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# Time and spectral resolution in resonance scattering and resonance fluorescence

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The theory of resonance Raman effect, resonantly enhanced two-photon absorption, and resonance fluorescence—valid also for strong fields—is treated in a unified and simplified way. Dressed states, Bloch equations, and perturbation theory are used to calculate line positions, and integrated intensities both for steady state and transient excitation. The case of adiabatic following is solved explicitly; it occurs when an off-resonance incident pulse is turned on and off slowly. It leads to the identification of Raman scattering, two-photon absorption, and Rayleigh scattering with an adiabatic process while fluorescence and consecutive two-photon absorption with nonadiabaticity. Time-dependent spectra are defined in a rigorous way. Our formulas agree in the various limits with those that appear in the literature.

## I. INTRODUCTION

Resonance fluorescence and Rayleigh scattering were among the first problems treated by the methods of quantum electrodynamics. The results of this treatment can be found today in textbooks such as that of Heitler.[1] Recently, there has been a revival of interest in the subject, because of new experimental techniques for making strong, coherent, narrow linewidth light sources that can also produce short pulses: tuneable dye lasers. These lasers have been used to produce nonlinear (multiphoton) phenomena, to explore details of the scattering very close to resonance, and to study the influence of collisions on spectra. In this process, some lively controversies have arisen and some misconceptions are still prevalent.

The present paper is an attempt to clarify some of the concepts involved and to discuss some of the expected effects, in a much simplified way using the simplest possible level schemes, dressed states, Bloch equations, and perturbation theory. This way line positions, integrated intensities, and time dependences (but not detailed line shapes) are calculated. In particular, it is shown how simultaneous time and spectral resolution can be used to study the scattered light. We hope that our treatment introduces a considerable simplification into the theory of these effects.

We concentrate on the off-resonance (near-resonance) case, where the scattered light can be meaningfully resolved into time-dependent spectral components. In particular, it is shown that when the spectrum of the exciting laser pulse does not overlap the absorption line, the pulse satisfies the adiabatic condition. As a result, in a collisionless three-level system only Raman scattering is present and the emission stops when the exciting pulse is turned off. Fluorescence (hot luminescence) is caused by nonadiabaticity, either because the spectrum of the exciting pulse overlaps the absorption line or collisions "interrupt" ("switch-off-and-on") the incident radiation. The fluorescence is emitted near the transition frequency and it decays with its own lifetime after the pulse is over. Thus we associate Raman emission with adiabaticity and fluorescence with the lack of it. Coherence of the source plays only a secondary role. (Raman scattering was studied with mercury lamps for many years.)

In resonance scattering (two-level case), the situation is similar: the scattering at the frequency of the exciting pulse, the Rayleigh scattering, is adiabatic; the fluorescence is nonadiabatic, it has the same causes and characteristics as in the three-level case. In addition, a three-photon Raman-type nonlinear process contributes to the emission near resonance.

Detailed line shapes and nonlinear effects in scattering from a two-level system in a strong incident field in the absence of collisions were first calculated by Mollow[2] in 1969, using a classical incident field. This is a problem of quantum electrodynamics in which perturbation has to be carried to "infinite" order. Later the calculation was extended,[3,4] and also done using quantum-mechanical coherent states[5–8] giving the same results. The problem was treated in terms of dressed states by Cohen-Tannoudji.[9] Our treatment was inspired by his earlier work,[10] and it is also close to Kazantsev's.[3]

The presence of collisions makes the theory considerably more complicated. The low-field case of the two-level system has been solved near line

center (the impact limit) by Huber,[11] Omont *et al.*,[12] and Mukamel *et al.*[13] The collisional aspects, including the nonimpact and high-field regions, have been treated by Yakovlenko and co-workers,[14] and by Kroll and Watson.[15] When the fields are not too high, their results agree with a theory by Mollow,[4] who introduced phenomenological relaxation constants into his treatment of the radiation problem.

The first experimental test of high-field collisionless resonance scattering was by Stroud[16] and has since been refined by Ezekiel[17] and Walther.[18] Good agreement with Mollow's theory was obtained. Gibbs and Venkatesan[17,19] have verified the old prediction[1] that the unshifted (Rayleigh) scattering can be narrower than the natural linewidth. The optical Stark effect, the shift of levels due to the strong incident field, has also been studied.[16–18,20–23] Scattering in the predominantly collisionally damped regime was studied by Carlsten and Szöke.[24] They made a detailed comparison with theory obtaining good agreement. Much better agreement is obtained when the pulsed nature of the incident radiation is properly accounted for, using the prescriptions of the present paper (Sec. IV C).

In a three-level system, Raman scattering can be seen without fluorescence, a fact discovered by Raman, but worth remembering. The recent flurry of activity started with a paper by Holzer *et al.*,[25] who observed a transition between resonance Raman scattering and fluorescence in iodine. This was followed by many papers attempting to clarify the concepts involved.[26–30] On the theoretical side Jacon and co-workers developed a general formalism to deal with the transition.[31] It was pointed out by Huber[32] and by Shen[33] that there is a distinct difference between Raman scattering and "hot luminescence" both in spectral and time behavior. Our results are similar to theirs. Very interesting experiments were conducted by Rousseau *et al.*,[34] who studied the time dependence of the emitted light and who observed both a short (prompt) and long (decaying) component. The present authors commented on that work,[35] and this article is, to some extent, an extension and continuation of that comment. More recently, Prosnitz *et al.*[23] studied the high-field behavior of the Raman emission and Liran *et al.*[36] studied the time dependence of the spectral components and, indeed, observed that it is the Raman (shifted) component that is short and the fluorescence that is long.

Stimulated processes in a three-level system, two-photon absorption, and Raman-type stimulated emission including line shapes, have been studied extensively by the methods of nonlinear optics[37] and by the semiclassical methods of susceptibility,[38] also including collisions.[39] Recently, Grischkowsky studied the time dependence of both two-photon and sequential absorption,[40] a work that is particularly relevant to ours. Also, Bjorkholm and Liao[41] studied the resonance two-photon absorption.

An important motivation for the present paper is the large activity in the field. Moreover, the theory is fairly complicated and, in the presence of collisions, it is not fully understood. It seems to us that an approach using simple concepts and showing connections among various experiments will help further development. In our paper we consider various cases in parallel; all intensities, line positions, and time dependences are worked out. In Sec. II, the dressed states and the self-consistent equations of motion are introduced for a two-level system using the Bloch formalism. In Sec. III, positions and intensities of the various spectral components are calculated using first-order perturbation theory. In Sec. IV the adiabatic following approximation is discussed, the equations of motion are solved for an adiabatic "square" pulse and time-dependent intensities are obtained. Also, the steady state and a nonadiabatic pulse are discussed. Section V presents a more rigorous approach to the definition of time-dependent spectra, using a filter function. A perturbation approach, giving our low field results very easily, is relegated to Appendix A, and the steady-state solution is displayed in Appendix B.

## II. DRESSED STATES AND EQUATIONS OF MOTION

Consider the nondegenerate two-level system of Fig. 1(a), where the lower state is the ground state.[42] The transition is dipole allowed, and the system is excited by an optical pulse of carrier frequency $\omega$ close to the resonance frequency $\omega_{21}$ with detuning

$$\Delta \equiv \omega - \omega_{21} . \tag{1}$$

One is interested in the time and frequency dependence of the scattered light and spontaneous emission. The system is assumed to be small in spatial extent and optically thin, and no stimulated emis-

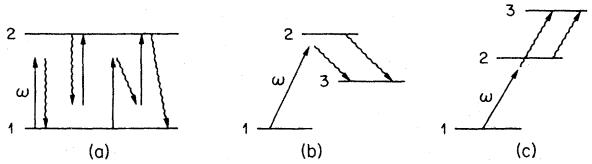


FIG. 1. Three processes considered in the present work: (a) Resonance scattering and fluorescence consisting of (i) scattering from the ground state, (ii) scattering from the excited state, (iii) a three-photon process taking the system to the upper state, (iv) upper state fluorescence. (b) Emission to a state 3 under near-resonant-excitation of the transition 1–2. (c) Absorption to a state 3 in the same conditions.

sion is considered. Thus the emission can be calculated as that from a single atom. The levels 1 and 2 with time-independent wave functions $|\psi_1\rangle$ and $|\psi_2\rangle$ form the basis set of our description. They are perturbed by the classical field

$$\vec{E} = \hat{x}\,\mathcal{E}(t)\cos(\omega t + \phi)\,, \tag{2}$$

that is taken to be linearly polarized; $\omega$ is constant, $\mathcal{E}$ is slowly varying, and for the present problem we consider only $\phi = 0$. With the appropriate transition matrix element $\vec{\mu} = \vec{p}(\sigma_+ + \sigma_-)$, where $\vec{p} = e\langle\psi_2|\vec{r}|\psi_1\rangle$, the Hamiltonian matrix is

$$\mathcal{H} = \tfrac{1}{2}\hbar\omega_{21}(\sigma_3 + I) - \vec{\mu}\cdot\vec{E}\,, \tag{3}$$

where the ground-state energy has been shifted to a convenient value and the $2\times 2$ Pauli matrices are defined as usual:

$$\sigma_+ = |\psi_2\rangle\langle\psi_1|\,,\quad \sigma_- = |\psi_1\rangle\langle\psi_2|\,,$$
$$\sigma_3 = |\psi_2\rangle\langle\psi_2| - |\psi_1\rangle\langle\psi_1|\,,\quad I = |\psi_2\rangle\langle\psi_2| + |\psi_1\rangle\langle\psi_1|\,.$$

Schrödinger's equation of motion, $i\hbar\dot{\psi} = \mathcal{H}\psi$, is transformed to a frame rotating at the field frequency by the unitary transformation $\mathfrak{U}_R = \exp[\tfrac{1}{2}i\omega t(\sigma_3 - 1)]$. The new Hamiltonian is

$$\mathcal{H}_R = \mathfrak{U}_R\mathcal{H}\mathfrak{U}_R^{-1} + i\hbar\frac{\partial\mathfrak{U}_R}{\partial t}\,\mathfrak{U}_R^{-1}$$
$$= -\tfrac{1}{2}\hbar\Delta\sigma_3 + \tfrac{1}{2}\hbar(\omega_{21} + \omega) - \tfrac{1}{2}p\mathcal{E}(\sigma_+ + \sigma_-)\,, \tag{4}$$

where $p = \vec{p}\cdot\hat{x}$, and where we have made the rotating wave approximation which consists of neglecting terms in $e^{\pm 2i\omega t}$. This approximation is good near resonance $|\Delta| \ll \omega_{21}$ and for fields which are not too strong $|p\mathcal{E}/\hbar| \ll \omega_{21}$. In the rotating frame, Schrödinger's equation becomes $i\hbar\dot{\psi}^R = \mathcal{H}_R\psi^R$ with $\psi^R = \mathfrak{U}_R\psi$.

A second unitary transformation $\mathfrak{U}_D$ is applied which diagonalizes the Hamiltonian when $\mathcal{E}$ is constant:

$$\mathfrak{U}_D = \cos\tfrac{1}{2}\theta + (\sigma_+ - \sigma_-)\sin\tfrac{1}{2}\theta\,, \tag{5}$$

with

$$\tan\theta = p\mathcal{E}/\hbar\Delta = \Omega/\Delta\,, \tag{6a}$$

where

$$\Omega = p\mathcal{E}/\hbar \tag{6b}$$

is the Rabi frequency. For later reference we also define

$$\Omega' = \Delta[1 + (\Omega/\Delta)^2]^{1/2} \tag{6c}$$

a quantity having the sign of $\Delta$, and usually called the effective field (in frequency units). Let us also note that

$$\sin\theta = \Omega/\Omega'\,, \tag{6d}$$

$$\cos\theta = \Delta/\Omega'\,. \tag{6e}$$

The angle $\theta$ is between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$. The new Hamiltonian $\mathcal{H}_D$ is

$$\mathcal{H}_D = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| + \tfrac{1}{2}i\hbar(\sigma_+ - \sigma_-)\dot{\theta}\,, \tag{7}$$

where

$$E_1 = \hbar\omega + \tfrac{1}{2}\hbar\delta\,, \tag{8a}$$

$$E_2 = \hbar\omega_{21} - \tfrac{1}{2}\hbar\delta\,, \tag{8b}$$

and where $\hbar\delta$ is the high-frequency Stark shift,[20]

$$\delta = \Delta(1 - \cos\theta)/\cos\theta = \Omega' - \Delta\,. \tag{8c}$$

The eigenstates are

$$|1\rangle = |\psi_1^R\rangle\cos\tfrac{1}{2}\theta - |\psi_2^R\rangle\sin\tfrac{1}{2}\theta\,, \tag{9a}$$

$$|2\rangle = |\psi_1^R\rangle\sin\tfrac{1}{2}\theta + |\psi_2^R\rangle\cos\tfrac{1}{2}\theta\,, \tag{9b}$$

and $\sigma_\pm$ are still $\sigma_+ = |2\rangle\langle 1|$, $\sigma_- = |1\rangle\langle 2|$. As seen from Eq. (7), the new states [Eq. (9)] diagonalize the Hamiltonian when $\dot{\theta} = 0$, which for slowly varying $\mathcal{E}$ amounts to the adiabatic approximation. When the field varies slowly, transitions between $|1\rangle$ and $|2\rangle$ whose rate is proportional to $\dot{\theta}^2$ can be neglected. Thus these states can properly be called adiabatic eigenstates. The conditions on $\dot{\theta}$ will be discussed in more detail below. These states are also called "dressed" states as they represent the eigenstates of the atom in the presence of the strong monochromatic field.[10] For a weak field, $|1\rangle$ tends to the ground state $|\psi_1^R\rangle$, and $|2\rangle$ to the excited state $|\psi_2^R\rangle$. Note that the ground-state energy includes the energy of one photon as required from the full quantum electrodynamics treatment. In that treatment the field mode corresponding to Eq. (2) is excited and the resulting states, $|1, n+1\rangle$ and $|2, n\rangle$, are obtained by a superposition of the atom-field product states $|\psi_1^R, n+1\rangle$ and $|\psi_2^R, n\rangle$ in a formula similar to Eq. (9), where $n$ is the photon number in the strong-field mode. The energies of these states are

$$E_{1,n+1} = (n+1)\hbar\omega + \tfrac{1}{2}\hbar\delta\,, \tag{8d}$$

$$E_{2,n} = n\hbar\omega + \hbar\omega_{21} - \tfrac{1}{2}\hbar\delta\,. \tag{8e}$$

Thus, it is seen that there is a large repetition of levels, depicted in Fig. 2.

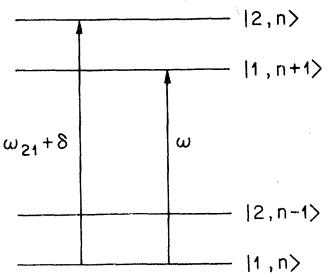


FIG. 2. Part of the field-atom eigenstates ladder obtained when interaction with only one mode is considered.

In order to calculate emission into other modes of the radiation field, it is necessary to know the population of these states, i.e., the equations of motion have to be solved. The rotating frame equations of motion derived from Eq. (4) can be written in the well-known Bloch form

$$\frac{d\vec{S}}{dt}=\vec{S}\times\vec{E}_{eff}-\vec{\Gamma}\cdot(\vec{S}-\vec{S}_0)\,. \tag{10}$$

Here,

$$\vec{S}\equiv\hat{x}(\rho_{12}^R+\rho_{21}^R)+i\hat{y}(\rho_{21}^R-\rho_{12}^R)+\hat{z}(\rho_{22}^R-\rho_{11}^R)\,, \tag{11a}$$

$$\vec{E}_{eff}\equiv\hat{x}\Omega+\hat{z}\Delta\,, \tag{11b}$$

where $\Omega=p\mathcal{E}/\hbar$ was defined in Eq. (6b), $\rho^R$ is the density matrix in the rotating frame, and $\vec{\Gamma}$ is the relaxation matrix caused by collisions and emission of radiation. The frame $(\hat{x},\hat{y},\hat{z})$ is an abstract frame not to be confused with the spatial coordinates. The effective field, $\vec{E}_{eff}$, has units of frequency, and its magnitude, $|\vec{E}_{eff}|=|\Omega'|$.

The relaxation matrix $\vec{\Gamma}$ will be introduced here phenomenologically as

$$\vec{\Gamma}\cdot(\vec{S}-\vec{S}_0)=\hat{x}\gamma_2 S_x+\hat{y}\gamma_2 S_y+\hat{z}\gamma_1(S_z+1)\,. \tag{12}$$

We assumed that in the absence of the field the atom relaxes to its ground state, $\vec{S}_0=-\hat{z}$. The relaxation is caused, in general, by radiation and collisions. In the case of pure radiative damping it has been shown[2,5–9] that $2\gamma_2=\gamma_1=1/\tau$, where $\tau$ is the radiative lifetime of the upper state. It has been shown, e.g., by Bloch,[43] that for collisional relaxation in the binary collision regime, a general $\vec{\Gamma}$ encompasses all the phenomena. (Actually, the description by a relaxation matrix applies to a more general class of systems.) It was pointed out recently that in the presence of collisions $\vec{\Gamma}$ depends, in general, both on the detuning $\Delta$ and on the field strength.[14,15,24] This large and complex subject will not be treated in this article. Note that in the absence of relaxation the solution of Eq. (10) for a constant $\mathcal{E}$ is a precession of $\vec{S}$ around $\vec{E}_{eff}$ at a constant angle $\alpha$ and constant angular frequency $|\vec{E}_{eff}|$. It is this visualization of the solution that makes the model so useful (Fig. 3).

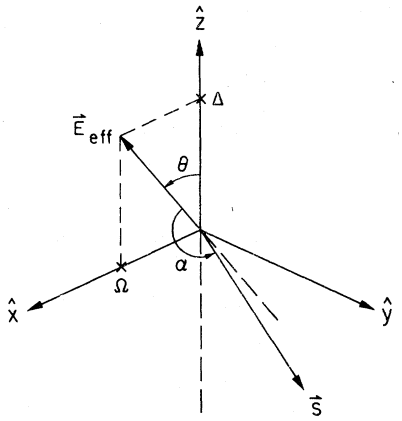


FIG. 3. Rotating frame in the abstract space $(\hat{x},\hat{y},\hat{z})$ showing $\vec{E}_{eff}$ in the $(\hat{x},\hat{z})$ plane with the definition of $\theta$ drawn for $\Delta>0$ and the definition of $\alpha$ which is the angle between $\vec{E}_{eff}$ and $\vec{S}$ for $\Delta>0$, or that between $-\vec{E}_{eff}$ and $\vec{S}$ for $\Delta<0$.

Equations (10) and (11) can be transformed to the dressed states by $\rho^D=\mathfrak{U}_D^{-1}\rho^R\mathfrak{U}_D$. It is easy to recognize that $\mathfrak{U}_D$ is a rotation around the $\hat{y}$ axis that causes the $\hat{x}$ component of the effective field to vanish (Fig. 3). In fact, $\mathfrak{U}_D$ is the spinor representation of the rotation group around $\hat{y}$. Thus, $\vec{S}^D$, which is expressed in terms of $\rho^D$ by a relation similar to Eq. (11a), is obtained from $\vec{S}$ by a rotation $-\theta$ around $\hat{y}$. It obeys an equation similar to Eq. (10) with

$$\vec{E}_{eff}^D\equiv\hat{z}\Omega'+\hat{y}\dot{\theta}\,, \tag{13}$$

where $\Omega'=\Delta/\cos\theta$ was defined in Eq. (6c). Using Eq. (12), one also finds

$$\vec{S}_0^D=\hat{x}\sin\theta-\hat{z}\cos\theta\,, \tag{14a}$$

and

$$\vec{\Gamma}^D=\begin{pmatrix}\gamma_2\cos^2\theta+\gamma_1\sin^2\theta & 0 & (\gamma_2-\gamma_1)\sin\theta\cos\theta\\ 0 & \gamma_2 & 0\\ (\gamma_2-\gamma_1)\sin\theta\cos\theta & 0 & \gamma_1\cos^2\theta+\gamma_2\sin^2\theta\end{pmatrix}. \tag{14b}$$

In particular, $\rho_{22}^D-\rho_{11}^D=S_z^D=S\cos\alpha$, where $S$ is positive and $\alpha$ is the angle between $\vec{S}^D$ and the positive $z$ axis in the dressed frame. Note that in the rotating system $\alpha$ is the angle between $\vec{S}$ and $\vec{E}_{eff}$ and that for a system near its ground state $\alpha\cong\pi$. Thus, using $\rho_{11}^D+\rho_{22}^D=1$, one obtains for the diagonal elements of $\rho^D$, i.e., the dressed-state populations,

$$\rho_{11}^D=\tfrac{1}{2}(1-S\cos\alpha)\,, \tag{15a}$$

$$\rho_{22}^D=\tfrac{1}{2}(1+S\cos\alpha)\,. \tag{15b}$$

In cases where a third level 3 is also considered [Figs. 1(b) and (c)], it is assumed that this level is connected to 2 by the dipole matrix element $\vec{\mu}_{23}=\langle\psi_2|\vec{\mu}|\psi_3\rangle$, whereas $\langle\psi_1|\vec{\mu}|\psi_3\rangle=0$. Also it is assumed that the field acting on the 2-3 transition is weak in the sense that $|\mu_{23}\mathcal{E}/\hbar(\omega-\omega_{23})|\ll 1$. The definition of $\mathfrak{U}_R$ is extended to level 3 by $\langle\psi_i|\mathfrak{U}_R|\psi_3\rangle=\delta_{i3}$.[48] The transformation to the rotating frame then leaves all matrix elements involving level 3 unchanged. With a similar extension of $\mathfrak{U}_D$, the diagonalization transformation modifies the off-

diagonal element $\mathcal{H}^R_{23}$ of the Hamiltonian in the following way:

$$\langle 2|\mathcal{H}^D|3\rangle = \langle 2|\mathfrak{u}_D \mathcal{H}^R \mathfrak{u}_D^{-1}|3\rangle = \mathcal{H}^R_{23}\cos\tfrac{1}{2}\theta\,, \quad (16a)$$

$$\langle 1|\mathcal{H}^D|3\rangle = -\mathcal{H}^R_{23}\sin\tfrac{1}{2}\theta\,, \quad (16b)$$

but the wave function $|3\rangle$ equals $|\psi_3^R\rangle$ and thus also $|\psi_3\rangle$. The energy of the third state [Fig. 1(b)] in the presence of $n$ photons of the exciting field and one emitted photon in mode $\vec{k}$ is written $E_{3,n,\vec{k}} = E_3 + n\hbar\omega + \hbar\omega_{\vec{k}}$.

In the first-order perturbation theory calculations that follow, we prefer to calculate matrix elements in the undiagonalized rotating frame using simply the fact that the wave functions [Eq. (9)] are the appropriate eigenstates. Identical results would, of course, be obtained by operating with the diagonal basis using Eq. (16), but the derivations might have somewhat less intuitive appeal.

## III. SCATTERING AND FLUORESCENCE

Scattering and fluorescence can be treated in a simple and transparent way using perturbation theory. This neglects important correlation effects[10] in the emission of successive photons as is particularly obvious from the ladder in Fig. 2, and thus does not lead to the correct line shapes. However, if the various spectral components can be resolved, their integrated intensities are obtained correctly, as well as their positions and the collisional contributions. There is a good reason for this as will be shown in Sec. V.

In scattering and fluorescence processes, photons are emitted into modes $\vec{k}$ of the radiation field other than the exciting one. These modes are in their vacuum state. The use of the dressed states enables one to count the spectral components very conveniently. As indicated above, all calculations are made using the basis set of the rotating frame wave functions and the treatment is restricted to the off-resonance case. We start with the emission in the three-level system of Fig. 1(b).

The quantum-mechanical emission rate from state $|1\rangle$ to $|3\rangle$ is calculated using Fermi's golden rule. The emission rate per atom is

$$W_R = \rho_{11}^D \frac{2\pi}{\hbar} \sum_{\vec{k}} |\langle 3|\mathcal{H}^{\rm int}_{\vec{k}}|1\rangle|^2\, \delta(E_{1,n+1} - E_{3,n,\vec{k}})$$

$$= \rho_{11}^D \left(\frac{\omega_R}{\omega_{23}}\right)^3 \left(\frac{4}{3}\frac{\omega_{23}^3}{\hbar c^3}\,\mu_{23}^2\right) \sin^2\frac{\theta}{2}$$

$$= \rho_{11}^D \left(\frac{\omega_R}{\omega_{23}}\right)^3 \frac{1}{\tau_{23}} \sin^2\frac{\theta}{2}\,, \quad (17)$$

where the sum over modes (integral over final states) is performed following Heitler.[1] The spontaneous emission rate which appears in parentheses in the second expression above has been replaced by $1/\tau_{23}$ in the third expression. Here $\tau_{23}$ is the spontaneous lifetime for the transition from 2 to 3. In the derivation of Eq. (17), the following relation was used:

$$\langle 3|\mu|1\rangle = \langle 3|\mu|\psi_1^R\rangle\cos\tfrac{1}{2}\theta - \langle 3|\mu|\psi_2^R\rangle\sin\tfrac{1}{2}\theta$$

$$= -\mu_{23}\sin\tfrac{1}{2}\theta\,,$$

as seen from Eq. (9a). The emission frequency results from the $\delta$ function in Eq. (17) and it is centered on

$$\omega_R = \omega_{23} + \Delta + \tfrac{1}{2}\delta\,. \quad (18)$$

This is a Raman process, whose frequency tracks the offset $\Delta$ of the incident field. It is shifted by the displacement of level $|1\rangle$ caused by the high-frequency Stark effect. For small $\mathcal{E}$, $\tan\theta \ll 1$, Eqs. (17) and (18) reduce to the usual Raman-scattering formula linear in incident intensity and at high intensities, $\tan\theta \gg 1$, Eq. (17) predicts saturation ($\sin^2\frac{1}{2}\theta \to \frac{1}{2}$).

A similar calculation gives the emission from state $|2\rangle$ to state $|3\rangle$,

$$W_F = \rho_{22}^D[\tfrac{4}{3}(\omega_F^3/\hbar c^3)\mu_{23}^2]\cos^2\tfrac{1}{2}\theta\,, \quad (19)$$

at the frequency

$$\omega_F = \omega_{23} - \tfrac{1}{2}\delta\,. \quad (20)$$

This can be called fluorescence proper: it is shifted only by the high-frequency Stark effect of level $|2\rangle$, and it reduces to spontaneous emission in the limit $\theta \ll 1$. In the high intensity limit, $\tan\theta \gg 1$, the states are mixed and the emission rate drops by a factor 2 ($\cos^2\frac{1}{2}\theta \to \frac{1}{2}$). It is already clear from the above that the adiabatic states of Eq. (9) play a crucial role in determining the spectral distribution of the scattered light: the adiabatic ground state causes only Raman emission and the adiabatic upper state (state $|2\rangle$) produces only fluorescence.

The emission obeys a sum rule. When $\omega_R \cong \omega_F \cong \omega_{23}$ the total emission rate is, from Eqs. (17) and (19),

$$W = W_R + W_F = (1/\tau_{23})(\rho_{11}^D \sin^2\tfrac{1}{2}\theta + \rho_{22}^D\cos^2\tfrac{1}{2}\theta)$$

$$= (1/2\tau_{23})(1 + S\cos\alpha\cos\theta) = (1/\tau_{23})\langle\rho_{22}^R\rangle\,, \quad (21)$$

where $\langle\ \rangle$ denotes here a time average. Thus, the total rate is proportional to the average population in state $|\psi_2^R\rangle$ (or in state $|\psi_2\rangle$).

If the third level is above level $|2\rangle$, an absorption measurement can be made as shown in Fig. 1(c). When the incident light near the transition to $|3\rangle$ is weak, the transition rate can be calculated using the golden rule. The absorption line from $|1\rangle$ to $|3\rangle$ integrated over angular frequencies is proportional to

$$\sum_{\vec{k}} |\langle 3|\mathcal{H}_{\vec{k}}^{\text{int}}|1\rangle|^2 \delta(E_{1,n+1}+\hbar\omega_{\vec{k}}-E_{3,n})\rho_{11}^{D},$$

which gives

$$\int \alpha_{\text{TP}}\, d\omega = m\rho_{11}^{D}\left(\frac{\lambda_{23}}{\lambda}\right)\left(\frac{4\pi^3\mu_{23}^2}{3\hbar\lambda_{23}}\right)\sin^2\frac{\theta}{2}, \tag{22}$$

where $m$ is a polarization factor which depends on the relative polarization of the strong field at $\omega$ and of the probing field at $\omega_{\vec{k}}$. The center frequency of this absorption is at

$$\omega_{\text{TP}} = \omega_{32} - \Delta - \tfrac{1}{2}\delta, \tag{23}$$

which is a two-photon (TP) absorption process. From $|2\rangle$ to $|3\rangle$ one obtains

$$\int \alpha_S\, d\omega = m\rho_{22}^{D}\left(\frac{4\pi^3\mu_{23}^2}{3\hbar\lambda_{23}}\right)\cos^2\frac{\theta}{2}, \tag{24}$$

with

$$\omega_S = \omega_{32} + \tfrac{1}{2}\delta, \tag{25}$$

which is a sequential absorption to level 3 via level $|\psi_2^R\rangle$. In the above calculations, possible Stark shifts on level 3 have been neglected.

Our calculation is restricted to the case where the lines are well resolved. Even in this case, interference effects occur. This problem received considerable attention because of the fine structure in Doppler broadened transition in the nonresolved case.[38,39,41]

The above approach also applies to resonance scattering and fluorescence in a two-level system [Fig. 1(a)]. In this case, the final states are also dressed states. Here again we use the energy of the quantum-field states of Fig. 2 and the Fermi golden-rule calculation of the transition probabilities. The initial states, $|1,n+1\rangle$ and $|2,n\rangle$, are given by Eqs. (9a), and (9b) in terms of $\psi^R$, their energy is given by Eqs. (8c) and (8d), whereas the final states are $|1,n,\vec{k}\rangle$ and $|2,n-1,\vec{k}\rangle$ with one scattered photon in mode $\vec{k}$ and one less photon in the exciting field. They are also constructed using Eqs. (9a) and (9b) and their energies are

$$E_{1,n,\vec{k}} = n\hbar\omega + \hbar\omega_{\vec{k}} + \tfrac{1}{2}\hbar\delta$$

and

$$E_{2,n-1,\vec{k}} = (n-1)\hbar\omega + \hbar\omega_{21} + \hbar\omega_{\vec{k}} - \tfrac{1}{2}\hbar\delta,$$

respectively. Defining the rate

$$1/\tau_{21} = \tfrac{4}{3}\,\omega_{21}^3 p^2/\hbar c^3, \tag{26}$$

one expresses the emission rates of the various processes as: (i) Scattering from $|1,n+1\rangle$ to $|1,n,\vec{k}\rangle$:

$$W_{R,1} = \rho_{11}^{D}\,(\omega/\omega_{21})^3(1/\tau_{21})(\tfrac{1}{2}\sin\theta)^2, \tag{27}$$

with the frequency,

$$\omega_R = \omega. \tag{28}$$

(ii) Scattering from $|2,n\rangle$ to $|2,n-1,\vec{k}\rangle$ with

$$W_{R,2} = \rho_{22}^{D}\,(\omega/\omega_{21})^3(1/\tau_{21})(\tfrac{1}{2}\sin\theta)^2, \tag{29}$$

and also,

$$\omega_R = \omega. \tag{30}$$

(iii) A three-photon process from $|1,n+1\rangle$ to $|2,n,\vec{k}\rangle$ with

$$W_3 = \rho_{11}^{D}\left(\frac{\omega_3}{\omega_{21}}\right)^3\frac{1}{\tau_{21}}\left(\frac{1-\cos\theta}{2}\right)^2, \tag{31}$$

at the frequency

$$\omega_3 = 2\omega - \omega_{21} + \delta = \omega + \Delta + \delta. \tag{32}$$

(iv) Fluorescence (spontaneous emission) from $|2,n\rangle$ to $|1,n,\vec{k}\rangle$ with

$$W_F = \rho_{22}^{D}\,(1/\tau_{21})[\tfrac{1}{2}(1+\cos\theta)]^2, \tag{33}$$

and the frequency

$$\omega_F = \omega_{21} - \delta = \omega - \Delta - \delta. \tag{34}$$

These four processes are drawn in Fig. 4(a), in the appropriate order. It is easy to see that in terms of the original states, they are represented by the processes in Fig. 4(b). The first two processes are Rayleigh scattering. The sum of their intensities,

$$W_R = W_{R,1} + W_{R,2} = (\omega/\omega_{21})^3(1/\tau_{21})(\tfrac{1}{2}\sin\theta)^2, \tag{35}$$

is independent of the state of the system. It is linear in the incident light intensity ($\sim\theta^2$) for $\theta \ll 1$ and, like all other components, it saturates

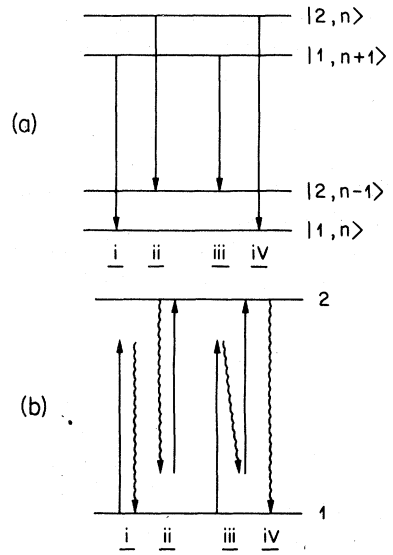


FIG. 4. Parallel between the four processes in the dressed-states ladder diagram (a) and the bare atomic-states diagram (b).

at high intensities. It is known from the work of Mollow[2] that at low intensities the scattering linewidth is as narrow as the incident light (see also Heitler[1]) and that at higher intensities it consists of two components, the second one proportional to the third power of the incident intensity and having a linewidth of the order of $\tau_{21}^{-1}$. Our treatment gives only the integrated intensity of both the narrow and broad components which do *not* correspond to $W_{R,1}$ and $W_{R,2}$ respectively (as discussed in Sec. IV).

In the three-photon process (iii), two incident photons are absorbed from the exciting field and one is emitted at the "sideband" frequency, leaving the atom in the excited state. For weak exciting intensity ($\theta \ll 1$) it is quadratic in the light intensity. It should be noted that this is a resonant *Stokes* Raman process, and as such it has gain. This fact was discovered already in 1961 by Rautian and Sobelman,[44] and has been pointed out anew since,[45] and observed experimentally.[46] The fluorescent component is proportional to the dressed upper-state population. The fluorescent lifetime is lengthened in the presence of the strong field by the factor $[2/(1+\cos\theta)]^2$. In the absence of collisions, the only process that populates the upper state is the three-photon process, therefore the (time) integrated intensities of the three-photon and fluorescence components are equal. There is also the possibility of a four-wave parametric process where two photons at $\omega$ are absorbed giving $\omega_3 + \omega_F$.[37] This is part of the cascades mentioned in connection with Fig. 2. Such processes interfere with those calculated using first-order perturbation theory and modify the linewidth.

If $\omega \cong \omega_F \cong \omega_3$, a sum rule is derived, giving the total rate for all processes:

$$W = W_R + W_F + W_3 = (1/\tau_{21})\tfrac{1}{2}(1 + S\cos\alpha\cos\theta) = (1/\tau_{21})\langle\rho_{22}^R\rangle , \tag{36}$$

with similar comments as those following Eq. (21). This formula actually shows that our calculation is consistent with the more fundamental derivation of $\gamma_1$. For a weak incident field only $W_R$ is important, and we get the correct expression $\gamma_1 = (\omega_L/\omega_{21})^3\tau_{21}^{-1}$.

When $S_x^2 + S_y^2 > 0$ in the rotating frame, the atomic dipole moment has a nonzero expectation value, therefore it radiates coherently. (This is usually called a classical or macroscopic dipole moment.) The radiation rate can be calculated, e.g., using Heitler,[1] and for a near constant $S_x = S\sin\theta$ it gives

$$W_{\text{coh}} = \frac{1}{\hbar\omega}\frac{1}{3}\frac{\omega^4 p^2}{c^3} = \left(\frac{\omega}{\omega_{21}}\right)^3 \frac{1}{\tau_{21}}\left(\frac{S\sin\theta}{2}\right)^2 . \tag{37}$$

When $S_x$, $S_y$ have a more complicated time variation, Eq. (37) has to be applied to each Fourier component (see Sec. IV D). Using the formula for classical radiation damping it can be seen easily that $\gamma_2 = \frac{1}{2}\gamma_1$, so this part is also consistent with our earlier expression. It should be emphasized that this coherent part is solely responsible for the index of refraction of the medium.[5] Also, in a medium with dimensions much larger than the wavelength, the amplitudes of the scattered fields should be added with their proper phases, giving rise to coherent phenomena[42] (superradiance, photon echoes, self-induced transparency).

## IV. PULSE AND STEADY-STATE SOLUTIONS

In this section, we will concentrate on the various components of the emission when they are spectrally resolved. In particular, results will be obtained for their time evolution under pulsed excitation. The condition for spectral resolution is that the offset be sufficiently large $|\Delta| \gg \gamma_{1,2}$ or, if this is not the case, that the Stark shift be sufficiently large, which for $\Delta = 0$ gives $\Omega \gg \gamma_{1,2}$ as seen from Eqs. (6) and (8). In order to make use of the expressions obtained above for the emission rates, it is necessary to know the diagonal elements of $\rho^D$. As pointed out before, the Bloch equations with the proper inclusion of relaxation terms provide a fully self-consistent picture, i.e., a picture which properly accounts for the contributions to $\rho^D$ of all relaxation and radiation processes. Our main emphasis will be on the adiabatic approximation which provides insight into the origin of the processes.

The adiabatic theorem states that for a pulse of light off resonance, which is switched slowly enough, the atomic system passes through a continuous succession of stationary states.[47,48] In the vector model this implies that $\vec{S}$ and $\vec{E}_{\text{eff}}$ are nearly parallel (or antiparallel) in the rotating frame, as can be seen from Eq. (15). [Actually $\cos\alpha = -\text{sgn}(\Delta)$, i.e., for $\Delta > 0$, $\cos\alpha = -1$ and for $\Delta < 0$, $\cos\alpha = 1$.] We will concentrate on the parallel case. Using the vector model, the conditions for adiabatic following[42,48,49] are seen in a pictorial way (Fig. 3). The speed of $\vec{S}$ on the unit sphere is $\alpha E_{\text{eff}}$ and this must compensate for the motion of $\vec{E}_{\text{eff}}$ which is $d\theta/dt$. We demand $\alpha \ll \theta$ which for small $\theta$ is stronger than $\alpha \ll 1$. Thus

$$\frac{d\theta}{dt} \approx \alpha E_{\text{eff}} \ll \theta E_{\text{eff}} , \tag{38a}$$

which for $\theta \ll 1$ reduces to

$$\left|\frac{1}{\mathcal{E}}\frac{d\mathcal{E}}{dt}\right| \ll |\Delta| . \tag{38b}$$

For large $\theta$ the condition is $|\mathcal{E}^{-1}d\mathcal{E}/dt| \ll |\Delta\theta/\sin\theta|$ which deviates appreciably from Eq. (38b) only at

very large angles. A second condition is on the magnitude of the relaxation. The same geometric argument yields that the motion on $\vec{S}$ caused by relaxation, $\theta\gamma_2$, has to be compensated by $\alpha E_{\text{eff}}$, or

$$|\Delta/\cos\theta| \gg \gamma_2 \ . \tag{39}$$

(More accurate calculations can be made using the steady-state solution given in Appendix B.) Thus, one has the general adiabatic condition that the Fourier components of the exciting pulse should not overlap appreciably the spectral components of the absorption line. These results are so important that they are derived again in Appendix A, from perturbation theory. It should be noted that the adiabatic condition is precisely the first condition for spectral resolution. In the case where $|\Delta| < \gamma_{1,2}$ but where the Stark shift is sufficiently large $|p\mathcal{E}/\hbar| \gg \gamma_{1,2}$ it is possible to attain spectral resolution without adiabaticity; this is usually called transient nutation.

In the adiabatic approximation $|\cos\alpha| = 1$ is a constant of the motion and the equations of motion reduce to a single one that we derive now. $S$ is the magnitude of $\vec{S}$, which can be calculated directly from Eq. (10)

$$\frac{1}{2}\frac{d}{dt}(S^2) = S_x\dot{S}_x + S_y\dot{S}_y + S_z\dot{S}_z$$

$$= -\gamma_2 S^2 - (\gamma_1 - \gamma_2)S_z^2 - \gamma_1 S_z \ , \tag{40}$$

which for $|\cos\alpha| = 1$ reduces to

$$\frac{dS}{dt} = -(\gamma_2 \sin^2\theta + \gamma_1 \cos^2\theta)S + \gamma_1 \cos\theta \ . \tag{41}$$

This is an extremely simple differential equation and the remainder of this section will mostly discuss its implications.

With the same approximation ($|\cos\alpha| = 1$) one should note that in the two-level case, Fig. 1(a), there is an expectation value to the dipole moment proportional to $S\sin\theta$ which radiates classically. The corresponding elastic Rayleigh component is proportional to the square of the dipole and is thus [see Eq. (37)]

$$W_{R,\text{elast}} = \left(\frac{\omega}{\omega_{21}}\right)^3 \frac{1}{\tau_{21}} \left(\frac{S}{2}\sin\theta\right)^2 \ . \tag{42}$$

This equation shows the well-known result that at low intensity ($|\theta| \ll 1$) the entire Rayleigh component [Eq. (35)] is elastic.[2,3] As the intensity is decreased, $W_{R,\text{elast}}/W_R$ decreases with $S^2$ whereas the inelastic part $W_{R,\text{inel}} = W_R - W_{R,\text{elast}}$ increases with $1 - S^2$. At saturation $S \cong 0$ and only the inelastic component remains. It is then field independent since $\sin^2\theta \cong 1$. The inelastic part can be compared to $W_{R,2}$ given by Eq. (29). One finds $W_{R,2}/W_{R,\text{inel}} = [2(1+S)]^{-1} \simeq \frac{1}{4}$ at low intensity.

### A. Short adiabatic pulse

When the incident field is far from resonance, it is easy to construct a pulse that is both adiabatic and shorter than the relaxation time, i.e., it satisfies the dual condition $|\Delta| \gg \tau_P^{-1} \gg \gamma_1, \gamma_2$, where $\tau_P$ is the length of a "monochromatic" laser pulse. To a good approximation, the solution of Eq. (40) is then $S = S_0 = 1$. Note that $\theta$ follows the pulse, $\theta = \arctan(p\mathcal{E}/\hbar\Delta)$. From Eq. (15) one immediately gets $\rho_{11}^D = 1$ and $\rho_{22}^D = 0$.

In a three-level system, Fig. 1(b), we get from Eqs. (17) and (19) that *during* the pulse $W_R = (\omega_R/\omega_{23})^3 \tau_{23}^{-1} \sin^2\tfrac{1}{2}\theta$; $W_F = 0$. After the pulse $\theta = 0$, and $W_R = W_F = 0$. Thus, there is Raman emission that terminates with the pulse but no fluorescence at all. This is the first example of the identification of the Raman effect with the adiabatic component. The absorption in the three-level system of Fig. 1(c) behaves similarly. There is two-photon absorption that follows the pulse but no sequential (two-step) absorption.

In a two-level system, we find Rayleigh scattering (all elastic) during the pulse, having the intensity $W_R = (\omega/\omega_{21})^3 \tau_{21}^{-1}(\frac{1}{2}\sin\theta)^2$ and three-photon scattering with intensity $W_3 = (\omega_3/\omega_{21})^3 \tau_{21}^{-1}[\frac{1}{2}(1 - \cos\theta)]^2$. Within the approximation $\rho_{22}^D = 0$ there is no fluorescence. (In fact, the three-photon process populates the upper state and with a better approximation one obtains from the Bloch equation the correct $\rho_{22}^D$ self-consistently, as will be seen later.) Within the present approximation $W_F = \tau_{21}^{-1} \int W_3\, dt \cong 0$. Both $W_R$ and $W_3$ terminate with the pulse. For small incident intensity $\theta \ll 1$, the Rayleigh scattering is linear in the intensity and the three-photon scattering is quadratic. For high intensities, $|p\mathcal{E}/\hbar\Delta| \gg 1$, they both saturate.

In an earlier Comment,[35] we calculated these basic processes for weak fields and coined the Raman and Rayleigh components as "adiabatic" parts. The three-photon component also shares this property, as seen above. The above results would also be obtained with an *incoherent* adiabatic excitation. Thus, the recent observation by Grischkowsky[40] on a three-level system [Fig. 1(c)] should be interpreted in terms of adiabaticity versus nonadiabaticity rather than coherence versus incoherence.

### B. Steady-state solution

When the exciting light is on for a long time ($t \gg \gamma_1^{-1}, \gamma_2^{-1}$) steady state is reached. The Bloch equations have a well-known simple algebraic solution for the general case, as shown in Appendix B. Here, we prefer to concentrate on the adiabatic case $|\Delta| \gg \gamma_{1,2}$. Results obtained in this way

are also valid for the other spectrally resolved case $|\Omega| \gg \gamma_{1,2} > |\Delta|$. This has to do with the fact that $S_z^D$ then becomes equal to the value of $S$ calculated in the adiabatic case (see Appendix B). The steady-state adiabatic value of $S$ follows immediately from Eq. (40):

$$S = \cos\theta/[\cos^2\theta + \eta \sin^2\theta] \ , \tag{43}$$

where we introduced after Mollow,[4]

$$\eta = \gamma_2/\gamma_1 \ . \tag{44}$$

This assumption is made *in lieu* of a theory, it is a strictly phenomenological one. In the weak-field case, near line center, Huber[12] and Omont *et al.*[13] found

$$\gamma_1 = 2(\gamma_N + \gamma_I), \quad \gamma_2 = \gamma_E + \gamma_N + \gamma_I \ , \tag{45}$$

where $\gamma_N$ is the radiative decay rate of the upper state, $\gamma_E$ is the rate of quasielastic collisions,[24] and $\gamma_I$ is the inelastic collision rate. In the collisionless case, it was found for arbitrary fields, that $\gamma_1 = 2\gamma_N$, $\gamma_2 = \gamma_N$.[2,5-9] Thus in the collisionless case $\eta = \frac{1}{2}$, while collisions make $\eta > \frac{1}{2}$.

The emission intensities will be calculated for a two-level system using Eqs. (15), (31), (33), and (35), and Eqs. (17) and (19) for the three-level system. From Eq. (15), one finds using Eq. (43) and $(\cos\alpha) = 1$,

$$\rho_{22}^D = \frac{1-S}{2} = \frac{1}{2}\left(1 - \frac{\cos\theta}{\cos^2\theta + \eta\sin^2\theta}\right)$$

$$= \frac{1}{2}\,\frac{\Delta^2 + \eta\Omega^2 - \Delta\Omega'}{\Delta^2 + \eta\Omega^2} \ , \tag{46a}$$

$$\rho_{11}^D = 1 - \rho_{22}^D = \frac{1}{2}\,\frac{\Delta^2 + \eta\Omega^2 + \Delta\Omega'}{\Delta^2 + \eta\Omega^2} \ . \tag{46b}$$

We first calculate the two-level case. The intensities are: (i) Rayleigh, from Eq. (31):

$$W_R = \left(\frac{\omega}{\omega_{21}}\right)^3 \frac{1}{\tau_{21}}\left(\frac{1}{2}\sin\theta\right)^2$$

$$= \frac{1}{4\tau_{21}}\left(\frac{\omega}{\omega_{21}}\right)^3 \frac{\Omega^2}{\Omega^2 + \Delta^2} \ . \tag{47}$$

(ii) Fluorescence, from Eq. (33):

$$W_F = \frac{1}{\tau_{21}}\,\rho_{22}^D \left(\frac{1+\cos\theta}{2}\right)^2$$

$$= \frac{1}{8\tau_{21}}\,\frac{\Delta^2 + \eta\Omega^2 - \Delta\Omega'}{\Delta^2 + \eta\Omega^2}\,\frac{(\Omega' + \Delta)^2}{\Omega^2 + \Delta^2}$$

$$= \frac{1}{8\tau_{21}}\,\frac{\Omega^2(\Omega' + \Delta)[\eta(\Omega' + \Delta) - \Delta]}{(\Omega^2 + \Delta^2)(\eta\Omega^2 + \Delta^2)} \ . \tag{48}$$

(iii) Three-photon scattering, from Eq. (35):

$$W_3 = \left(\frac{\omega_3}{\omega_{21}}\right)^3 \frac{1}{\tau_{21}}\,\rho_{11}^D \left(\frac{1-\cos\theta}{2}\right)^2$$

$$= \left(\frac{\omega_3}{\omega_{21}}\right)^3 \frac{1}{8\tau_{21}}\,\frac{\Delta^2 + \eta\Omega^2 + \Delta\Omega'}{\Delta^2 + \eta\Omega^2}\,\frac{(\Omega' - \Delta)^2}{\Omega^2 + \Delta^2}$$

$$= \left(\frac{\omega_3}{\omega_{21}}\right)^3 \frac{1}{8\tau_{21}}\,\frac{\Omega^2(\Omega' - \Delta)[\eta(\Omega' - \Delta) + \Delta]}{(\Omega^2 + \Delta^2)(\eta\Omega^2 + \Delta^2)} \ . \tag{49}$$

These last equations [Eqs. (47)–(49)], are identical to those obtained by Mollow in 1969 for the pure radiative case,[2] $\eta = \frac{1}{2}$, and in the more general case recently,[50] using a more fundamental but less intuitive approach. Note that only $\eta = \gamma_2/\gamma_1$ appear explicitly in these equations. This is in accordance with the adiabatic approximation. It should be mentioned that for $\eta = \frac{1}{2}$, $W_F = W_3$ as expected from the discussion above, and when $\eta > \frac{1}{2}$ elastic collisions contribute to an enhanced fluorescence component. In recent work of Carlsten and Szöke,[24] there is a detailed discussion of these equations and they are compared with experiments.

In the three-level case [Fig. 1(b)] one finds using Eqs. (17) and (19): (i) Raman emission:

$$W_R = \left(\frac{\omega_R}{\omega_{23}}\right)^3 \frac{1}{\tau_{23}}\,\rho_{11}^D\,\frac{1-\cos\theta}{2}$$

$$= \frac{1}{4\tau_{23}}\left(\frac{\omega_R}{\omega_{23}}\right)^3 \frac{\Delta^2 + \eta\Omega^2 + \Delta\Omega'}{\Delta^2 + \eta\Omega^2}\left(1 - \frac{\Delta}{\Omega'}\right)$$

$$= \frac{1}{4\tau_{23}}\left(\frac{\omega_R}{\omega_{23}}\right)^3 \frac{\Omega^2[\eta(\Omega' - \Delta) + \Delta]}{\Omega'(\Delta^2 + \eta\Omega^2)} \ . \tag{50}$$

(ii) Fluorescence:

$$W_F = \frac{1}{\tau_{23}}\,\rho_{22}^D\,\frac{1+\cos\theta}{2} = \frac{1}{4\tau_{23}}\,\frac{\Omega^2[\eta(\Omega' + \Delta) - \Delta]}{\Omega'[\Delta^2 + \eta\Omega^2]} \ . \tag{51}$$

In the pure radiative case, $\eta = \frac{1}{2}$, the Raman emission is much stronger than the fluorescence which is quadratic in the incident intensity for weak fields. For elastic collisions such that $\gamma_E = \gamma_N$, and $\gamma_I$ is negligible, one has $\eta = 1$ and the Raman emission equals the fluorescence intensity. For large $\eta$ the fluorescence becomes much stronger than the Raman emission. In the three-level system, only the dynamics of the two levels connected with the strong field are solved, the emission to the third level is considered to be a probe.

In the absorption case [Fig. 1(c)] similar results are obtained; the appropriate integrated absorption lines have the same dependence of $\Omega$, $\Omega'$, $\Delta$, and $\eta$ as shown in Eqs. (50) and (51).

### C. Adiabatic square pulse

Let us introduce the concept of an adiabatic square pulse. It has rise and fall times that are long compared with $|\Delta|^{-1}$, but a duration $\tau_P$ that

is long compared to the rise and fall times. The detuning $|\Delta|$ has to be larger than $\gamma_{1,2}$. During the pulse itself, the field amplitude $\mathcal{E}$ is constant. Many experimental situations are well approximated with such a pulse. It can be easily constructed, e.g., by gating a cw dye laser. In fact, for a sufficiently large $\Delta$ it is hard to visualize an experimentally made pulse that does not satisfy the adiabatic condition. (To the best of our knowledge, the power spectrum of all gated optical pulses falls off in the wings at least exponentially.)

The great advantage of the adiabatic square pulse is that the equations of motion are easily solved in the general case. During the risetime $S=1$, and $\theta$ increases to its value given by $\mathcal{E}$. These are then the initial conditions for the solution of Eq. (41):

$$S(t)=\frac{\cos\theta}{\cos^2\theta+\eta\sin^2\theta}+\left(1-\frac{\cos\theta}{\cos^2\theta+\eta\sin^2\theta}\right)\times\exp[-\gamma_1(\cos^2\theta+\eta\sin^2\theta)t]\ , \tag{52}$$

where

$$\theta(t)=\arctan(p\mathcal{E}/\hbar\Delta),\quad 0\leq t\leq\tau_p\ .$$

During the fall time of the pulse $S=S(\tau_p)$ and $\theta$ decreases to zero. After the pulse, $S$ decays to its steady-state value:

$$S(t)=1+[S(\tau_p)-1]\exp[-\gamma_1(t-\tau_p)]\ , \tag{53}$$

with

$$\theta(t)=0,\quad t>\tau_p\ .$$

These equations (52) and (53) give the explicit time dependence of $S(t)$. Remembering that $\cos\alpha$ is a constant in the adiabatic approximation, Eq. (15) can be used to obtain $\rho_{11}^D$, $\rho_{22}^D$, and the emitted intensity calculated using Eqs. (31), (33), and (35) for the two-level case, and Eqs. (17) and (19) for the three-level system. Rather than doing this, a qualitative discussion will be given of the general features of the time dependence of the various spectral components and some illustrative examples will be provided.

First, it should be noted that various regimes exist for Eqs. (52) and (53). These are: (i) weak pulses ($|\theta|\ll 1$) versus strong pulses; (ii) short pulses [$\gamma_1(\cos^2\theta+\eta\sin^2\theta)\tau_p\ll 1$] versus long pulses; (iii) saturating pulses [$\cos\theta/(\cos^2\theta+\eta\sin^2\theta)\ll 1$] versus nonsaturating pulses. For weak pulses, the saturation condition is $\eta\theta^2\gg 1$. For strong pulses it can be written $\eta\sin^2\theta\gg\cos\theta$.

Let us now consider the three-level system, Fig. 1(b). For a weak, nonsaturating pulse,

$$S(t)\cong 1-(\eta-\tfrac{1}{2})\theta^2[1-\exp(-\gamma_1 t)],\quad 0\leq t\leq\tau_p \tag{54}$$

if the pulse is also short, $S(t)\cong 1-(\eta-\frac{1}{2})\theta^2\gamma_1 t$, for $0\leq t\leq\tau_p$. The Raman signal follows the pulse,

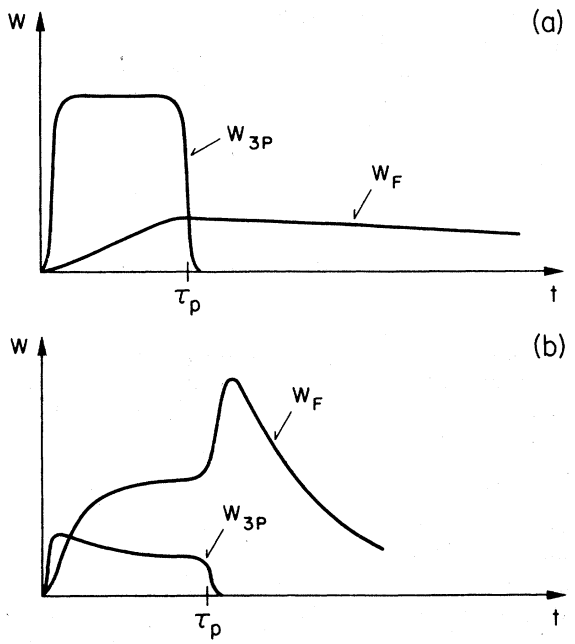


FIG. 5. Time-dependent three-photon scattering and fluorescence produced by an adiabatic square pulse of duration $\tau_p$. Rayleigh component is not shown and simply follows the pulse: (a) weak short nonsaturating excitation with $\eta=\frac{1}{2}$. (b) strong long saturating pulse with $\tan\theta=3$, $\gamma_1\tau=3$, $\eta=3$.

as $\rho_{11}^D\cong 1$ and is proportional to $(\frac{1}{2}\theta)^2$. The fluorescence from Eq. (19) is proportional to $\eta-\frac{1}{2}$, which is the nonradiative part of the relaxation; it vanishes for radiative decay only; it integrates the pulse and decays slowly afterwards.[36] This behavior is illustrated in Fig. 5(a). That figure is actually drawn for the resonance fluorescence case [Fig. 1(a)] but the Raman case [Fig. 1(b)] is qualitatively similar. For $\eta=1$ the integrated Raman signal equals the integrated fluorescence signal. The ratio $W_F(\tau_P)/W_R=2\tau_p(2\gamma_2-\gamma_1)$ for $\tau_p\ll\gamma_1^{-1}$. It is independent of the detuning $\Delta$ as long as $\eta$ is independent of $\Delta$, explaining the results of Williams *et al.*[34] For large detunings, collisions become less effective to supply or absorb the energy required to produce transitions between the dressed states $|2,n\rangle$ and $|1,n+1\rangle$.[24,35] If the weak nonsaturating pulses are long, $\rho_{22}^D(\tau_P)\cong\frac{1}{2}(\eta-\frac{1}{2})\theta^2$, and $W_F(\tau_P)/W_R=(2\gamma_2-\gamma_1)/\gamma_1$.

For strong pulses, there is a sudden increase in fluorescence when the pulse terminates. Indeed $\rho_{22}^D$ does not change rapidly, but the decay rate of state $|2\rangle$ suddenly increases when $\theta$ returns to zero at $\tau_P$, as seen in Eqs. (19) and (33). This effect is particularly strong for the resonance fluorescence case of Fig. 1(a) and is seen in Fig. 5(b) for the case of a strong, long, saturating pulse.

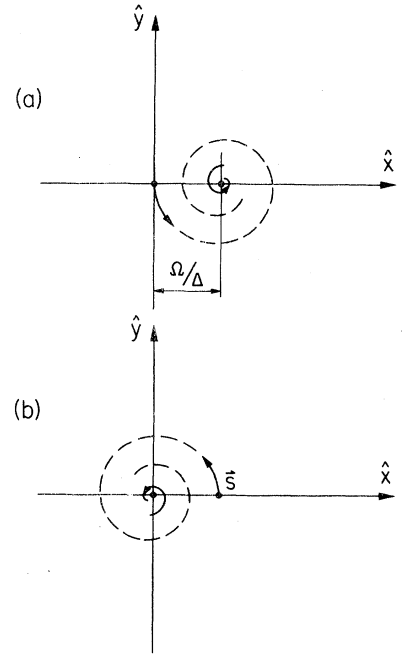


FIG. 6. Nonadiabatic excitation by a weak step. Motion of $\vec{S}$ is pictured by following the intersection of $\vec{S}$ with a plane tangent to the bottom of the Bloch sphere and designated by $(\hat{x},\hat{y})$. (a) Step is turned on; (b) step is turned off after a long time.

In the case of resonance scattering [Fig. 1(a)], both the Rayleigh component and the three-photon component exist only during the pulse.[24] The integrated intensity of the Rayleigh component is constant, but its coherence and spectral composition will change with time as predicted by Eqs. (41) and (42). This will be particularly strong when the pulse is saturating. For weak, nonsaturating, short pulses

$$W_3 \simeq \tfrac{1}{16}\theta^4 ,$$

whereas

$$W_F(\tau_P) \simeq 1/2(\eta - \tfrac{1}{2})\theta^2\gamma_1\tau_P \quad \text{for} \quad \eta > \tfrac{1}{2} .$$

This gives

$$W_F(\tau_P)/W_3 = 8(\eta - \tfrac{1}{2})\gamma_1\tau_P\Delta^2/\Omega^2 .$$

For long pulses

$$W_F(\tau_P) \simeq 1/2(\eta - \tfrac{1}{2})\theta^2$$

and thus

$$W_F(\tau_P)/W_3 = 8(\eta - \tfrac{1}{2})\Delta^2/\Omega^2 .$$

The short-pulse case is represented in Fig. 5(a). Again, by a relative measurement of the two sidebands observed in resonance scattering specific information can be obtained on the dependence of $\gamma_2$ on detuning.

### D. Nonadiabatic excitation

As it was pointed out in the beginning of this section, if the pulse has spectral overlap with $\omega_{21}$ nonadiabatic excitation results, and there is emission around $\omega_{21}$. This subject has received detailed attention in a number of theoretical papers.[5]

In principle, the Bloch equations [Eq. (10)] have to be solved, and this can be done at least numerically. As an illustrative example, we investigate the application of a weak ($\theta \ll 1$) step pulse and the switching off of such a pulse after a long time. Consider the rotating coordinate system in Fig. 6. When a step pulse is applied nonadiabatically, $\vec{E}_{\text{eff}}$ moves to its new position suddenly and stays there. $\vec{S}$ starts precessing around it, and it spirals in a time comparable to $\gamma_2$, as depicted in Fig. 6(a). It is easy to see that there is initially an equal amount of Rayleigh scattering and fluorescence. Considering the quantities $S_x$, $S_y$, and their time dependence, it is also easily seen that there is a *coherent* emission both at $\omega$ and at $\omega_{12}$. The coherence of the emission shows up in the definite phase relation between the two emitted fields, and the fact that in a macroscopic system (with dimensions $\gg \lambda$) the emission at both frequencies is directional. In addition, there is a side emission coming from density fluctuations.

When the pulse is suddenly turned off, after having been on for a long time, $\vec{S}$ starts free precession and it emits at $\omega_{12}$ a decaying exponential. This emission is also coherent (super-radiant) in the same sense as above. These, and similar effects in the optical spectrum have been studied by Brewer and co-workers in elegant experiments.[52] Also, very similar considerations give the results of Refs. 51.

The above example illustrates again that it is the adiabaticity that distinguishes Raman emission, two-photon absorption, Rayleigh, and three-photon scattering from fluorescence and stepwise absorption. When the adiabatic condition is not satisfied, coherent emission may result at the resonance frequency $\omega_{21}$.

## V. RIGOROUS CALCULATION OF TIME-DEPENDENT SPECTRA AND SUM RULES

Time-dependent spectra can be defined rigorously in an operational manner. In the absorption case of Fig. 1(c), one can measure the time dependence of the intensity of a weak monochromatic probing beam of tuneable frequency near $\omega_{32}$. Sequential absorption and two-photon absorption will be seen, caused by the pulse of carrier frequency $\omega$. In the emission case of Figs. 1(a) and (b), spectral definition will be achieved by means of a spectroscopic instrument. Using a sufficiently

wide bandwidth (with a sufficiently wide slit in the spectrometer), there remains information to be gained from the time evolution of the intensity transmitted by the spectrometer. On this basis, one can develop a rigorous description of time-dependent spectra. We shall concentrate here on the emission case.

Let $E(t)$ be the amplitude of the emitted field, which is in the form of a pulse. It is Fourier transformable, at least in the sense of generalized functions, giving

$$e(\omega)=\int_{-\infty}^{+\infty} E(t)e^{i\omega t}dt\,. \tag{55}$$

Let $f(\omega)$ be the transfer function of the spectrometer. This acts on the signal amplitude, giving a filtered field

$$v(\omega)=e(\omega)f(\omega)\,, \tag{56}$$

or

$$V(t)=\int_{-\infty}^{+\infty} E(t')F(t-t')\,dt'\,, \tag{57}$$

where

$$F(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} f(\omega)e^{-i\omega t}\,d\omega \tag{58}$$

is the Fourier transform of the filter function $f(\omega)$. Causality demands that $F(t-t')$ in Eq. (57) be zero for $t'>t$. The simplest possible filter is thus

$$F(t)=\alpha e^{-i\omega_1 t-\alpha t}\Theta(t) \tag{59a}$$

or

$$f(\omega)=\alpha/[\alpha+i(\omega_1-\omega)]\,, \tag{59b}$$

where $\Theta(t)$ is the unit step starting at $t=0$. One sees that $\alpha$ determines the width of the transfer function about its center frequency $\omega_1$, and its peak transmission is unity. The integrated transmission of the filter for white light is proportional to its width,

$$\int_{-\infty}^{+\infty} |f(\omega)|^2\,d\omega=\pi\alpha\,. \tag{59c}$$

The response to white noise is a Lorentzian spectrum centered on $\omega_1$. The use of other similar filter functions would not qualitatively modify the considerations made below and thus we shall limit the discussion to the above filter.

The intensity detected after the filter is, using Eqs. (57) and (59a)

$$I(t;\omega_1,\alpha)=|V(t)|^2$$
$$=\alpha^2\int_{-\infty}^{+\infty} E(t')E^*(t'')e^{-(i\omega_1+\alpha)(t-t')}\,e^{(i\omega_1-\alpha)(t-t'')}\Theta(t-t')\Theta(t'-t'')\,dt'\,dt''\,. \tag{60a}$$

The upper limit of integration is actually $t$, and the $(t',t'')$ plane is divided into two regions characterized by $t'>t''$ and $t'<t''$, respectively. With an interchange of the integration variables in the second region, followed by a change of variable $t'=t''+\tau$, one obtains

$$I(t;\omega_1,\alpha)=2\alpha^2\int_{-\infty}^{t} dt'e^{-2\alpha(t-t')}$$
$$\times\,\mathrm{Re}\int_0^{\infty} E(t')E^*(t'-\tau)e^{i\omega_1\tau-\alpha\tau}\,d\tau\,. \tag{61}$$

The instantaneous intensity is always finite for a pulse. Using the Fourier transform relation,

$$I(t;\omega_1,\alpha)=|V(t)|^2$$
$$=\frac{1}{(2\pi)^2}\int\int d\omega\,d\omega'\,V(\omega)\,V^*(\omega')e^{-i(\omega-\omega')t}$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\,|e(\omega)|^2\,|f(\omega)|^2\,, \tag{60b}$$

and the normalization, Eq. (59c), the power spectrum can be defined as

$$I(\omega_1)\equiv\lim_{\alpha\to 0}\frac{1}{\alpha}I(t;\omega_1,\alpha)=|e(\omega_1)|^2\,. \tag{62a}$$

For a stationary field, i.e., when the correlation function, $E(t)E^*(t-\tau)$ depends only on the time difference, $\tau$, from Eq. (61) we get the usual definition,

$$I(\omega_1)=\mathrm{Re}\int_0^{\infty} E(t')E^*(t'-\tau)e^{i\omega_1\tau}\,d\tau\,. \tag{62b}$$

We will rather be interested in the other extreme, i.e., $\alpha$ large compared to $\gamma_{1,2}$ and $\tau_p^{-1}$. Referring in particular to the case of Fig. 1(a) contact is made with Mollow's theory when one notes that, in our notation,

$$\langle E(t')E^*(t'-\tau)\rangle\propto\langle\sigma_+(t'-\tau)\,\sigma_-(t')\rangle\equiv g(\tau;t'-\tau)\,. \tag{63}$$

The Heisenberg operators $\sigma_+$ and $\sigma_-$ will be taken in the rotating frame so that all frequencies will already be shifted by $\omega$. In particular, the filter frequency $\omega_1$ is the offset with respect to $\omega$. It should first be noted that Eq. (61) can reproduce the steady-state result of Mollow. Let $\mathcal{E}(t)$ be an adiabatic pulse applied around $t=0$ and consider $I(t)$ at large $t$. Let $\alpha$ also be small but such that

$\alpha t \gg 1$. Then the range of $t'$ in the first integration in Eq. (61) is from $\sim t - (2\alpha)^{-1}$ to $t$. The range of $\tau$ in the second integration is from 0 to $\sim\alpha^{-1}$. Over this range Eq. (63) depends only on the time difference $\tau$ and one finds

$$I(\omega_1) \propto \mathrm{Re}\int_0^\infty g(\tau;\sim t)\, e^{i\omega_1\tau}\, d\tau\,, \tag{64}$$

where the initial values for the correlation function $g$ in Eq. (64) are the steady-state values. This is just the spectrum as a function of $\omega_1$, as calculated by Mollow.[2]

Now, let us consider the general transient case. The expression for $g(\tau;t')$ is obtained following Mollow.[2] One uses the evolution operator $U(t,t')$, where $t - t' = \tau > 0$. One has

$$\rho^R(t) = U(t,t')\,\rho^R(t')\,U^{-1}(t,t') \tag{65}$$

and

$$g(\tau;t') = \langle\sigma_+(t')\,\sigma_-(t)\rangle = \mathrm{tr}[\rho^R(t')\sigma_+ U^{-1}(t,t')\,\sigma_- U(t,t')]$$
$$= \rho^R_{12}(t')U^{-1}_{11}\,U_{21} + \rho^R_{22}(t')U^{-1}_{11}\,U_{22}\,. \tag{66}$$

The needed values of $U$, which depend only on the time difference $\tau$, are obtained from a comparison of Eqs. (65), (10), and (11). Specifically, the equations of motion are Laplace transformed and the resulting algebraic equations are solved for $\rho^R(s)$, where $s$ is the Laplace variable, in terms of the initial values $\rho^R(t')$. A comparison with the matrix elements of Eq. (65) gives all the Laplace transforms, $\mathfrak{L}[U^{-1}_{ij}U_{kl}]$. In particular, one finds

$$a(s) \equiv \mathfrak{L}[U^{-1}_{11}U_{21}] = \frac{i\Omega}{2}\,\frac{(s+\gamma_1)(s+\gamma_2+i\Delta)}{sf(s)}\,, \tag{67a}$$

$$b(s) \equiv \mathfrak{L}[U^{-1}_{11}U_{22}] = \frac{\frac{1}{2}\Omega^2 + (s+\gamma_1)(s+\gamma_2+i\Delta)}{f(s)}\,, \tag{67b}$$

where

$$f(s) \equiv (s+\gamma_1)(s+\gamma_2+i\Delta)(s+\gamma_2-i\Delta) + \Omega^2(s+\gamma_2)\,. \tag{67c}$$

For simplicity's sake we have defined the quantities $a(s)$ and $b(s)$ whose inverse transforms $A(\tau)$ and $B(\tau)$ enter in Eq. (66). One thus has

$$g(\tau;t') = \rho^R_{12}(t')A(\tau) + \rho^R_{22}(t')B(\tau)\,. \tag{68}$$

By combining Eq. (68), (63), and (61) one obtains the time-dependent spectrum

$$I(t;\omega_1,\alpha) = 2\alpha^2\int_{-\infty}^{t} dt'\, e^{-2\alpha(t-t')}\,\mathrm{Re}\int_0^\infty \rho^R_{12}(t'-\tau)A(\tau)e^{-(\alpha-i\omega_1)\tau}\,d\tau$$
$$+ 2\alpha^2\int_{-\infty}^{t} dt' e^{-2\alpha(t-t')}\,\mathrm{Re}\int_0^\infty \rho^R_{22}(t'-\tau)B(\tau)e^{-(\alpha-i\omega_1)\tau}\,d\tau\,. \tag{69}$$

Let us now concentrate on situations where the time evolution of $\rho^R$ is slow compared to $\alpha^{-1}$. This corresponds precisely to a measurement of the individual spectral components in the adiabatic case as discussed in the previous sections. In such circumstances, $\rho^R$ can be considered as constant over the relevant range of $\tau$ in Eq. (69), and thus can be pulled out of the second integral. Similarly, it can be considered constant over the relevant range of $t'$, and one ends up with

$$I(t;\omega_1,\alpha) \simeq \alpha\rho^R_{12}(t)\,\mathrm{Re}a(\alpha - i\omega_1)$$
$$+ \alpha\rho^R_{22}(t)\,\mathrm{Re}b(\alpha - i\omega_1)\,, \tag{70}$$

where we have used the definitions of the Laplace transforms $a(s)$ and $b(s)$, and where we have remarked that $\rho^R_{12}$ is real in the adiabatic case ($S_y \cong 0$). In fact, using Eqs. (11) and (6), $\rho^R_{12} = -\frac{1}{2}S\sin\theta$ and $\rho^R_{22} = \frac{1}{2}(1 - S\cos\theta)$. Finally, it should be remarked that within the same adiabatic approximation, $\Omega$ can be considered as a slow function of $\mathcal{E}$ in $a(\alpha - i\omega_1)$ and $b(\alpha - i\omega_1)$. In order to follow the time evolution produced by relaxation, it is necessary to have $\alpha \ll \gamma_{1,2}$, and, in order to achieve spectral resolution, it is necessary to have $\alpha \ll |\Delta|$ or $|\Omega'|$, where $\Omega'$ was defined in Eq. (47). Under such conditions, it is easy to calculate Eq. (70) using the above approximations together with Eq. (67). One finds a three-peak spectrum with peaks at $\omega = 0$ and $\omega = \pm\Omega'$. With the broad slit ($\alpha \gg \gamma_{1,2}$) the value of $I(t;\omega_1,\alpha)$ at the peak is the integral of the spectrum over the peak width. What one finds is summarized in Table I. The last line in this table is obtained from the two previous lines using $\sin\theta = \Omega/\Omega'$, $\cos\theta = \Delta/\Omega'$, and the values of $\rho^R_{12}$ and $\rho^R_{22}$ given above. The result is proportional to the rates given in Eqs. (35), (31), and (33). The only difference is that the factors in $(\omega/\omega_{21})^3$ have now disappeared. This is a minor change for the shifts of usual interest.

The sum rule is established directly from (63).[2,3,9,53] The instantaneous total intensity is proportional to the equal-time correlation function

$$\langle\sigma_+(t)\,\sigma_-(t)\rangle = \mathrm{tr}[\rho^R(t)\,|\psi^R_2\rangle\langle\psi^R_1|\,|\psi^R_1\rangle\langle\psi^R_2|\,] = \rho^R_{22}(t) \tag{71}$$

which should be compared to Eq. (36).

## APPENDIX A: ADIABATIC APPROXIMATION IN PERTURBATION THEORY, DISPERSION FORMULA

In this appendix the adiabatic approximation for weak fields will be derived. This is interesting for several reasons. First it makes connection with

TABLE I. Calculations for the spectral components with wide slits.

| Position<br>Process | $\omega=0$<br>Rayleigh | $\omega=\Omega'$<br>Three-photon | $\omega=-\Omega'$<br>Fluorescence |
|---|---|---|---|
| $\propto \mathrm{Re}\, a(\alpha-i\omega_1)$ | $-\frac{\frac{1}{2}\Omega\Delta}{\Omega'^2+\alpha^2}$ | $-\frac{\Omega\Omega'^2(\Omega'-\Delta)+\alpha^2\Omega(\Omega'+\frac{1}{2}\Delta)}{(\Omega'^2+\alpha^2)(4\Omega'^2+\alpha^2)}$ | $\frac{\Omega\Omega'^2(\Omega'+\Delta)+\alpha^2\Omega(\Omega'-\frac{1}{2}\Delta)}{(\Omega'^2+\alpha^2)(4\Omega'^2+\alpha^2)}$ |
| $\propto \mathrm{Re}\, b(\alpha-i\omega_1)$ | $\frac{\frac{1}{2}\Omega^2+\alpha^2}{\Omega'^2+\alpha^2}$ | $\frac{2\Omega'(\Omega'-\Delta)(\Omega'^2+\alpha^2)-\Omega^2\Omega'^2}{(\Omega'^2+\alpha^2)(4\Omega'^2+\alpha^2)}$ | $\frac{2\Omega'(\Omega'+\Delta)(\Omega'^2+\alpha^2)-\Omega'^2\Omega^2}{(\Omega'^2+\alpha^2)(4\Omega'^2+\alpha^2)}$ |
| | | $+\frac{\alpha^2(\frac{1}{2}\Omega^2+\Omega'^2+\alpha^2)}{(\Omega'^2+\alpha^2)(4\Omega'^2+\alpha^2)}$ | $+\frac{\alpha^2(\frac{1}{2}\Omega^2+\Omega'^2+\alpha^2)}{(\Omega'^2+\alpha^2)(4\Omega'^2+\alpha^2)}$ |
| $I(t;\omega_1,\alpha)$ for | | | |
| $\alpha \ll \lvert\Delta\rvert$ and/or $\lvert\Omega'\rvert$ | $\sim(\frac{1}{2}\sin\theta)^2$ | $\sim\frac{1}{2}(1+S)[\frac{1}{2}(1-\cos\theta)]^2$ | $\sim\frac{1}{2}(1-S)[\frac{1}{2}(1+\cos\theta)]^2$ |

well-known results showing in particular how they are modified in the adiabatic case. As perturbation theory formulas were used in the initial steps of many papers, it is then very clear how to specialize the final results of those papers for the adiabatic case. Second, several recent authors have have not gone beyond the weak field case, and it is quite instructive to derive the adiabatic limit of their expressions. Third, the spectra of light sources are not Lorentzian in most experiments; resonance lamps have exponential wings, the spectrum of a gated monochromatic laser follows the spectrum of the modulator which is typically exponential (6–12 $dB$/octave).

In first-order time-dependent perturbation theory, the time-dependent solution of Schrödinger's equation, $\psi(t)$ of the Hamiltonian, Eq. (3), is expanded in the wave functions of the atomic states (without the field)

$$\psi(t)=b_1(t)\,\psi_1+b_2(t)\,\psi_2\,, \tag{A1}$$

where at $t\to-\infty$ the atom is in its ground state, $b_1=1$, $b_2=0$. We follow Heitler's notation.[1] The incident field is expanded in a Fourier integral,

$$E(t)=\mathcal{E}(t)e^{-i\omega t}=\frac{1}{2\pi}\int_{-\infty}^{\infty}e(\omega')e^{-i\omega' t}d\omega'\,. \tag{A2}$$

For every Fourier component, the steady-state solution in first-order perturbation theory is given by $b_1=1$,

$$b_2(\omega')=\mu_{12}e(\omega')/\hbar(\omega'-\omega_{12}+\tfrac{1}{2}i\Gamma)\,. \tag{A3}$$

where we introduced a Weisskopf–Wigner-type relaxation rate, $\Gamma$.[1] Therefore the general solution of $b_2(t)$ is given by Fourier transformation:

$$b_2(t)=\frac{1}{2\pi}\int b_2(\omega')e^{-i\omega' t}d\omega'$$

$$=\frac{1}{2\pi}\int\frac{\mu_{12}e(\omega')e^{-i\omega' t}}{\hbar(\omega'-\omega_{21}+\frac{1}{2}i\Gamma)}d\omega'\,, \tag{A4}$$

under the condition that $\mathcal{E}(t)$ drops to zero fast enough when $t\to-\infty$. The adiabatic approximation is valid when the Fourier components of the field do not overlap the absorption profile. If the mean frequency of the field is denoted by $\omega$ as above, and $\Delta\omega$ is the "range" of values of $\omega'$ where $\lvert e(\omega')\rvert$ is large, then the adiabatic condition means $\lvert\omega-\omega_{12}\rvert \gg \Delta\omega$, $\Gamma$. Under these conditions, in first approximation the denominator in Eq. (A4) can be taken as $\omega-\omega_{21}+i\Gamma$, a constant, giving

$$b_2(t)\cong\frac{\mu_{12}}{\hbar(\omega-\omega_{21}+i\Gamma/2)}\frac{1}{2\pi}\int e(\omega')e^{-i\omega' t}d\omega'$$

$$=\frac{\mu_{12}E(t)}{\hbar(\omega-\omega_{21}+\frac{1}{2}i\Gamma)}\,, \tag{A5}$$

it can be seen that the upper-state amplitude follows the incident field adiabatically. A more accurate solution can be obtained by expanding the denominator:

$$\frac{1}{\omega'-\omega_{21}+\frac{1}{2}i\Gamma}=\frac{1}{\omega-\omega_{21}+\frac{1}{2}i\Gamma}+\frac{\omega-\omega'}{(\omega-\omega_{21}+\frac{1}{2}i\Gamma)^2}+\cdots\,, \tag{A6}$$

giving, after some rearrangement,

$$b_2(t)=\frac{\mu_{12}\mathcal{E}(t)e^{-i\omega t}}{\hbar(\omega-\omega_{21}+\frac{1}{2}i\Gamma)}-\frac{i\mu_{12}}{\hbar(\omega-\omega_{21}+\frac{1}{2}i\Gamma)^2}\frac{d\mathcal{E}(t)}{dt}e^{-i\omega t}+\cdots\,. \tag{A7}$$

This shows that the critical parameter in the expansion is

$$\frac{\lvert d\mathcal{E}(t)/dt\rvert}{\lvert\omega-\omega_{21}\rvert}\,;$$

also that sharp derivatives cause nonadiabaticity. The second term is out of phase. It should be noted

that it was implicitly assumed that the spectrum of the field $e(\omega')$ is nonLorentzian.

There are several simple generalizations of the above. The formula for the resonance Raman effect from second-order perturbation theory can be treated similarly, giving, in the adiabatic approximation

$$I_R(t) \sim |\mu_{12}\mu_{23}/\hbar\Delta|^2 I_L(t). \tag{A8}$$

Similar extensions can be done for the two-photon absorption and the Kramers-Heisenberg dispersion formula. It should be noted that all our results in the main part of the paper can be reproduced in the low-field limit.

Another extension can be made for the quantum-electrodynamic formalism introduced by Kroll.[54] Using the formalism of Mukamel and Jortner[51] one can obtain the formulas for the pulse:

$$\phi(t) = \int dk\, A_k e^{i(\bar{k}-k)t}, \tag{A9}$$

where $A_k$ are the quantum-mechanical field operators (vector potential). The photon counting rate is

$$F = \Gamma P_s(t) = \Gamma |V_{gs}|^2 |\Phi_s(t)|^2, \tag{A10}$$

where $|V_{gs}|^2$ is the matrix element, and the "exact" solution is

$$\Phi_s(t) = \int_{-\infty}^{t} d\tau\, \phi(t) \exp[-\tfrac{1}{2}\Gamma(t-\tau) - i\Delta\tau]. \tag{A11}$$

The detuning $\Delta = (\bar{k} - E_s)/\hbar$. Substituting Eq. (A9) into Eq. (A11), we get

$$\Phi_s(t) = \int_{-\infty}^{t} d\tau \int dk A_k \times \exp[-\tfrac{1}{2}\Gamma(t-\tau) + i(E_s - k)(t-\tau)]$$
$$= \int dk \frac{A_k \exp[i(E_s - k)t]}{i(E_s - k) + \frac{1}{2}\Gamma}, \tag{A12}$$

a formula similar to Eq. (A4), it can also be treated similarly.

## APPENDIX B: STEADY-STATE SOLUTIONS OF THE BLOCH EQUATIONS

For reference we list here the steady-state solutions of Eq. (10). In the rotating frame:

$$S_x^R = -\Delta\Omega/(\Delta^2 + \gamma_2^2 + \eta\Omega^2),$$
$$S_y^R = -\gamma_2\Omega/(\Delta^2 + \gamma_2^2 + \eta\Omega^2), \tag{B1}$$
$$S_z^R = -(\Delta^2 + \gamma_2^2)/(\Delta^2 + \gamma_2^2 + \eta\Omega^2).$$

In the dressed-state frame,

$$\vec{S}^D = (S_x^R \cos\theta - S_z^R \sin\theta)\hat{x} + S_y^R \hat{y} + (S_x^R \sin\theta + S_z^R \cos\theta)\hat{z},$$

giving

$$S_x^D = (\sin\theta)\gamma_2^2/(\Delta^2 + \gamma_2^2 + \eta\Omega^2),$$
$$S_y^D = S_y^R, \tag{B2}$$
$$S_z^D = -(\cos\theta)(\Delta^2 + \gamma_2^2 + \Omega^2)/(\Delta^2 + \gamma_2^2 + \eta\Omega^2).$$

It can be seen that for $\Omega' \gg \gamma_2$ both $S_x^D, S_y^D \ll 1$. Also note that for $\Delta \ll \gamma_2$ and $\Omega \gg \gamma_1, \gamma_2$ (strong field, on resonance) the largest component is $S_y^R$, it is of the order $\gamma_2/(\eta\Omega)$, therefore a highly nonadiabatic situation prevails, $\alpha \cong 90°$.

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[1]W. Heitler, *The Quantum Theory of Radiation* (Oxford, U.P., Oxford, 1954).

[2]B. R. Mollow, Phys. Rev. 188, 1969 (1969).

[3]A. P. Kazantsev, Zh. Eksp. Teor. Fiz. 66, 1229 (1974) [Sov. Phys.-JETP 39, 601 (1974)].

[4]B. R. Mollow, Phys. Rev. A 2, 76 (1970); 13, 758 (1976).

[5]S. S. Hassan and R. K. Bullough, J. Phys. B 8, L147 (1975).

[6]B. R. Mollow, Phys. Rev. A 12, 1919 (1975).

[7]H. J. Carmichael and D. F. Walls, J. Phys. B 9, 1199 (1976); M. E. Smithers and H. S. Freedhoff, J. Phys. B 8, 2911 (1975).

[8]J. H. Kimble and L. Mandel, Phys. Rev. A 13, 2123 (1976).

[9]C. Cohen-Tannoudji, *Proceedings of the 2nd Laser Spectroscopy Conference, Megève* (Springer-Verlag, Berlin, 1975); in a conference Prof. Cohen-Tannoudji referred to an extension of that treatment, but no text was available to us at the time of submission of this paper.

[10]C. Cohen-Tannoudji, *Cargèse Lectures in Physics* (Gordon and Breach, London, 1968) Vol. 2.

[11]D. L. Huber, Phys. Rev. 178, 93 (1969).

[12]A. Omont, E. W. Smith, and J. Cooper, Astrophys. J. 175, 185 (1972).

[13]S. Mukamel, A. Ben-Reuven, and J. Jortner, Phys. Rev. A 12, 947 (1975); Chem. Phys. Lett. 38, 394 (1976).

[14]V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 66, 1550 (1974) [Sov. Phys.—JETP 39, 759 (1974)]; 68, 479 (1975) [41, 233 (1975)].

[15]N. M. Kroll and K. M. Watson, Phys. Rev. A 13, 1018 (1976); A. M. F. Lau, *ibid.* 13, 139 (1976).

[16]F. Schuda, C. R. Stroud, Jr., and M. Hercher, J. Phys. B 7, L198 (1974).

[17]F. Y. Wu, R. E. Grove, and S. Ezekiel, Phys. Rev. Lett. 35, 1426 (1975).

[18]H. Walther, on *Proceedings of the 2nd Laser Spectroscopy Conference, Megève, France*, 1975 (Springer-Verlag, Berlin, 1975).

[19]H. M. Gibbs and T. N. C. Venkatesan, IEEE J. Quantum Electron. 11, 91D (1975).

[20]S. H. Autler and C. H. Townes, Phys. Rev. 100, 703 (1955); A. M. Bonch-Bruevich and V. A. Khodovoi, Usp. Fiz. Nauk. 93, 71 (1967) [Sov. Phys. Usp. 10, 637 (1968)].

[21]A. Schabert, R. Keil, and P. E. Toschek, Opt. Com-

mun. 13, 265 (1975).
[22]P. F. Liao and J. E. Bjorkholm, Phys. Rev. Lett. 34, 1 (1975); Opt. Commun. 16, 392 (1976), and references therein.
[23]D. Prosnitz, D. W. Wildman and E. V. George, Phys. Rev. A 13, 891 (1976).
[24]J. L. Carlsten and A. Szöke, Phys. Rev. Lett. 36, 667 (1976); J. Phys. B 9, L231 (1976); J. L. Carlsten, A. Szöke, and M. Raymer, Phys. Rev. A 15, 1029 (1977).
[25]W. Holzer, W. F. Murphy, and J. H. Bernstein, J. Chem. Phys. 52, 399 (1970); W. Kiefer and J. H. Bernstein, J. Mol. Spectrosc. 43, 366 (1972); J. Chem. Phys. 57, 3017 (1972).
[26]D. A. Fouche and R. K. Chang, Phys. Rev. Lett. 29, 536 (1972).
[27]R. L. St. Peters, S. D. Silverstein, M. Lapp and C. M. Penney, Phys. Rev. Lett. 30, 191 (1973).
[28]P. F. Williams and D. L. Rousseau, Phys. Rev. Lett. A 30, 951 (1973); P. Robrish, H. Rosen, and O. Chamberlain, Phys. Lett. A 51, 434 (1975).
[29]L. S. Ditman, R. W. Gammon, and T. D. Wilkerson, Opt. Commun. 13, 154 (1975).
[30]A good review is by P. P. Shorygin, Usp. Fiz. Nauk. 109, 293 (1973) [Sov. Phys. Usp. 16, 99 (1974)].
[31]M. Jacon, *Advances in Raman Spectroscopy* (Heyden and Sons, London, 1972), Vol. 1, p. 324; D. van Labeke, M. Jacon, M. Berjot, and L. Bernard, J. Raman Spectrosc. 2, 219 (1974); M. Jacon and D. van Labeke, Mol. Phys. 29, 1241 (1975).
[32]D. L. Huber, Phys. Rev. B 1, 3409 (1969); Phys. Lett. A 40, 311 (1972).
[33]Y. R. Shen, Phys. Rev. B 9, 622 (1974).
[34]P. F. Williams, D. L. Rousseau, and S. H. Dworetsky, Phys. Rev. Lett. 32, 196 (1974); D. L. Rousseau, A. D. Patterson, and P. F. Williams, *ibid.* 34, 1306 (1975); D. L. Rousseau and P. F. Williams, J. Chem. Phys. 64, 3519 (1976); P. A. Hackett, Phys. Rev. Lett. 36, 1403 (1976); D. L. Rosseau *et al.*, Phys. Rev. Lett. 37, 1441 (1976).
[35]A. Szöke and E. Courtens, Phys. Rev. Lett. 34, 1053 (1975).
[36]Y. Liran, private communication.
[37]See, e.g., Y. R. Shen, Rev. Mod. Phys. 48, 1 (1976) for a recent review and extensive list of references.
[38]See, e.g., M. S. Feld and A. Javan, Phys. Rev. 177, 540 (1969); M. S. Feld, *Fundamental and Applied Laser Physics* (Wiley, New York, 1973); T. Hänsch, and P. Toschek, Z. Phys. (Leipz.) 236, 213 (1970); I. M. Beterov and V. P. Chebotaev, *Progress in Quantum Electronics* (Pergamon, New York, 1974); Vol. 3 also their lists of references.
[39]See, e.g., P. R. Berman, Phys. Rev. A 13, 2191 (1976); R. Salomaa and S. Stenholm, J. Phys. B 9, 1221 (1976); also their lists of references.
[40]D. Grischkowsky, Phys. Rev. A 14, 802 (1976).
[41]J. E. Bjorkholm and P. F. Liao, Phys. Rev. Lett. 33, 128 (1974); Phys. Rev. A 14, 757 (1976); also W. K. Bischel, P. J. Kelly, and C. K. Rhodes, Phys. Rev. Lett. 34, 300 (1975).
[42]Our notation follows closely that of E. Courtens, *Laser Handbook* (North Holland, Amsterdam, p. 1260. 1972),
[43]F. Bloch, Phys. Rev. 105, 1206 (1957); A. G. Redfield, IBM J. Res. Develop. 1, 19 (1957).
[44]S. A. Rautian and I. I. Sobelman, Zh. Eksp. Teor. Fiz. 41, 456 (1961) [Sov. Phys.-JETP 14, 328 (1962)]; also see A. Javan, Phys. Rev. 107, 1579 (1957).
[45]P. P. Sorokin *et al.*, Appl. Phys. Lett. 10, 44 (1967); see also later work by B. R. Mollow, Phys. Rev. A 5, 2217 (1974); S. L. McCall, *ibid.* A 9, 1515 (1974); and reviews by Ya. B. Zeldovich, Usp. Fiz. Nauk. 110, 139 (1973) [Sov. Phys. Usp. 16, 427 (1973)]; I. B. Beterov and R. I. Sokolovskii, Usp. Fiz. Nauk 110, 169 (1973) [Sov. Phys. Usp. 16, 339 (1973)].
[46]N. N. Badalyan, V. A. Iradyan, and M. E. Movsesyan, Zh. Eksp. Teor. Fiz. Pisma Red. 8, 518 (1968) [JETP Lett. 8, 316 (1968)]; V. M. Arutyunian *et al.*, Zh. Eksp. Teor. Fiz. 66, 509 (1974) [Sov. Phys.-JETP 39, 243 (1974)]; D. W. Aleksandrov *et al.*, Zh. Eksp. Teor. Fiz. Pis'ma Red. 18, 102 (1973) [JETP Lett. 18, 58 (1973)]; A. M. Bonch-Bruevich, V. A. Khodovoi, and N. A. Chigir, Zh. Eksp. Teor. Fiz. 67, 2069 (1974) [Sov. Phys.-JETP 40, 1027 (1975)].
[47]A. Messiah, *Quantum Mechanics* (North Holland, Amsterdam, 1958), Vol. II.
[48]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., Oxford, 1961).
[49]D. Grischkowsky, Phys. Rev. Lett. 24, 866 (1972); D. Grischkowsky and J. A. Armstrong, Phys. Rev. A 6, 1566 (1972); D. Grischkowsky, M. M. T. Loy, and P. F. Liao, *ibid.* 12, 2514 (1975).
[50]B. R. Mollow, Phys. Rev. A 15, 1023 (1977).
[51]S. Mukamel and J. Jortner, J. Chem. Phys. 62, 3609 (1974); J. M. Friedman and R. M. Hochstrasser, Chem. Phys. 6, 155 (1974); J. O. Berg, C. A. Langhoff, and A. W. Robinson, Chem. Phys. Lett. 29, 305 (1974); H. Metiu, J. Ross, and A. Nitzan, J. Chem. Phys. 63, 1289 (1975); P. A. Hackett and R. A. Black, Chem. Phys. Lett. 37, 339 (1976).
[52]R. G. Brewer and R. L. Shoemaker, Phys. Rev. Lett. 27, 631 (1971); Phys. Rev. A 6, 2001 (1972); P. R. Berman, J. M. Levy, and R. A. Brewer, *ibid.* 11, 1668 (1975); R. G. Brewer and E. L. Hahn, *ibid.* 11, 1641 (1975); R. G. Brewer and A. Z. Genack, Phys. Rev. Lett. 36, 959 (1976).
[53]B. J. Feldman and M. S. Feld, Phys. Rev. A 12, 1013 (1975).
[54]N. M. Kroll, in *Quantum Optics and Electronics*, edited by C. deWitt, A. Blandin, and C. Cohen-Tannoudji (Gordon and Breach, London, 1965).