PHYSICAL REVIEW VOLUME 188, NUMBER 2 10 DECEMBER 1969

# Coherent Resonance Fluorescence Excited by Short Light Pulses

DAVID C. BURNHAM
*NASA Electronics Research Center, Cambridge, Massachusetts 02139*

AND

RAYMOND Y. CHIAO*
*Department of Physics, University of California, Berkeley, California 94720*

(Received 18 February 1969; revised manuscript received 29 August 1969)

Assuming infinite relaxation times and negligible pulse attenuation, we calculate the ringing produced when a resonant light pulse passes through a medium. These assumptions imply that each atom of the medium is excited identically and will therefore radiate coherently. Two models are used for the atoms of the medium: the classical harmonic oscillator and the two-level quantum-mechanical atom. The validity of the various approximations is discussed in detail.

## INTRODUCTION

THE advent of picosecond light pulses from mode-locked lasers[1] offers the possibility of investigating phenomena which have previously been hidden by short relaxation times. In this paper we will calculate the result of passing a resonant light pulse through a medium under the assumption of infinite relaxation times and negligible absorption of the incident pulse. The induced coherent fluorescence produces a ringing after the original pulse (illustrated in Fig. 1). Our calculation examines a limiting case with an analytical solution for the general problem of a light pulse interacting with a resonant medium. We neglect any modification of the incident pulse by the medium, as is considered in work on self-induced transparency[2] and coherence effects in laser amplifiers.[3] We also study effects occurring only after the exciting pulse and do not consider the precursers[4] which occur before the main pulse in a dispersive medium. Dicke[5] has considered the problem discussed in this paper; he calculated the radiation rate immediately after the pulse passes but did not follow the decay of the atomic excitation. Lynch *et al.*[6] have studied a problem related to ours, namely, the ringing produced by resonant filtering of naturally decaying $\gamma$ rays. They fit their experimental data with a theory based on a harmonic oscillator medium. Our theory differs from theirs in that we assume a $\delta$-function incident pulse, while they considered a pulse which rises abruptly and decays exponentially.

We first discuss the assumptions of our calculation and show how they lead to simple boundary conditions for our problem. We simultaneously solve Maxwell's equations and the harmonic oscillator equation for these boundary conditions and obtain a single analytical solution. The harmonic oscillator is then generalized to a two-level quantum-mechanical atom, and a family of solutions depending on one excitation parameter is obtained. The limitations of the assumptions leading to our solutions are treated in detail. Finally, possible experimental implications of this work are discussed.

## ASSUMPTIONS

The following five assumptions, often made in calculations of this type, are not independent, although their relationships are not trivially obvious. Actually, the first two assumptions are sufficient to define our problem.

### 1. Long Relaxation Times

Our calculation considers only times short compared to the characteristic decay times $T_1$, $T_2$, and $T_2^*$ of the medium. For an individual atom, $T_1$ describes the decay of excited-state population and $T_2$ the decay of radiating dipole moment. $T_1$ is equal to or shorter than the lifetime for spontaneous radiation; since the ringing we will calculate is due to stimulated emission, our calculation will require stimulated radiation to completely dominate spontaneous radiation for times of interest. An ensemble of independent atoms can have a more rapid decay of dipole moment than $T_2$ because of a spread in frequency for different atoms. An additional

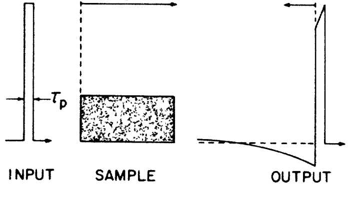

FIG. 1. Ringing produced by interaction of a pulse with the medium.

---

* Alfred P. Sloan Fellow.

[1] W. H. Glenn and M. J. Brienza, Appl. Phys. Letters **10**, 221 (1967); J. A. Armstrong, *ibid.* **10**, 16 (1967).

[2] S. L. McCall and E. L. Hahn, Phys. Rev. Letters **18**, 908 (1967); S. L. McCall and E. L. Hahn, Phys. Rev. **183**, 457 (1969); G. L. Lamb, Jr., Phys. Rev. Letters **25A**, 181 (1967).

[3] J. P. Wittke and P. J. Warter, J. Appl. Phys. **35**, 1668 (1964); C. L. Tang and B. D. Silverman, *Physics of Quantum Electronics* (McGraw-Hill Book Co., New York, 1966); F. T. Arechi and R. Bonfacio, IEEE J. Quantum Electron. **QE-1**, 169 (1965); F. Hopf and M. O. Scully, Phys. Rev. **179**, 399 (1969).

[4] A. Somerfeld, Ann. Physik **44**, 177 (1914); L. Brillouin, *ibid.* **44**, 203 (1914).

[5] R. H. Dicke, Phys. Rev. **93**, 99 (1954).

[6] F. J. Lynch, R. E. Holland, and M. Hammermesh, Phys. Rev. **120**, 513 (1960).

decay time $T_2^*$ inversely proportional to this spread occurs for inhomogeneously broadened solids and for Doppler-broadened gases. We ignore any differences between these two kinds of broadening.

### 2. Small Attenuation

We assume that the medium is short enough that the exciting pulse is essentially unattenuated and thus appears identical to each atom in the sample.

### 3. Maxwell's Equations

We use a macroscopic polarization in Maxwell's equations to treat the radiative effects of the atoms. When the density of randomly positioned atoms is not large enough to reconstruct the incident wavefront, this approximation fails and the atoms will radiate in all directions (Rayleigh scattering), not just the forward direction. Rayleigh scattering is dominated by spontaneous emission from the atoms and, therefore, is negligible under the conditions of our problem where stimulated emission dominates spontaneous emission (assumption 1). In other words, if the fluorescent ringing can be observed, the atomic density will be high enough to neglect Rayleigh scattering. Additional discussion appears later.

### 4. No Backward Wave

We assume that the effect of any backward-traveling wave is negligible. If the sample is much thicker than a wavelength, any backward wave radiated by the bulk medium will be small compared to the forward wave, because contributions from different portions of the medium are out of phase and therefore cancel. In addition, the discontinuity of the refractive index at the boundaries of the medium must be small in order to prevent significant reflections at the boundaries. We neglect the small broadband reflection which occurs at the boundary of a dense medium; its lowest-order effect is to produce a slight reduction in the incident and transmitted intensities. However, the refractive index associated with the resonant levels can become very large. Neglecting this reflection is justified under the assumption of long $T_1$ (assumption 1), as is discussed later.

### 5. Slowly Varying Envelope

We assume that the envelope of the radiated field and the atomic polarization varies slowly not only compared to an oscillation period, but also compared to the length of the exciting pulse $\tau_p$. The latter assumption will be shown to be equivalent to assuming small attenuation (assumption 2).

### Boundary Conditions

We assume that the medium is semi-infinite in the $+z$ direction and that the exciting pulse travels in the $+z$ direction, just passing position $z=0$ at time $t=0$ (see Fig. 1). Since each ground-state atom sees the same pulse (assumption 2) and does not radiate while the pulse is applied (assumption 4), the final electronic displacement $X(t,z)$ of each atom is the same (both phase and amplitude) immediately after the pulse passes. This boundary condition is

$$X(t=z/c,\, z)=X_0\,, \tag{1}$$

where $c$ is the velocity of light (we assume that the index of refraction of the host medium is unity). We note that Eq. (1) says nothing directly about the frequency, shape or magnitude of the exciting pulse. Because of our assumptions, all such information is condensed to a single parameter $X_0$. However, as is shown later, $X_0$ will be zero unless the pulse contains frequency components close to resonance with the atomic system.

An additional boundary condition arises because we have neglected backward waves. After the exciting pulse passes the beginning of the medium ($z=0$), the electric field there is zero:

$$E(t>0,\, z=0)=0\,. \tag{2}$$

## HARMONIC OSCILLATOR MEDIUM

### Equations of Motion

We assume that the atoms of the medium can be represented as harmonic oscillators of frequency $\omega_0$. The harmonic oscillator is a good approximation to a two-level quantum-mechanical atom for small excitation, as will be discussed later. The equation of motion for the electronic displacement is

$$\frac{\partial^2 X(t,z)}{\partial t^2}+\gamma\frac{\partial X(t,z)}{\partial t}+\omega_0^2 X(t,z)=\frac{ef^{1/2}}{m}E(t,z)\,, \tag{3}$$

where $\gamma=1/T_1$ is the energy damping rate, $E$ is the linearly polarized electric field, $f$ is the oscillator strength, $e$ is the electronic charge, and $m$ is the electronic mass. Maxwell's equations couple the electric field to the electronic polarization which is equal to $Nf^{1/2}eX$, where $N$ is the atomic density.

$$\left(\frac{\partial}{\partial z}+\frac{1}{c}\frac{\partial}{\partial t}\right)\left(\frac{\partial}{\partial z}-\frac{1}{c}\frac{\partial}{\partial t}\right)E(t,z)=\frac{4\pi f^{1/2}eN}{c^2}\,\frac{\partial^2 X(t,z)}{\partial t^2}\,. \tag{4}$$

### Dispersion Relation

A plane-wave solution for coupling the harmonic oscillator to Maxwell's equations leads to a dispersion relation between the wavelength $\lambda$ and frequency $\omega$ of light, i.e., a dispersion in the index of refraction $n(\omega)=2\pi c/\omega\lambda(\omega)$. For a linear medium, the solution for a light pulse can be obtained by summing plane-wave solutions; with the proper approximations this procedure leads to our harmonic oscillator solution [Eqs.

(18) and (19)]. Since we will generalize to the nonlinear two-level atom, we will usually work in the time rather than the frequency domain.

We write Eq. (3) in the frequency domain:

$$X(\omega)=(ef^{1/2}/m)E(\omega)(\omega_0^2+i\omega\gamma-\omega^2)^{-1}, \tag{5}$$

where we have defined the Fourier transforms

$$X(\omega)=\int_{-\infty}^{+\infty} dt X(t)e^{-i\omega t}, \tag{6a}$$

$$E(\omega)=\int_{-\infty}^{+\infty} dt E(t)e^{-i\omega t}. \tag{6b}$$

Equation (5) leads to the dispersion relation in the usual fashion (neglecting local field corrections):

$$n^2=1+\omega_p^2(\omega_0^2-\omega^2+i\omega\gamma)^{-1}, \tag{7}$$

where we have defined the plasma frequency

$$\omega_p^2=4\pi fe^2N/m. \tag{8}$$

Near resonance where $\omega\cong\omega_0$, the index of refraction can become very large or very small (or even imaginary, i.e., totally reflecting). Any of these possibilities will produce a large index discontinuity and hence a large reflection at the boundaries of our sample. The strict assumption of small reflection therefore requires

$$\omega_p^2\ll\gamma\omega_0=\omega_0/T_1. \tag{9}$$

The plasma frequency must be much less than the geometrical mean of the oscillator frequency and its spontaneous decay width.

Condition (9) can be relaxed without affecting our calculation. Unless the density is extremely high, the spectral width for which reflection will be large is of order $\gamma$. Totally reflecting a spectral band of width $\gamma$ from the incident pulse will produce a "ringing" following the pulse for a time $\sim\gamma^{-1}=T_1$. The ratio of the amplitude of this ringing to the incident amplitude is of order $\tau_p/T_1$. Since the amplitude ratio for our calculated bulk ringing is $\tau_p/\tau_R$ [Eq. (20b)] with $\tau_R\ll T_1$ [Eq. (42)], the surface ringing can be neglected.

### Time Domain Solution

The solution we are seeking must satisfy the two differential Eqs. (3) (with $\gamma=0$ from assumption 1) and (4) and the boundary conditions Eqs. (1) and (2). We assume a slowly varying amplitude for $E$ and $X$:

$$E(t,z)=\exp[i\omega_0(t-z/c)]\mathcal{E}(t,z), \tag{10a}$$

$$X(t,z)=\exp[i\omega_0(t-z/c)]\mathcal{X}(t,z). \tag{10b}$$

Equations (10) assume that only the wave propagating in the forward direction is important. The Appendix treats the case of a slab much thinner than a wavelength where the backward wave is equally important.

If we neglect appropriate derivatives of the slowly varying amplitudes $\mathcal{X}$ and $\mathcal{E}$, we obtain the following forms for Eqs. (3) and (4):

$$\frac{\partial\mathcal{X}(t,z)}{\partial t}=\frac{-if^{1/2}e}{2m\omega_0}\mathcal{E}(t,z), \tag{11}$$

$$\left(\frac{\partial}{\partial z}+\frac{1}{c}\frac{\partial}{\partial t}\right)\mathcal{E}(t,z)=\frac{-i2\pi f^{1/2}Ne\omega_0}{c}\mathcal{X}(t,z). \tag{12}$$

Let us change our time variable to $\tau=t-z/c$, the time after the end of the exciting pulse (see Fig. 1). The boundary condition of Eq. (1) becomes $\mathcal{X}(\tau=0,z)=X_0$ and the derivatives in Eqs. (11) and (12) become

$$\frac{\partial}{\partial t}\rightarrow\frac{\partial}{\partial\tau},\quad \frac{\partial}{\partial z}+\frac{1}{c}\frac{\partial}{\partial t}\rightarrow\frac{\partial}{\partial z}.$$

Equations (11) and (12) can then be combined to give

$$\frac{\partial^2\mathcal{X}(\tau,z)}{\partial z\partial\tau}=-\frac{\omega_p^2}{4c}\mathcal{X}(\tau,z)=-Q\mathcal{X}(\tau,z), \tag{13}$$

where the plasma frequency was defined by (8). The reason for the occurrence of the plasma frequency here is that we are calculating the exchange of energy between the radiation field and the atomic system. All the electrons oscillate coherently with respect to their positive ion cores just as in a longitudinal plasma oscillation.

The two boundary conditions (1) and (2) for our problem can be put into a form which is symmetrical between $\tau$ and $z$. By integrating the differential equation (11) with $\mathcal{E}(t,z=0)=0$ (assumption 2), one obtains

$$\mathcal{X}(t,z=0)=\mathcal{X}(\tau,z=0)=X_0. \tag{14}$$

These boundary conditions are consistent with a solution of the form

$$\mathcal{X}(\tau,z)=Y(q), \tag{15}$$

where we have defined $q=2(Q\tau z)^{1/2}$. The dependence of $\mathcal{X}$ on the product $\tau z$ becomes apparent if one integrates Eqs. (11) and (12) to give an integral form

$$\mathcal{X}(\tau,z)=X_0-Q\int_0^z dz'\int_0^\tau d\tau'\mathcal{X}(\tau',z'), \tag{16}$$

which can be iterated to give a power series in $\tau z$. This $\tau z$ dependence also occurred in the resonant filtering calculations of Lynch *et al.*[6]

With the change of variable (15), the partial differential of Eq. (13) is reduced to an ordinary differential equation:

$$Y''+Y'/q+Y=0, \tag{17}$$

which is Bessel's equation of zero order. The boundary conditions become $Y(0)=X_0$ and $Y'(0)=0$. The solu-

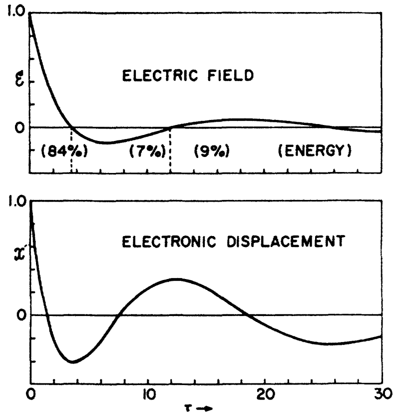

FIG. 2. Electric field and electronic displacement versus time delay after the exciting pulse. The time and amplitude normalizations are discussed in the text. The atoms are treated as harmonic oscillators.

tion for the electronic displacement envelope is

$$\mathcal{X}(\tau,z)=X_0J_0(\omega_p(\tau z/c)^{1/2})\,, \tag{18}$$

where $J_0$ is the zero-order Bessel's function. The electric field envelope, according to Eq. (11), is just the derivative of the displacement:

$$\mathcal{E}(\tau,z)=-i(m\omega_0X_0\omega_p/f^{1/2}e)(z/\tau c)^{1/2}J_1(\omega_p(\tau z/c)^{1/2})\,, \tag{19}$$

where we have used the relationship $J_1=-J_0'$. These solutions can be put in a normalized form for the values of $\mathcal{E}$ and $\mathcal{X}$ at the end of a sample of length $Z$:

$$\mathcal{X}(\tau)=X_0J_0(2(\tau/\tau_R)^{1/2})\,, \tag{20a}$$

$$\mathcal{E}(\tau)=-\mathcal{E}_1J_1(2(\tau/\tau_R)^{1/2})/(\tau/\tau_R)^{1/2}\,, \tag{20b}$$

where we have defined a radiation time

$$\tau_R=4c/\omega_p^2Z \tag{21}$$

and have used Eq. (33) to give

$$\mathcal{E}_1=\mathcal{E}_0\tau_p/\tau_R\,. \tag{22}$$

The two curves of Eqs. (20) are shown in Fig. 2 for $\tau_R=1$ with the normalizations $X_0=\mathcal{E}_1=1$ which give unity at $\tau=0$ and $\int d\tau\, \mathcal{E}^2(\tau)=1$. At time $\tau=\tau_R$, 62% of the energy stored in the sample has been radiated. Most of the energy (84%) is lost before the first zero in $\mathcal{E}$. Since oscillations of the Bessel functions in Eq. (20) are approximately periodic in their arguments, the oscillation periods in Fig. 2 increase as $\tau^{1/2}$. The oscillations are caused by the exchange of energy between the radiation field and the medium. The rate for interchange is proportional to the product $\mathcal{E}\mathcal{X}$ and thus decreases as energy is lost from the sample. A consequence of this rate decrease is that the electric field (representing power $\sim\mathcal{E}^2$ flowing out of the sample) decreases more rapidly than the electronic displacement (representing energy $\sim\mathcal{X}^2$ stored in the sample).

As long as $z\gg\lambda$, only the product $Nz\sim\tau_R^{-1}$ characterizes the ringing produced by the medium. The single parameter of the solution in Eq. (18) is proportional to $(Nz\tau)^{1/2}$, the square root of the number of atoms excited times the time they have had to radiate. As the effective sample thickness $Nz$ increases, the oscillations become more rapid. Our calculated functional dependence on the product $\tau z$ breaks down in the region $z\lesssim\lambda$ where both forward and backward waves are required as in the Appendix.

### Doppler Effect

In many cases (e.g., low-pressure gases) the first relaxation process which limits the validity of our result is Doppler or inhomogeneous broadening which causes the radiating dipole movements to get out of phase. A complete treatment of this process is complex because broadening affects both the absorption and the emission of radiation in the ringing following the initial pulse. However, two limiting cases are easily analyzed.

The first case where the dephasing time $T_2^*$ is long, is just the case we have analyzed in the previous sections. The solutions of Eqs. (18) and (19) are approximately valid for $\tau<T_2^*$. As $\tau$ exceeds this limit, the dephasing effect destroys the macroscopic polarization and thereby decouples the electronic displacement of each atom from the radiation field. Thus, the radiated field dies away and the displacement becomes fixed. The energy left in the atoms is then lost by the much slower process of incoherent spontaneous radiation ($T_1$).

In the second limiting case ($\tau_R\gg T_2^*$) the dephasing effect dominates the coherent fluorescence, and the macroscopic polarization is damped before the ringing of Eq. (18) can develop. In this case the displacement is approximately fixed at its initial magnitude $X_0$ ($\tau\sim0$ in Fig. 2), and the macroscopic polarization decays only because of dephasing:

$$\mathcal{X}(\tau,z)=X_0\int_{-\infty}^{+\infty}d(\Delta\omega)g(\Delta\omega)e^{i\Delta\omega\tau}=X_0G(\tau)\,, \tag{23}$$

where $\Delta\omega=\omega-\omega_0$ and $g(\Delta\omega)$ is the spectral line shape. We can define the dephasing time from the autocorrelation function $G(\tau)$ as the time for the polarization to decay to half its initial value: $G(T_2^*)=\frac{1}{2}$. The radiated field becomes

$$\mathcal{E}(\tau,z)=-i2\pi f^{1/2}Ne\omega_0X_0G(\tau)z/c \tag{24}$$

by integration of Eq. (11). This second limit where radiation damping is neglected is assumed in treatments of photon echo[7,8] (which do not necessarily assume $\tau_p\ll T_2^*$ as we do here) where sending a second pulse a

---

[7] I. D. Abella, N. A. Krunit, and S. R. Hartman, Phys. Rev. 141, 391 (1966).

[8] M. Scully, M. J. Stephen, and D. C. Burnham, Phys. Rev. 171, 213 (1968).

time $T$ later through a two-level system causes a recovery of macroscopic polarization at time $2T$.

## TWO-LEVEL MEDIUM

### Equations of Motion

The equations of motion for two-level atoms interacting with a radiation field have been derived by many authors.[2,3] Instead of a formal derivation, we will show how our previous equations become modified by the properties of two-level systems. All possible states of a two-level system can be represented by a vector **P** of fixed length[9] (the electric dipole moment for the transition is $\mu = f^{1/2}eP$) as illustrated in Fig. 3. We define the angle of excitation $\theta$ as the angle between **P** and the ground state $\mathbf{P}_b$ which points in the $+z$ direction. The projection of **P** on the $z$ axis is related to the energy $W$ stored in the atom: $W = \frac{1}{2}\hbar\omega_0(\cos\theta - 1)$. The electronic displacement is the projection of **P** on the $xy$ plane where the azimuthal angle gives the phase of the displacement. When the applied field is on resonance with the atom, only one component of the displacement couples to the field. In our transformation to slowly varying amplitudes (10) we effectively went to a rotating coordinate system where **P** is fixed in the $xz$ plane. With the two-level replacement for the electronic displacement $\mathcal{X} = P\sin\theta$, the field equation (12) becomes

$$\frac{\partial \mathcal{E}}{\partial z}(\tau,z) \propto P\sin\theta(\tau,z), \tag{25}$$

where the excitation angle $\theta$ depends on time and position. In the rotating coordinate system, the electric field drives the angle $\theta$ directly instead of $\mathcal{X}$ and the atomic equation (11) becomes

$$\frac{\partial \mathcal{X}(\tau,z)}{\partial \tau} \longrightarrow P\frac{\partial \theta(\tau,z)}{\partial \tau} \propto \mathcal{E}(\tau,z). \tag{26}$$

We note that for small excitation ($\theta \cong \sin\theta$) these equations reduce to the previous ones for harmonic oscillators. Equation (13) becomes the well-known[2] nonlinear equation for the interaction of two-level atoms with a resonant field in the absence of all relaxation phenomena:

$$\frac{\partial^2\theta(\tau,z)}{\partial\tau\partial z} = -\frac{\omega_p{}^2}{4c}\sin\theta(\tau,z). \tag{27}$$

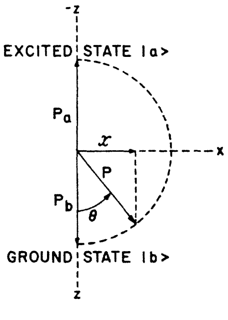

FIG. 3. Diagram of the vector model for a two-level atom.

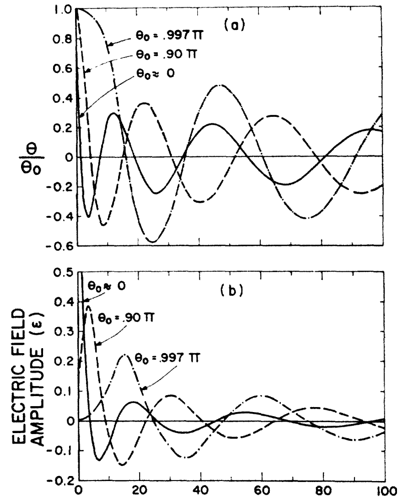

FIG. 4. Excitation angle (a) and electric field amplitude (b) versus time delay ($\tau_R = 1$) after the exciting pulse for three values of initial excitation $\theta_0$. The field $\mathcal{E}$ has been normalized to give $\int d\tau\, \mathcal{E}^2(\tau) = 1$ so that $\mathcal{E}^2$ represents the fraction of the energy radiated per unit time. The curve for $\theta_0 = 0$ extends to $\mathcal{E} = 1$ at $\tau = 0$ as in Fig. 2.

The boundary condition $\mathcal{X}(0,z) = X_0$ now becomes $\theta(0,z) = \theta_0 = \sin^{-1}(X_0/P)$, where $\theta_0$, the initial excitation angle, is an additional parameter which will characterize the solutions for a two-level system.

### Solution

The same transformation which led to Bessel's equation (17) before now gives

$$Y'' + Y'/q + \sin Y = 0, \tag{28}$$

with the boundary conditions $Y(0) = \theta_0$ and $Y'(0) = 0$. The relevant range for the initial conditions is $0 \leq \theta_0 \leq \pi$. The desired solutions for Eq. (28) are functions $F(q,\theta_0)$ which approach Bessel's functions for small $\theta_0$:

$$F(q,\theta_0) \xrightarrow[\theta\to 0]{} \theta_0 J_0(q)\,; \quad F'(q,\theta_0) \xrightarrow[\theta_0\to 0]{} -\theta_0 J_1(q). \tag{29}$$

The functions $F$ have been computed using a second order Runge-Kutta method to integrate Eq. (28). For $\theta_0 = 0.01$, the result for $0.01\,F(q,0.01)$ agreed with tabulated values of $J_0$ to the fourth decimal place. $F(q,\theta_0)$ was particularly simple to integrate because its quasiperiodic oscillation [see Fig. 5(b) which shows the zeros of $F(q,\theta_0)$ versus $\theta_0$] allowed a fixed-grid spacing. Solving directly for $\theta(\tau)$ would be considerably more difficult.

Figure 4(a) shows three different solutions for the excitation angle in the normalized form:

$$\theta(\tau)/\theta_0 = F[2(\tau/\tau_R)^{1/2},\theta_0]/\theta_0. \tag{30}$$

---

[9] R. P. Feynman, F. L. Vernon, Jr., and R. W. Hellwarth, J. Appl. Phys. 28, 49 (1957).

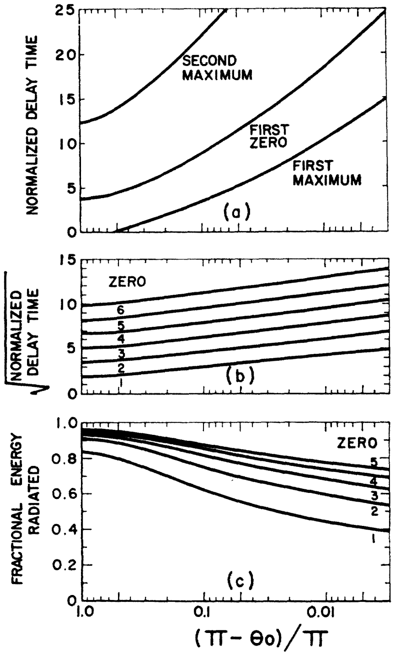

FIG. 5. Characteristics of the radiated electric field as a function of the initial excitation angle $\theta_0$. The separation from the singular point $\theta_0=\pi$ decreases logarithmically to the right. The results for the harmonic oscillator solution appear at the left edge. (a) Delay time for the first zero and the first two maxima. (b) Square root of the delay time for the first six zeros. (c) The fraction of the excitation energy radiated by the $N$th zero ($N=1$–$5$).

Figure 4(b) shows the corresponding electric field normalized to $\int d\tau\, \mathcal{E}^2(\tau)=\tau_R$:

$$\mathcal{E}(\tau)=-F'(2(\tau/\tau_R)^{1/2},\theta_0)/[2(1-\cos\theta_0)\tau/\tau_R]^{1/2}. \quad (31)$$

Figures 5(a) and 5(b) show how the solutions depend on $\theta_0$. Figure 5(c) shows the fraction of the stored energy radiated in each pulse of the ringing. The predominant characteristic of these solutions is that as $\theta_0$ becomes larger, the energy is radiated more slowly from the sample. Moreover, as $\theta_0$ increases, each pulse of the ringing contains a smaller fraction of the total energy. For $\theta_0>\frac{1}{2}\pi$ the electronic polarization increases as the atoms begin to radiate, and a maximum appears before the first zero. When $\theta_0$ approaches the unstable stationary point $\theta_0=\pi$, the initial electronic polarization becomes very small and the ringing begins very slowly.

A simple physical interpretation can be made for the calculated ringing. Atoms located at position $Z$ have excitation $\theta_0$ at $\tau=0$. As they radiate away their stored energy, $\theta$ decreases to zero. They then begin to absorb energy radiated by atoms at positions $z<Z$ and become excited with opposite phase. When the incident radiation has been attenuated to zero, the atoms again radiate but with their new opposite phase. This process repeats as the excitation angle $\theta$ rings down to zero.

## DISCUSSION OF ASSUMPTIONS

We will discuss the small attenuation and small Rayleigh-scattering assumptions only for a harmonic-oscillator medium. The approaches can be easily generalized to the two-level medium, although numerical results could require computer calculation.

### Small Attenuation of Incident Pulse

Let us assume a square resonant incident pulse of length $\tau_p$ and amplitude $\mathcal{E}_0$ as shown in Fig. 1. We can then integrate Eqs. (11) and (12) under our assumption of small attenuation ($\mathcal{E}\cong\mathcal{E}_0$). For $\tau$ inside the exciting pulse ($-\tau<\tau_p<0$), one obtains

$$\mathfrak{X}(\tau,z)=-i(f^{1/2}e/2m\omega_0)\,\mathcal{E}_0(\tau+\tau_p)\,, \quad (32)$$

$$X_0=\mathfrak{X}(0,z)=-i\,\mathcal{E}_0(f^{1/2}e/2m\omega_0)\tau_p\,, \quad (33)$$

$$\mathcal{E}(\tau,z)=\mathcal{E}_0[1-(\tau+\tau_p)/\tau_R]. \quad (34)$$

The electric field decreases linearly in time until $\tau=0$, when the $\mathcal{E}_0$ term disappears and the solution in Eq. (20b) begins. The assumption that the attenuation is small requires

$$\tau_p/\tau_R=\omega_p{}^2\tau_p z/4c\ll 1. \quad (35)$$

This inequality sets a limit on the maximum value of the effective thickness $Nz$ which is inversely proportional to $\tau_p$. As $\tau_p$ decreases, less energy is absorbed by each atom [Eq. (33)]. In the frequency domain, a shorter $\tau_p$ implies a broader spectrum which has less resonant energy [see Eq. (44)]. A comparison of Eq. (35) with Eq. (20) shows that the small attenuation assumption leads to an amplitude varying slowly in time $\tau_p$ (assumption 5).

### Small Rayleigh Scattering

The relationship of spontaneous (Rayleigh scattering) and stimulated radiation to the validity of the macroscopic Maxwell's equations will be illustrated by two examples before we calculate the energy lost by scattering in our problem.

The radiated electric field at a field point $\mathbf{R}(\mathbf{n}=\mathbf{R}/R)$ from an oscillator at the origin is[10]

$$E(\mathbf{R},t)=(ef^{1/2}/Rc^2)\mathbf{n}\times[\mathbf{n}\times\ddot{\mathbf{x}}(t-R/c)]\,, \quad (36)$$

which gives the usual dipole pattern. The energy in a single harmonic oscillator will spontaneously decay at rate

$$\gamma=1/T_1=\tfrac{2}{3}e^2f\omega_0{}^2/mc^3. \quad (37)$$

If one applies a strong resonant electromagnetic wave of the correct phase to the oscillator (the classical analog of stimulated emission), the energy can be lost in a time much less than $T_1$. Since the radiated electric field is just the same (depending only on $\ddot{\mathbf{x}}$) as for spontaneous

---

[10] J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., New York, 1962) Chap. 17, pp. 468–472.

decay, the energy radiated into the dipole pattern is significantly reduced. The missing energy appears in the forward direction where the radiated field interferes constructively with the stimulating field.

If one considers a collection of $\mathcal{N}$ randomly positioned oscillators excited coherently, the ratio $\mathcal{R}$ of the power radiated in the forward direction (where the electric fields from each oscillator add in phase) to the power in other directions can be shown to be roughly

$$\mathcal{R}=\tfrac{3}{16}\mathcal{N}(\lambda/D)^2, \tag{38}$$

where $D$ is the transverse dimension of the collection. The condition for the coherent forward radiation to dominate ($\mathcal{R}\gg 1$) requires many atoms in each cross section of area $\lambda^2$ through the sample. In other words, in order for the atoms to reconstruct the exciting wave front, one must be able to see many atoms per square wavelength. When the coherent radiation dominates ($\mathcal{R}\gg 1$) the atoms radiate much faster than by incoherent spontaneous emission. The reason for this increased radiation rate is that the atoms stimulate each other to radiate. Thus again we see that stimulated emission produces radiation in the forward direction.

Instead of assuming uniform atomic excitation as above, we can use our solution to the ringing problem (18) to integrate the total spontaneous energy decay from a sample of unit cross sectional area, using Eq. (37) for the spontaneous decay rate:

$$W_s=\gamma\int_0^T d\tau\int_0^Z N dz\tfrac{1}{2}m\omega_0{}^2\mathcal{X}^2(\tau,z), \tag{39}$$

where we have defined a cutoff time $T\lesssim T_1$ which limits the integral to times where our Bessel function solution (18) is valid. In addition, we will consider correctly only those atoms which have coherently radiated away most of their energy in time $T$, i.e., we adopt the asymptotic expression for Bessel's functions:

$$J_n(z)\approx(2/\pi z)^{1/2}\cos[z-\tfrac{1}{2}\pi(n+\tfrac{1}{2})].$$

We use the integral relationship $\int J_0{}^2(z)z\,dz=\frac{1}{2}z^2\times[J_0{}^2(z)+J_1{}^2(z)]$ and obtain the following result for the energy radiated incoherently:

$$W_I=(32/3\pi)^{1/2}(NZ\lambda^2)^{-1/2}(T/T_1)^{1/2}[\tfrac{1}{2}NZm\omega_0{}^2\mathcal{X}^2(0)]. \tag{40}$$

The factor in brackets in (40) is the total energy stored in the sample. In order for our use of the macroscopic Maxwell's equations to be justified, the energy in (40) must be much less than the stored energy:

$$NZ\lambda^2\gg(33/3\pi)(T/T_1). \tag{41}$$

We again obtain the result that the number of atoms per square wavelength $NZ\lambda^2$ must be much greater than a number or order unity, the exact value of which depends on how long one wishes to observe the ringing from the sample.

Let us compare condition (41) with assumption (1) for observing the fluorescent ringing:

$$\tau_R\ll T_1, \tag{42}$$

i.e., ringing must occur in a time short compared to $T_1$. Equation (42) can be rewritten as a density condition

$$NZ\lambda^2\gg 8\pi/3. \tag{43}$$

Thus this condition for seeing ringing is sufficient to insure negligible Rayleigh scattering, especially if one is interested in times considerably shorter than $T_1$.

### Resonant Excitation

In this section we show that the exciting pulse must be close to resonance in order to leave the atomic system excited after the pulse passes.

#### *Harmonic Oscillator*

Using Eqs. (5) and (6), the excitation of a harmonic oscillator by an incident electric field pulse ending at time $t=0$ can be shown to be

$$X_0=X(0)=(if^{1/2}e/2m\omega_0)E(\omega_0) \tag{44}$$

in the limit $\gamma\to 0$. Thus only the resonant part of the incident pulse produces excitation which remains after the pulse passes.

#### *Two-Level System*

One might suspect that a very intense off-resonant pulse $[E(\omega_0)\cong 0]$ could excite a two-level atom by power broadening. In the rotating coordinate system (Fig. 3), the effective field which acts on the atom is $\Omega=[(\Delta\omega)^2+(\mu\mathcal{E}/\hbar)^2]^{1/2}$, where $\Delta\omega$ is the distance off resonance, $E$ is the applied field along the $x$ axis, and $\mu$ is the electric dipole moment $[\mu^2=(e^2f\hbar/2m\omega_0)]$. This field $\Omega$ makes an angle $\psi=\tan^{-1}(\mu\mathcal{E}/\hbar\Delta\omega)$ with the $z$ axis. A very intense electric field pulse will change $\psi$ from zero to $\frac{1}{2}\pi$ and then back to zero. We consider a smooth pulse envelope $\{$e.g., Gaussian $\mathcal{E}(t)=\mathcal{E}_0\exp\times[-(t/\tau p)^2]\}$ in order to minimize the spectral width of $E(\omega)\{\mathcal{E}(\Delta\omega)\propto\mathcal{E}_0\exp[-(\Delta\omega\tau_p)^2]$ for our Gaussian pulse$\}$.

The atom will not remain excited after the pulse passes unless the adiabatic condition $\dot{\psi}\ll\Omega$ has been violated. Thus for significant excitation we require

$$\frac{1}{\Omega}\frac{d\psi}{dt}\sim 1. \tag{45}$$

Let us assume a general pulse form $\mathcal{E}=\mathcal{E}_0f(t)$. If we maximize the left-hand side of Eq. (45) with respect to $\mathcal{E}_0$ we obtain

$$\tfrac{2}{3}3^{-1/2}(\tau_p\Delta\omega)^{-1}[\tau_pf'(t)/f(t)]\sim 1, \tag{46}$$

with $\mathcal{E}_0=\hbar\Delta\omega/\sqrt{2}\mu f(t)$. If we are far off resonance ($\tau_p\Delta\omega\gg 1$), then Eq. (46) is true only for large logarith-

TABLE I. Density limits.

| Approximation | Condition | Equation |
|---|---|---|
| Strict small reflection | $NZ\lambda^2 \ll (2\pi^2/3)(z/\lambda)$ | (9) |
| Small attenuation | $NZ\lambda^2 \ll (8\pi/3)(T_1/\tau_p)$ | (35) |
| Small Rayleigh scattering | $NZ\lambda^2 \gg (32/3\pi)(T/T_1)$ | (41) |
| Small spontaneous decay | $NZ\lambda^2 \gg 8\pi/3$ | (43) |

mic slopes $r = \tau_p f'(t)/f(t) \gg 1$. In the case of a Gaussian pulse, one has $r = t/\tau_p$ and $\mathcal{E} \ll \mathcal{E}_0$ holds for $r \gg 1$. The peak field value required to satisfy Eq. (46) is

$$\mathcal{E}_0 = (\hbar\Delta\omega/\sqrt{2}\mu)\exp[(27/4)(\Delta\omega\tau_p)^2]. \qquad (47)$$

As $\Delta\omega$ becomes significantly larger than the spectral width of the pulse, the intensity required for excitation increases drastically. The functional dependence (47) on $\Delta\omega\tau_p$ is essentially the same as that for the value of $\mathcal{E}_0$ required to achieve a given value of $E(\omega_0)$ [as in Eq. (44)]. Thus we see that off-resonant excitation is no more possible with the nonlinearities of the two-level atom than with the harmonic oscillator.

## DISCUSSION OF RESULTS

### Experimental Values

Let us consider the conditions for the experimental observation of fluorescent ringing. The first requirement for the validity of our calculations is the existence of an effective two-level system,[11] i.e., the coupling of only two levels to the field or the coupling of pairs of levels with identical matrix elements (see the discussion of Ref. 12). Our solution is valid for times $\tau$ in the range $\tau_p < \tau < T_{\min}$, where $T_{\min}$ is the minimum time among $T_1$, $T_2$, and $T_2{}^*$. In order for our solution to have a significant range of experimental validity one must have $\tau_p \ll T_{\min}$. In addition, we have upper and lower limits on the density $N$ because of various approximations (see Table I).

We will consider the case of Na vapor in detail ($T_1 = T_2 = 10^{-8}$ sec, $\omega_0 = 3.2\times10^{15}$ sec$^{-1}$). Since $T_2{}^*$ for room-temperature Na vapor is $2\times10^{-10}$ sec, one might obtain the exciting pulse from a mode-locked laser with $\tau_p = 2\times10^{-12}$ sec. In this case our solution would be valid for times one hundred times longer than the exciting pulse, if one neglects the fine structure of the Na *D* lines (which would produce some additional ringing and a more stringent restriction on $\tau_p$). For the values $f = 1$ and $Z = 10$ cm, the small attenuation approximation (35) produces an upper limit on the density,

$$N_L = cm/\pi f e^2 \tau_p z = 2\times10^{12}\ \mathrm{cm}^{-3}, \qquad (48)$$

which corresponds to a pressure of $5\times10^{-5}$ Torr and $N_L Z\lambda^2 = 7\times10^4$. This value is less than $Z/\lambda = 1.6\times10^5$ so that the small reflection condition is satisfied. At $5\times10^{-6}$ Torr, a cell of volume 10 cm$^3$ excited to $\theta_0 = \frac{1}{2}\pi$ has a stored energy of about $2\times10^{-7}$ J. The radiation time $\tau_R$ for the first 62% of this energy is

$$\tau_R = (N_L/N)\tau_p = 20\times10^{-12}\ \mathrm{sec}. \qquad (49)$$

The initial radiated power is therefore about $6\times10^3$ W. The rest of the ringing takes place at considerably smaller power levels. The experimental observation of these power levels in the presence of the stronger exciting pulse will be difficult.

### Photon Echo

As mentioned in the section on Doppler effect, the usual discussion[7,8] of photon echo ignores radiative damping effects. The energy radiated when the atoms are in phase is assumed to be much less than the stored energy. This assumption implies

$$\tau_R \gg T_2{}^*. \qquad (50)$$

If the exciting pulse (assumed to be unattenuated $\tau_p \ll \tau_R$) is significantly shorter than $T_2{}^*$, the conditions for the calculated ringing can be satisfied and one can have the radiation damped case

$$\tau_p < \tau_R < T_2{}^*, \qquad (51)$$

where the photon echo will be much smaller than expected.[8] The condition (50) can always be achieved by shortening the sample length, since $\tau_R \sim (NZ)^{-1}$.

### Amplifying Medium

In our treatment of a two-level system, we assumed that the system started in the ground state and then was excited to angle $\theta_0$ by the incident pulse. However, the same situation can be produced by starting with all atoms in the excited state (an amplifier) and deexciting them by an angle $(\pi - \theta_0)$ by means of the incident pulse. Thus the same ringing can result from a thin amplifier as from a thin attenuator. It is unlikely that such an experiment could be performed using the same material as an oscillator to produce the incident pulse and as the thin amplifier. An oscillator generally cannot produce a pulse much shorter than its inverse bandwidth, and we have assumed that the incident pulse is much shorter than the inverse bandwidth. Variations in host (e.g., Nd$^{+++}$ in glass or YAG) or temperature (as in ruby) could perhaps allow large enough bandwidth differences for such an experiment to work.

## ACKNOWLEDGMENTS

We have had useful discussions with E. Hahn who (with S. McCall) has independently derived the solutions discussed in this paper. One of the authors (RYC) would like to acknowledge helpful discussions with C. H. Townes and A. Szöke.

---

[11] The harmonic oscillator result will hold for any set of energy levels as long as the response is linear.

[12] C. K. Phodes, A. Szöke, and A. Javan, Phys. Rev. Letters **21**, 1151 (1968).

## APPENDIX

We wish to treat the case of a thin slab ($\Delta z \ll \lambda$) of excited harmonic oscillators. The surface density of oscillators is $\sigma = N\Delta z$. The displacement can be represented in terms of a slowly varying envelope:

$$X(t,z) = \exp(i\omega_0 t)\delta(z)\mathfrak{X}(t)\,, \qquad \text{(A1)}$$

where $\delta(z)$ is the Dirac $\delta$ function. We require a solution that is symmetric in the forward and backward directions. Once can verify that such a solution for Eqs. (4) and (A1) is

$$E(t,z) = -i\pi e f^{1/2}\omega_0^2 c^{-2}\{\theta(z)\exp[i\omega_0(t-z/c)] + \theta(-z)\exp[i\omega_0(t+z/c)]\}\,, \qquad \text{(A2)}$$

where derivatives of $\mathfrak{X}(t)$ have been dropped and $\theta(z)$ is the step function. The harmonic oscillator equation (3) for $\gamma = 0$ becomes

$$\frac{d\mathfrak{X}(t)}{dt} = -\tfrac{1}{2}\Gamma\mathfrak{X}(t)\,, \qquad \text{(A3)}$$

with $\Gamma = \pi f\omega_0\sigma/mc^2$, where we have kept only first derivatives of $\mathfrak{X}(t)$. Equation (A3) leads to exponential decay of the stored energy $W$:

$$W(t) = W(0)e^{-\Gamma t}. \qquad \text{(A4)}$$

The decay rate $\Gamma$ is proportional to the number of oscillators, as is characteristic of a coherent process.

---

PHYSICAL REVIEW VOLUME 188, NUMBER 2 10 DECEMBER 1969

# Optical and Electron-Spin-Resonance Studies of Fourth-Nearest-Neighbor Chromium Ion Pairs in Ruby*†

M. J. Berggren
*Department of Physics, Stanford University, Stanford, California 94305*

AND

G. F. Imbusch‡
*Bell Telephone Laboratories, Murray Hill, New Jersey 07974*

AND

P. L. Scott
*Natural Sciences Division, University of California, Santa Cruz, California 95060*

(Received 19 June 1969)

The fine structure of the optical fluorescence spectrum arising from the fourth-nearest-neighbor chromium ion pair system in ruby is studied using high-resolution optical spectroscopy, ordinary electron-spin resonance, and optically detected electron-spin resonance. The ground-state energy levels of this system are found to be describable by a simple spin Hamiltonian of the form

$$\mathcal{H} = g\beta\,\mathbf{H}\cdot\mathbf{S} + J/2[S(S+1) - 15/2] + D_S[S_z^2 - \tfrac{1}{3}S(S+1)] + E_S[S_x^2 - S_y^2],$$

where the directions of the symmetry axes, $D_S$, and $E_S$ each depend on the spin $S$ in a predictable way, requiring only two adjustable parameters: $D_c$ (the usual second-order crystal-field term of axial symmetry) and $D_E$ (a similar term arising from the anisotropic exchange interaction). The value of $D_c$ is found to be $-0.191 \pm 0.005$ cm$^{-1}$, which is equal to that for the isolated ion. The value of $D_E$ is found to be $-0.021 \pm 0.005$ cm$^{-1}$. A phonon-assisted energy-transfer mechanism is postulated to account for the existence of the optically detected spin-resonance spectrum.

## I. INTRODUCTION

A SUBSTANTIAL amount of attention has been given to the subject of chromium ion pairs in ruby ($\alpha$-$Al_2O_3$:$Cr^{3+}$) over the past several years. In particular, experimental work on the optical spectrum,[1] and on the paramagnetic resonance spectrum,[2–5] as well as theoretical work on systems of such pairs of

---

* Work supported in part by the Advanced Research Projects Agency, under Contract No. SD 87 G-704, and in part by the Office of Naval Research, under Grant No. N00014-68-A-0381-0002.

† Based on part of the Ph.D. dissertation of M. J. Berggren, Stanford University, 1969 (unpublished).

‡ Present address: University College, Galway, Ireland.

[1] L. F. Mollenauer and A. L. Schawlow, Phys. Rev. **168**, 309 (1968); and references therein.

[2] L. Rimai, H. Statz, M. J. Weber, G. A. de Mars, and G. F. Koster, Phys. Rev. Letters **4**, 125 (1960); J. Appl. Phys. **32**, 2185 (1961); J. Phys. Soc. Japan **17**, Suppl. B-1, 430 (1962).

[3] Yu. L. Shelekin, M. P. Votinov, and B. P. Berkovskii, Fiz. Tverd. Tela. **8**, 589 (1966); **9**, 2119 (1967) [English transls.: Soviet Phys.—Solid State **8**, 469 (1966); **9**, 1663 (1967)].

[4] W. Gunsser, W. Hille, and A. Knappwost, Z. Phys. Chem. **58**, 316 (1968).

[5] A. Jelenski, H. Szymczak, and J. Twarowski. *Proceedings of the International Conference on Magnetic Resonance and Relaxation, Fourteenth Colloque Ampere, Ljubljona, Yugoslavia, 1966*, edited by R. Blinc (North-Holland Publishing Co., Amsterdam, 1967), p. 1205.