this section we computed ρ_g to first order in γ^2. We now calculate Π to first order in γ^2. Equation (5.10) to first order in γ^2 is

$$\dot{\delta\Pi} + \nu\delta\Pi = -i[\Pi_p, \chi^I] - [\Pi_p, \chi^R]_+ + S \ , \qquad (6.11)$$

where $\delta\Pi = \Pi - \Pi_p$. The density matrix Π_p is given by Eq. (6.1). We find $\delta\Pi(\omega)$ by setting the coefficient of $\exp(-i\omega t)$ in Eq. (6.11) equal to zero, which yields

$$(i\omega+\nu)\langle\vec{k}i|\,\delta\Pi(\omega)\,|i'\vec{k}+\vec{\kappa}\rangle = \sum_{\vec{k},\bar{i}} \{(-i)[\langle\vec{k}i|\,\Pi_p\,|\bar{i}\vec{k}\rangle\langle\vec{k}\bar{i}\,|\chi^I|\,i'\vec{k}+\vec{\kappa}\rangle - \langle\vec{k}i|\,\chi^I\,|\bar{i}\vec{k}\rangle\langle\vec{k}|\,\Pi_p\,|i'\vec{k}+\vec{\kappa}\rangle]$$

$$-\langle\vec{k}i|\,\Pi_p\,|\bar{i}\vec{k}\rangle\langle\vec{k}\bar{i}\,|\chi^R|\,i'\vec{k}+\vec{\kappa}\rangle - \langle\vec{k}i|\,\chi^R\,|\bar{i}\vec{k}$$

$$\times\langle\vec{k}\bar{i}\,|\,\Pi_p\,|\,i'k+\kappa\rangle\}_\omega + \langle\vec{k}i|\,S(\omega)\,|\,i'\vec{k}+\vec{\kappa}\rangle \ , \qquad (6.12)$$

where $\langle\vec{k}i|\,S(\omega)\,|\,i'\vec{k}+\vec{\kappa}\rangle \equiv 2\pi\mathfrak{N}\gamma^2 \sum_{\mu,m,m'} \int d\vec{v}\,\delta(\Omega_k - \omega_0 + \vec{k}\cdot\vec{v})$

$$\times\langle\mu|\,\vec{\epsilon}_{i'}{}^{\dagger}(\vec{k}+\vec{\kappa})\cdot\vec{D}\,|m\rangle\langle m|\,\rho_e(\omega)\,|m'\rangle\langle m'|\,\vec{\epsilon}_i(\vec{k})\cdot\vec{D}\,|\mu\rangle \ , \qquad (6.13)$$

and where $\langle m|\,\rho_e(\omega)\,|m'\rangle = \sum_{\nu,\bar{k}} \langle m|\,\vec{\epsilon}_j(\vec{k})\cdot\vec{D}\,|\nu\rangle\langle\nu|\,\rho_g\,|\nu\rangle\langle\nu|\,\vec{\epsilon}_{j'}(\vec{k}')\cdot\vec{D}\,|m'\rangle$

$$\times\langle\vec{k}j|\,\Pi_p(\omega)\,|j'\vec{k}+\vec{\kappa}\rangle\,[\Gamma_e + i(\Omega_{mm'}+\omega)]^{-1} \ . \qquad (6.14)$$

The subscript ω denotes the Fourier transform of the square bracket with respect to time. Since χ is proportional to $\gamma^2\rho_g$, we must take only the zeroth order in γ^2 of ρ_g, which means that the ρ_g in χ in Eq. (6.12) is diagonal. Equation (6.12) is a complete solution for the modulated part of the optical radiation because $\Pi_p(\omega)$ and ρ_g are given. The "off-diagonality" in wave number of $\delta\Pi(\omega)$ is due to correlations between optical photons differing by wave number κ, $\langle a_i{}^{\dagger}(\vec{k})a_i(\vec{k}+\kappa)\rangle$, in exactly the same way as "off-diagonality" in polarization, $\langle a_i{}^{\dagger}(\vec{k})a_j(\vec{k})\rangle$ is due to correlations between photons of the same wave number but different polarizations or spin states.

We can simplify Eq. (6.12) for $\delta\Pi(\omega)$ by taking the representation where the polarization state i is a right circular polarized photon which we denote by $i=+$. The expression for $\delta\Pi(\omega)$ in this spin representation is

$$\langle\vec{k}+|\,\delta\Pi(\omega)\,|+,\vec{k}+\vec{\kappa}\rangle = (i\omega+\nu)^{-1}[-\langle\vec{k}+|\,\Pi_p(\omega)\,|+,\vec{k}+\vec{\kappa}\rangle$$

$$\times(\langle\vec{k}+\vec{\kappa},+|\,\chi^R\,|+,\vec{k}+\vec{\kappa}\rangle + \langle\vec{k}+|\,\chi^R\,|+\vec{k}\rangle) + \langle\vec{k}+|\,S(\omega)\,|+,\vec{k}+\vec{\kappa}\rangle], \qquad (6.15)$$

where $\langle\vec{k}+|\,S(\omega)\,|+,\vec{k}+\vec{\kappa}\rangle = \sum_{m,\mu} \int d\vec{v}\,\delta(\Omega_k - \omega_0 + \vec{k}\cdot\vec{v})$

$$\times[\langle\mu|\,\vec{\epsilon}_+{}^{\dagger}(\vec{k}+\vec{\kappa})\cdot\vec{D}\,|m\rangle\langle m|\,\rho_e(\omega)\,|m\rangle\langle m|\,\vec{\epsilon}_+(\vec{k})\cdot\vec{D}\,|\mu\rangle] \ , \qquad (6.16)$$

and where $\langle m|\,\rho_e(\omega)\,|m\rangle = \sum_{\nu,\bar{k}} \langle m|\,\vec{\epsilon}_+(\bar{\vec{k}})\cdot\vec{D}\,|\nu\rangle\langle\nu|\,\rho_g\,|\nu\rangle\langle\nu|\,\vec{\epsilon}_+{}^{\dagger}(\vec{k})\cdot\vec{D}\,|m\rangle$

$$\times\langle\bar{\vec{k}}+|\,\Pi_p(\omega)\,|+,\bar{\vec{k}}+\vec{\kappa}\rangle[\Gamma_e + i(\Omega_{mm'}+\omega)]^{-1} \ . \qquad (6.17)$$

The imaginary term in Eq. (6.15) vanished because the difference between $\langle \vec{k}+|\chi^I|+\vec{k}\rangle$ and $\langle \vec{k}+\vec{\kappa},+|\chi^I|+,\vec{k}+\vec{\kappa}\rangle$ vanishes. The solution of (6.11) for the unmodulated part of the beam $\delta\Pi(\omega=0)$ is

for the unmodulated part of the beam $\delta\Pi(\omega=0)$ is

$$\nu\langle \vec{k}i|\,\delta\Pi(0)\,|i'\vec{k}\rangle = \sum_{\vec{k},\bar{i}} \{-i[\langle \vec{k}i|\,\Pi_p(0)\,|\bar{i}\,\vec{\bar{k}}\rangle\langle \vec{\bar{k}}\,\bar{i}\,|\chi^I(0)|\,i'\vec{k}\rangle - \langle \vec{k}i\,|\chi^I(0)|\,\bar{i}\,\vec{\bar{k}}\rangle\langle \vec{\bar{k}}\,\bar{i}\,|\chi^I(0)|\,i'\vec{k}\rangle]$$

$$-\langle \vec{k}i|\,\Pi_p(0)\,|\bar{i}\,\vec{\bar{k}}\rangle\langle \vec{\bar{k}}\,\bar{i}\,|\chi^R(0)|\,i'\vec{k}\rangle - \langle \vec{k}i|\chi^R(0)|\,\bar{i}\,\vec{\bar{k}}\rangle\langle \vec{\bar{k}}\,\bar{i}\,|\,\Pi_p(0)\,|\,i'\vec{k}\rangle + \langle \vec{k}i|\,S(0)\,|\,i'\vec{k}\rangle\,, \quad (6.18)$$

where the variable 0 refers to $\omega=0$.

In the representation where $i=+$ represents a right circularly polarized photon, Eq. (6.18) becomes

$$\langle \vec{k}+|\,\delta\Pi(0)\,|+\vec{k}\rangle = \nu^{-1}[-2\langle \vec{k}+|\,\Pi_p(0)\,|+\vec{k}\rangle\langle \vec{k}+|\,\chi^R(0)\,|+\vec{k}\rangle + \langle \vec{k}+|\,S(0)\,|+\vec{k}\rangle]\,. \quad (6.19)$$

Equations (6.12) and (6.18) or (6.15) and (6.19) depend on only the zeroth-order expressions for Π and ρ_g and constitute a complete solution of the problem to order γ^2. They contain the same information as the solution of ρ_g to order γ^2 in Eq. (6.8). Thus, to order γ^2 we can solve for either $\delta\Pi$ or ρ_g, the choice being a matter of convenience. Higher-order solutions require knowing both ρ and Π and require joint solutions of the coupled Eqs. (5.10) and (4.17).

The total change in intensity of the beam to order γ^2 is

$$\Delta I = \nu\sum_k[\langle \vec{k}|\,\Pi(0)\,|\vec{k}\rangle - \langle \vec{k}|\,\Pi_p(0)\,|\vec{k}\rangle + 2^{-1}(\langle \vec{k}|\,\Pi(\omega)\,|\vec{k}+\vec{\kappa}\rangle$$

$$-\langle \vec{k}|\,\Pi_p(\omega)\,|\vec{k}+\vec{\kappa}\rangle + \langle \vec{k}|\,\Pi(\omega)\,|\vec{k}+\vec{\kappa}\rangle - \langle \vec{k}|\,\Pi_p(\omega)\,|\vec{k}+\vec{\kappa}\rangle)]\,, \quad (6.20)$$

where ΔI, $\langle \vec{k}|\,\Pi(0)\,|\vec{k}\rangle$, etc., are two-by-two operators in spin space. When we substitute Eqs. (6.12) and (6.18) in (6.20), we obtain

$$\Delta I = \nu\sum_k\{-2\langle \vec{k}|\,\Pi_p(0)\,|\vec{k}\rangle\langle \vec{k}|\,\chi^R\,|\vec{k}\rangle + \langle \vec{k}|\,S(0)\,|\vec{k}\rangle - [\langle \vec{k}|\,\Pi_p(\omega)\,|\vec{k}+\vec{\kappa}\rangle\langle \vec{k}+\vec{\kappa}|\,\chi^R\,|\vec{k}+\vec{\kappa}\rangle$$

$$+\langle \vec{k}|\,\Pi_p(\omega)\,|\vec{k}+\vec{\kappa}\rangle\langle \vec{k}+\vec{\kappa}|\,\chi^R\,|\vec{k}+\vec{\kappa}\rangle] + 2^{-1}[\langle \vec{k}|\,S(\omega)\,|\vec{k}+\vec{\kappa}\rangle + \langle \vec{k}|\,S(\omega)\,|\vec{k}+\vec{\kappa}\rangle]\}$$

$$= -I_a(0) + I_e(0) - I_a(\omega) + I_e(\omega)\,, \quad (6.21)$$

where $I_a(0)$ is light absorbed at zero frequency modulation, $I_e(0)$ is light emitted at zero frequency modulation, $I_a(\omega)$ is light absorbed at frequency modulation ω, $I_e(\omega)$ is light emitted at frequency modulation ω.

The symbols $\langle \vec{k}|\,\chi^R\,|\vec{k}\rangle$ and the various I's are two-by-two operators in the spin space. The expression for Eq. (2.1) in the time domain is

$$\Delta I(t) = -I_a(0)(1+d\cos\omega t) + I_e(0)(1+d\cos\omega t)\,,$$

where we use $\Pi_p(\omega)=d\Pi_p(0)$. Both the absorbed and emitted light are modulated at frequency ω. We would obtain the same result for $\Delta I(t)$ if we applied an rf magnetic field to the system. However, the two cases differ in that a magnetic field the ω dependence comes from $\chi^r(\omega)$ while in the Bell-Bloom effect the ω dependence comes from the $\Pi_p(\omega)$.

VII. SPATIAL DEPENDENCE OF Π

The dominant spatial dependence of Π is a consequence of the spatial variation of $\rho(\vec{x}, t)$. If the spatial variation of $\rho(\vec{x}, t)$ over the modulation wavelength κ^{-1} is small or if the time variation over the time (L/C) is small, then we can neglect retardation effects within the sample. We express the polarization matrix at a detection point outside the sample in terms of the free space Green's function appropriate to the geometry as follows:

$$\Pi(\vec{x}t) - \Pi_p(\vec{x}, t)$$

$$= \int_A \int_0^t G_0[\vec{x} - \vec{x}', t - t'] Q(\vec{x}' t')\, dt'\, dA', \qquad (7.1)$$

where $Q(\vec{x}, t) = -i[\Pi(\vec{x}, t), \xi^I(\vec{x}, t)]$

$$- [\Pi(\vec{x}, t), \xi^R(\vec{x}, t)]_+ + L(\vec{x}, t)\,,$$

and where the $\vec{x}'$ integration is over the surface of the system that emits light to the detector. In a one-dimensional geometry where the light beam is along the x axis and the sample is contained between $x = 0$ and $x = L$, the Green's function is

$$G_0[\vec{x} - \vec{x}', t - t'] = \delta(y - y')\delta(z - z') \times \delta[x - x' - c(t - t')], \quad \text{for } t > t' \qquad (7.2)$$

$$= 0, \quad \text{for } t < t'.$$

In this section, we return to dimensional variables. When we substitute Eq. (7.2) in (7.1), we obtain

$$\Pi(z, t) - \Pi_p(z, t) = Q[L, t - (z - L)c^{-1}]\,. \qquad (7.3)$$

The problem of retardation effects within the sample is more complicated. The solution of Eq. (5.10) for the point $\vec{x}$ within the sample is

$$\Pi(\vec{x}, t) - \Pi_p(\vec{x}, t) = \int_0^t \exp\{-(t - t')(\nu + c\vec{n}\cdot\nabla)\}\, Q(\vec{x}, t')\, dt'$$

$$= \int_0^t \exp[-\nu(t - t')]\, Q[\vec{x} - c\vec{n}(t - t'), t']\, dt'$$

$$= \int_v d^3x' \exp[-\nu(t - \vec{n}\cdot(\vec{x} - \vec{x}')c^{-1})] \times Q[\vec{x}', t - n\cdot(\vec{x} - \vec{x}')c^{-1}]\,, \qquad (7.4)$$

where $\vec{n}$ is a unit vector in the direction of propagation and v is the volume of the sample.

If $\rho(\vec{x}, t)$ varies over distance of the order of κ^{-1}, then it is necessary to retain the spatially dependent terms $\exp[i(\vec{k} - \vec{k}')\cdot\vec{x}]$ in the equations of motion for Π and ρ. Consequently, we can neglect spatial variation if $|\kappa| L \equiv |\vec{k} - \vec{k}'| L \ll 1$. The inclusion of spatial variation is straightforward. When spatial effects are important we must include a $\vec{v}\cdot\nabla$ term in the equation of motion for ρ.

VIII. DISCUSSION

We made five approximations in this paper, four of which are essential and a fifth, which is for algebraic convenience. The five approximations are represented by five dimensionless parameters which must be small compared with 1. The first approximation is that the lifetime of the ground state is long compared with the lifetime of the excited state and it is represented by the inequality $(\Gamma_g/\Gamma_e) \ll 1$. This approximation allows us to neglect particle-particle and particle-field correlations. The same approximation justifies the adiabatic solution for the excited-state matrix elements $\langle m|\rho_e|m'\rangle$ in terms of the ground-state matrix elements $\langle \mu|\rho_g|\nu\rangle$. The second approximation is that the width of the radiation is much greater than the inverse lifetime of the ground state and it is represented by the inequality $(\Gamma_g/\delta) \ll 1$. This approximation justifies treating the absorption process by the atom perturbatively. The third approximation is the Wigner-Weisskopf approximation, which justifies treating spontaneous emission perturbatively and it is represented by the inequality $(\Gamma_e/\omega_0) \ll 1$. The fourth approximation, $\delta \gg \omega_e, \omega_g$, is made for convenience because it allows us to replace the various arguments of the $\delta_\pm$ functions by the same argument $(\Omega_k - \omega_0 - \vec{k}\cdot\vec{v})$. Our general equations for ρ and R, Eqs. (2.16) and (2.17), are valid even if $\delta \ll \omega_e, \omega_g$. We need a fifth approximation to play the role for photons that the approximation $\delta \gg \Gamma_g$ plays for atoms. At first glance the appropriate approximation would seem to be $\omega_D \gg \gamma^2 \mathfrak{N} \omega_D^{-1}$ because ω_D^{-1} is the interaction time for a photon and $\gamma^2 \mathfrak{N} \omega_D^{-1}$ is the photon-relaxation time. The approximation $\omega_D \gg \gamma^2 \mathfrak{N} \omega_D^{-1}$ is sufficient to justify the use of the first-order perturbation theory in the equation of motion for Π. However, experimentally the values of are often sufficiently large that the inequality is reversed. Consequently, we must either justify a weaker condition or use higher-order perturbation theory for the photons than we used for the atoms. The answer is that the weaker assumption $\omega_D \gg \gamma^2 \mathfrak{N} \omega_D^{-1} (\Gamma_g/\Gamma_e)$ is valid experimentally and justified theoretically. The need for an inequality comes from the requirement that there exists a time t long compared with the interaction time τ_i in order to obtain the energy conservation δ function and short compared with a relaxation time τ_γ in order not to have to go to higher-order perturbation theory. A rough estimate of the second-order relaxation time is $\gamma^2 \omega_D^{-1} \times (\gamma^2 \mathfrak{N} \omega_D^{-2})$, which can be written in the form $\gamma^2 \mathfrak{N} \omega_D^{-1} (\tau_i/\tau_\gamma)$. Consequently, when τ_i is no longer negligible compared with τ_γ we must include higher-order irreducible diagrams. A more careful analysis of the second-order irreducible diagrams involving two different atoms, the γ^4 terms, show that one of the two atoms has to be excited to get a nonvanishing contribution. The second-order correction factor is not $(\gamma^2 \mathfrak{N} \omega_D^{-2})$, but $(\gamma^2 \mathfrak{N}_e \omega_D^{-2})$, where $\mathfrak{N}_e = (\Gamma_g/\Gamma_e)\mathfrak{N}$ is the number of excited atoms. Consequently, our approximation that t be sufficiently short so higher-order processes are justifiably negligible is not $t \ll \gamma^2 \mathfrak{N} \omega_D^{-1}$ but $t \ll \gamma^2 \mathfrak{N} \omega_D^{-1} (\Gamma_g/\Gamma_e)$. The factor (Γ_g/Γ_e) is less than 10^{-3} in optical pumping experiments and justifies the first-order kinetic

equations for the densities used in experiments.

The usual theoretical treatment of optical pumping for linear problems is to take as zeroth order the given external beam and some initial density matrix, then to solve for ρ to first order in γ^2. We showed that the same physics is contained in the first-order solution of the radiation polarization matrix $\langle \vec{k}i|\,\Pi|\,i'\vec{k}'\rangle$. In a future publication, we plan to show that the experiments[11,12] with electromagnetic fields approximately resonant with either excited- or ground-state level separation can also be completely described by the appropriate radiation polarization matrix. In the rf field experiments, the coherence comes from the generator of the rf signal instead of from the light modulator. However, the net result is the same, i.e., the modulation of the signal on absorption or emission is a result of nonvanishing correlations between optical photons differing in frequency by the rf frequency.

As the intensity of the external optical beam is increased so that $(\gamma^2\mathfrak{N}/\omega_D\nu)$ becomes of the order or greater than 1, then multiple scattering becomes important and the coupled nonlinear equations must be used. The condition $(\gamma^2\mathfrak{N}/\omega_D\nu)\gtrsim 1$ is equivalent to $k_0 L \gtrsim 1$, where k_0 is the absorption per unit length at line center and L is the thickness of the sample. Some years ago, Holstein[13] obtained an expression for the linewidth of resonant radiation imprisoned in gases. In a future publication, we will show Holstein's equations correspond to the diagonal matrix elements of our equations for ρ and Π. Equations (5.7) and (6.10) also explain the resonant narrowing when coherence,[14] i.e., offdiagonality, is present in the atomic system. Furthermore, our equations show that the line narrowing is due to separate absorption and emission processes described by the first-order Born approximation without any two-atom atom-field correlation.

Two recent papers[2,15] with quite different approaches use derivations in which the treatment of the electromagnetic radiation is its interaction involving the use of ensembles for which the electromagnetic field is nonvanishing. The resultant equations of Ref. 2 are equivalent to the linearization of our equations for Π without the emission term $L\Pi$. The resultant equations of Ref. 15 are equivalent to the linearization of our equations for ρ without the mission term $B\rho$. The use of ensembles with nonvanishing electric fields for "thermal-like" beams require the answering of some subtle questions. However, one of the results of the present paper is to show that the results of Refs. 2 and 15, which depend on χ and ξ, respectively, are independent of any assumptions about the existence of electromagnetic fields. Our equations, which contain the results of Refs. 2 and 15 as limits, depend only on first-order perturbation theory and the second moments of radiation density matrix $\langle a_i^\dagger(\vec{k})a_j(\vec{k}')\rangle$. A further advantage of the present work is that the terms $\langle a_j(\vec{k}')a_i^\dagger(\vec{k})\rangle$ gives rise to the spontaneous emission terms $L\Pi$ and $B\rho_g$ which are absent in both papers.

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*Research reported in this paper was sponsored in part by the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research. A preliminary report on the results of this paper appeared in Bull. Am. Phys. Soc. 14, 31 (1969).

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