

## Quantum-Theoretical Comparison of Nonlinear Susceptibilities in Parametric Media, Lasers, and Raman Lasers†

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The steady-state response of a nonlinear medium to several simultaneously applied monochromatic electromagnetic fields is described by the density matrix method. A Fourier series expansion in terms of ascending powers of the amplitudes of the applied fields is especially useful to describe the parametric response in spectral regions, where the absorption is small. As the resonances of the material system are approached, the general formalism exhibits the mixture and interference between parametric processes and single- and multiple-photon absorption and emission processes. Previously discussed examples of the two-level and three-level system are generalized. The reaction of the general nonlinear medium on the electromagnetic fields is incorporated.

### I. INTRODUCTION

IN an ideal lossless medium only parametric processes occur, as transitions between energy levels of the material system are confined to  $\delta$ -function type singularities as a function of the frequency of the photons. The energy of the photons remains conserved. Nonlinear scattering processes in which three or more photons participate were considered by Blaton<sup>1</sup> and Guttinger.<sup>2</sup> The corresponding nonlinear part of the dielectric polarization, which results from the interference between all such nonlinear scattering processes by all atoms in the crystal lattice, was calculated by Armstrong *et al.*<sup>3</sup> for a lossless medium.

If one wishes to generalize this theory to include damping, one is immediately confronted with the fact that the parametric processes become interwoven with processes in which one or more photons are absorbed or emitted. Since the damping mechanism is statistical in nature and results from the interaction with random photon and phonon fields about which our information is far from complete, the use of the density matrix formalism is appropriate. Karplus and Schwinger<sup>4</sup> used it to describe the saturation of microwave resonances. This may be considered as a kind of nonlinear effect in which successive absorption and emission of quanta at the same frequency takes place.

This formalism was extensively developed, especially in the study of nuclear magnetic relaxation.<sup>5-10</sup> The interest here will be limited to dilute systems, in which the interaction between particles is very small compared

to the energy separation between levels, and also small compared to differences in spacing between energy levels of an individual particle. Equally spaced levels are not considered here. These assumptions are usually well met in the optical region of the spectrum, and may on occasions also be valid in dilute paramagnetic materials at microwave frequencies. Furthermore, the random interaction Hamiltonian will usually have a constant spectral density over a frequency range larger than the linewidth of individual transitions. They are physically caused by radiative and nonradiative processes in which photons and/or phonons are absorbed and emitted. The interaction with random or thermal radiation fields and the lattice vibrations includes the effects of spontaneous emission. In the parlance of magnetic relaxation the case of interest corresponds to the limit of "rapid motion in an isotropic medium." Under these circumstances the effect of the random Hamiltonian on the motion of the density matrix is given by phenomenological damping terms,

$$(\partial\rho_{aa}/\partial t)_{\text{random}} = \sum_n R_{aann}\rho_{nn} = \sum_n w_{an}\rho_{nn} - \sum_n w_{na}\rho_{aa} \quad (1.1)$$

$$(\partial\rho_{ab}/\partial t)_{\text{random}} = -R_{abab}\rho_{ab} = -\Gamma_{ab}\rho_{ab}. \quad (1.2)$$

The  $\mathfrak{N}$  diagonal elements relax in a combined fashion leading to  $\mathfrak{N}-1$  longitudinal relaxation times. Their inverses are the eigenvalues of the determinant of the  $w_{nn}$ . Each off-diagonal element decays with a characteristic transverse relaxation time  $\Gamma_{ab}^{-1}$  which has, in general, both adiabatic and nonadiabatic contributions. The latter are caused by the finite lifetime related to the transition probabilities  $w_{an}$ ,  $w_{bn}$ . In the case of only two energy levels one has  $\Gamma_{\text{nonad}} = (1/2T_1) = (w_{ab} + w_{ba})$ . The former corresponds to a random modulation of the splitting  $h\nu_{ba}$ , due to diagonal elements of the random perturbation Hamiltonian as may e.g., be caused by lattice vibrations. In the special case that the only random perturbation is nonadiabatic and corresponds to spontaneous emission of photons from levels  $a$  and  $b$  to other lower levels, the relaxation terms may be

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<sup>1</sup> J. Blaton, *Z. Physik* **69**, 835 (1931).

<sup>2</sup> P. Guttinger, *Helv. Phys. Acta* **5**, 237 (1932).

<sup>3</sup> J. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, *Phys. Rev.* **127**, 1918 (1962). [The factor  $\frac{1}{2}$  in the last two terms of Eq. (2.9) of this paper should be omitted.]

<sup>4</sup> R. Karplus and J. Schwinger, *Phys. Rev.* **73**, 1020 (1948).

<sup>5</sup> R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).

<sup>6</sup> R. K. Wangsness and F. Bloch, *Phys. Rev.* **89**, 278 (1953).

<sup>7</sup> F. Bloch, *Phys. Rev.* **102**, 104 (1956).

<sup>8</sup> A. G. Redfield, *IBM Journal* **1**, 19 (1957).

<sup>9</sup> See, for example, A. Abragam *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961).

<sup>10</sup> P. S. Hubbard, *Rev. Mod. Phys.* **33**, 249 (1961).

expressed by the anticommutator,

$$\left(\frac{\partial}{\partial t}\right)_{\text{damping}} \rho = -(\Gamma\rho + \rho\Gamma), \quad (1.3)$$

where  $\Gamma$  is a diagonal matrix.

In the field of magnetic resonance, relaxation theory has been developed to an advanced stage<sup>9</sup> in which the interaction between individual spins may have a large influence on the relaxation behavior. When the interaction between individual atoms or ions is ignored, the relaxation terms retain the same form in the presence of applied periodic fields. There is, strictly speaking, a slight modification because the system tends to relax to thermal equilibrium at the instantaneous value of the applied fields in the limit of relaxation by rapid motion. The assumption that the relaxation terms always retain the form given by Eqs. (1.1) and (1.2) is, however, a very good approximation for the physical situations encountered in lasers and nonlinear optical devices. Effects of inhomogeneous broadening, strain broadening of optical lines, etc., can always be taken into account by integrating the final results of this report over a distribution of the resonant frequencies of the atomic system.

The total Hamiltonian will consist of the part  $\mathcal{H}_A$  which determines the unperturbed energy levels of the atomic system, the interaction  $\mathcal{H}_{\text{coh}}$  of this system with one or more applied monochromatic fields, and a random Hamiltonian  $\mathcal{H}_{\text{random}}$ , which includes not only the photon and phonon relaxation processes already discussed, but also applied random pump fields. If a laser crystal is e.g., surrounded by a flash lamp, it is subjected to random fields characterized by different temperatures depending on whether the solid angle subtends an element of the flash lamp or not. In this case, the transition probabilities due to random fields obey the relationship

$$w_{ab} = \sum_{\Omega} w_{ab}^{\Omega}$$

$$w_{ba} = \sum_{\Omega} w_{ba}^{\Omega},$$

with

$$w_{ba}^{\Omega} = w_{ab}^{\Omega} \exp\{-h\nu_{ba}/kT^{\Omega}\}.$$

The equation of motion for the density matrix can thus be written,

$$i\hbar\dot{\rho} = [\mathcal{H}_A, \rho] + [\mathcal{H}_{\text{coh}}, \rho] + i\hbar(\partial\rho/\partial t)_{\text{random}}, \quad (1.4)$$

where the last term is given by Eqs. (1.1) and (1.2). In this form various authors have discussed the response of a material system subjected simultaneously to two applied periodic fields. Particular attention has been paid to two- and three-level maser systems. Javan,<sup>11</sup> Winter,<sup>12</sup> and Yatsiv<sup>13</sup> emphasize the importance of two-quantum Raman processes which may occur in

<sup>11</sup> A. Javan, *Phys. Rev.* **107**, 1579 (1957).

<sup>12</sup> J. M. Winter, *J. Phys. Radium* **19**, 802 (1958); and A. Javan, *ibid.* **19**, 806 (1959).

<sup>13</sup> S. Yatsiv, *Phys. Rev.* **113**, 1538 (1959).

such systems. Anderson<sup>14</sup> clearly describes a basic parametric process for a three-level system. Clogston<sup>15</sup> has given a formula which contains all these processes. Although he emphasizes the operation of a three-level maser, he did not omit the parametric term, as Fain<sup>16</sup> has asserted. The latter<sup>17</sup> has also used the density matrix formalism to discuss the operation of maser oscillators. Kastler<sup>18</sup> and his co-workers<sup>19,20</sup> have extensively used this formalism to describe the simultaneous action of radiofrequency and optical fields, as have Wilcox and Lamb.<sup>21,22</sup> For a two-level system the density matrix formalism is identical with the classical Bloch equations for magnetic resonance.<sup>23</sup> Harmonic generation in ferromagnetic resonance, a parametric process, was studied theoretically and experimentally at an early date by Ayres, Vartanian, and Melchor.<sup>24</sup>

All these papers—and many others which cannot be referred to here—emphasize one or more aspects of the general steady-state response of an atomic system subjected to a number of simultaneous periodic perturbations. Usually the interest has been focused on situations at or near resonances of the atomic system. In this report special emphasis will be given to the parametric case in which none of the frequencies is near resonance. A systematic general procedure is presented in Sec. II. All previous results may be derived by it, if approximations suitable in each particular situation are made. The nonlinear steady-state response of a two-level system will be considered in Sec. III. Both parametric and Raman-type processes are exhibited. The well-known example of a three-level system subjected to simultaneous fields at three frequencies is reconsidered in Sec. IV, and generalizations of the results of Clogston<sup>15</sup> and Javan<sup>12</sup> are obtained. A brief account of this work was presented at the Paris conference on quantum electronics.<sup>25</sup> The reaction of the nonlinear medium on the electromagnetic fields is described in Sec. V. All maser, Raman maser, and parametric effects are taken into account in this formulation.

<sup>14</sup> P. W. Anderson, *J. Appl. Phys.* **28**, 1049 (1957).

<sup>15</sup> A. M. Clogston, *J. Chem. Phys. Solids* **4**, 271 (1958).

<sup>16</sup> V. M. Fain, Ya. I. Khanin, and E. G. Yashchin, *Zh. Eksperim. i Teor. Fiz.* **41**, 986 (1961) [translation: *Soviet Phys.—JETP* **14**, 700 (1962)].

<sup>17</sup> V. M. Fain and Ya. I. Khanin, *Zh. Eksperim. i Teor. Fiz.* **41**, 1498 (1961) [translation: *Soviet Phys.—JETP* **14**, 1069 (1962)].

<sup>18</sup> A. Kastler, in *Rendiconti S. I. F. XVII Corso* (Academic Press Inc., New York, 1962), p. 167.

<sup>19</sup> J. P. Barrat, *J. Phys. Radium* **20**, 541, 633, 657 (1959).

<sup>20</sup> C. Cohen-Tannoudji, in *Rendiconti S. I. F., XVII Corso* (Academic Press Inc., New York, 1962), p. 240.

<sup>21</sup> L. R. Wilcox and W. E. Lamb, *Phys. Rev.* **119**, 1915 (1960).

<sup>22</sup> W. E. Lamb and T. M. Sanders, *Phys. Rev.* **119**, 1901 (1960).

<sup>23</sup> R. P. Feynman, F. L. Vernon, and R. W. Hellwarth, *J. Appl. Phys.* **28**, 49 (1957).

<sup>24</sup> W. P. Ayres, P. H. Vartanian, and J. L. Melchor, *J. Appl. Phys.* **27**, 188 (1956).

<sup>25</sup> N. Bloembergen, in *Proceedings of the Third International Conference on Quantum Electronics* (Dunod Cie., Paris, and Columbia University Press, New York, 1963).

## II. GENERAL CALCULATION OF NONLINEAR CONDUCTIVITIES AND SUSCEPTIBILITIES

A steady-state solution for the density matrix in ascending powers of the coherent periodic perturbations may be found from the following hierarchy of equations,

$$\begin{aligned} i\hbar\dot{\rho}^{(0)} &= [\mathcal{H}_{A,\rho}^{(0)}] + i\hbar(\partial/\partial t)\rho_{\text{damping}}^{(0)}, \\ i\hbar\dot{\rho}^{(1)} &= [\mathcal{H}_{A,\rho}^{(1)}] + i\hbar(\partial/\partial t)\rho_{\text{damping}}^{(1)} + [\mathcal{H}_{\text{coh},\rho}^{(0)}], \\ i\hbar\dot{\rho}^{(n)} &= [\mathcal{H}_{A,\rho}^{(n)}] + i\hbar(\partial/\partial t)\rho_{\text{damping}}^{(n)} + [\mathcal{H}_{\text{coh},\rho}^{(n-1)}]. \end{aligned} \quad (2.1)$$

The first equation gives the density matrix in thermodynamic equilibrium. The linear response of the system is determined by the second equations;  $\rho^{(1)}$  contains the same frequencies as  $\mathcal{H}_{\text{coh}}$ . In second approximation the steady response  $\rho^{(2)}$  contains sum, difference, and second harmonic frequencies, as well as dc terms. The dc terms are a first approximation to incipient saturation effects and arise as the beat between positive and negative frequency terms in the  $\mathcal{H}_{\text{coh}}$  and  $\rho^{(1)}$ , respectively. Insertion of  $\rho^{(2)}$  into the equation for  $\rho^{(3)}$  gives the Fourier components in the next approximation, etc. Note that in the steady-state the differentiation on the left side is replaced simply by  $-i\sum(\pm n_i\omega_i)$ , where the  $(+\omega_i)$ -component has a time dependence  $\exp(-i\omega_i t)$ , the  $(-\omega_i)$ -component varies as  $\exp(+i\omega_i t)$  and  $n_i$  is an integer. Each successive step corresponds, therefore, to a very simple algebraic operation, relating the Fourier components in each approximation to those of the preceding one. Price<sup>26</sup> has discussed the general nonlinear response in the time domain as an iterated integration over the unit impulse response function, but the steady-state response to periodic forces is most easily calculated in the frequency domain.

Although this formalism is not restricted to electromagnetic interactions and would apply equally well, for example, to the response of a system to applied periodic mechanical vibrations, the explicit form for  $\mathcal{H}_{\text{coh}}$  used in the following discussion will correspond to the semiclassical, nonrelativistic interaction of a bound electron with charge  $-e$  and a finite number of electromagnetic modes,

$$\mathcal{H}_{\text{coh}} = \frac{e}{2mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e\hbar}{mc} \mathbf{s} \cdot \nabla \times \mathbf{A} + \frac{e^2}{2mc^2} \mathbf{A} \cdot \mathbf{A}, \quad (2.2)$$

with the vector potential of the electromagnetic waves given by

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{2} \sum_{m=1}^M [\mathbf{A}_m(\mathbf{r}) \exp(-i\omega_m t) + \mathbf{A}_m^*(\mathbf{r}) \exp(i\omega_m t)], \quad (2.3)$$

$$\mathbf{A}_m(\mathbf{r}) = (c/i\omega_m) \mathbf{E}(\mathbf{k}_m, \omega_m) \exp(i\mathbf{k}_m \cdot \mathbf{r}). \quad (2.4)$$

<sup>26</sup> P. J. Price, Phys. Rev. **130**, 1792 (1963); also P. L. Kelley, J. Phys. Chem. Solids **24**, 607 (1963).

The current density operator is given by<sup>27</sup>

$$\mathbf{j}(\mathbf{r}_0) = -\frac{e}{2m} \left\{ \left[ \delta(\mathbf{r}-\mathbf{r}_0) \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right) + \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right) \delta(\mathbf{r}-\mathbf{r}_0) \right] + 2i[\delta(\mathbf{r}-\mathbf{r}_0)(\mathbf{p} \times \mathbf{s}) - (\mathbf{p} \times \mathbf{s})\delta(\mathbf{r}-\mathbf{r}_0)] \right\}, \quad (2.5)$$

where

$$\delta(\mathbf{r}-\mathbf{r}_0) = |\mathbf{r}_0\rangle \langle \mathbf{r}_0|.$$

The Fourier components of the current density in wave vector space are

$$\mathbf{j}(\mathbf{k}) = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) \mathbf{j}(\mathbf{r}). \quad (2.6)$$

They have matrix elements

$$\begin{aligned} \mathbf{j}_{n'n} &= \langle n' | \mathbf{j}(\mathbf{k}) | n \rangle = -\frac{e}{2m} \langle n' | \exp(-i\mathbf{k} \cdot \mathbf{r}) \\ &\times \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right) + \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right) \exp(-i\mathbf{k} \cdot \mathbf{r}) \\ &- 2i\hbar \mathbf{s} \times \mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{r}) | n \rangle. \end{aligned} \quad (2.7)$$

The expectation value of the current density as a function of the time is given by

$$\langle \mathbf{j}(\mathbf{k}, t) \rangle = \text{Tr}(\mathbf{j}(\mathbf{k}, t) \rho(t)) = \sum_n \sum_{n'} \mathbf{j}_{n'n}(\mathbf{k}, t) \rho_{n'n}(t). \quad (2.8)$$

This expectation value can again be decomposed into Fourier components of successive higher approximations.<sup>28</sup> The  $n$ th approximation can be written as

$$\begin{aligned} \langle \mathbf{j}^{(n)}(\mathbf{k}, t) \rangle &= \sum_n \sum_{n'} (\mathbf{j}_0(\mathbf{k}))_{n'n'} \rho_{n'n}^{(n)}(t) \\ &+ \sum_n \sum_{n'} (\mathbf{j}_1(\mathbf{k}, t))_{n'n'} \rho_{n'n}^{(n-1)}(t), \end{aligned} \quad (2.9)$$

where  $\mathbf{j}_1(\mathbf{k})$  is that part of the current-density operator linear in the field amplitude.

The linear conductivity tensor is defined by the ratio of the first-order approximation to the current density expectation value at frequency  $\omega$  with wave vector  $\mathbf{k}$  and the amplitude of the electric field with the same frequency and wave vector

$$\langle \mathbf{j}^{(1)}(\mathbf{k}, \omega) \rangle = \boldsymbol{\sigma}(\omega, \mathbf{k}) \mathbf{E}(\mathbf{k}, \omega). \quad (2.10)$$

In a similar manner higher order conductivity tensors are defined,

$$\begin{aligned} \langle \mathbf{j}^{(n)}(\mathbf{k} = \sum_{i=1}^n \mathbf{k}_i, \omega = \sum_{i=1}^n \omega_i) \rangle \\ = \boldsymbol{\sigma}^{NL}(\mathbf{k}_1 \cdots \mathbf{k}_n, \omega_1 \cdots \omega_n) \mathbf{E}(\mathbf{k}_1, \omega_1) \cdots \mathbf{E}(\mathbf{k}_n, \omega_n). \end{aligned} \quad (2.11)$$

<sup>27</sup> See, for example, A. Messiah, *Quantum Mechanics* (Interscience Publishers, Inc., New York, 1961).

<sup>28</sup> Y. R. Shen, Phys. Rev. (to be published).

Note that a particular applied frequency  $\pm\omega_n$  may be repeated several times. Therefore, the third-order current density will contain e.g., a component at the frequency  $\omega_1$  which is proportional to  $\mathbf{E}(\omega_1)\mathbf{E}^*(-\omega_1)\mathbf{E}(\omega_1)$  and which may be regarded as a saturation correction to  $j^{(1)}(\omega_1)$ .

The expectation value of both the linear and nonlinear parts of the current density may be inserted as a source term in Maxwell's equations,

$$\begin{aligned}\nabla \times \mathbf{e} &= -\frac{1}{c} \frac{\partial \mathbf{b}}{\partial t} \\ \nabla \times \mathbf{b} &= -\frac{1}{c} \frac{\partial \mathbf{e}}{\partial t} + \frac{4\pi}{c} \langle \mathbf{j}(\mathbf{r}, t) \rangle,\end{aligned}\quad (2.12)$$

where  $\mathbf{e}$  and  $\mathbf{b}$  are the vacuum fields.

A detailed discussion of the influence of the nonlinear source terms on the propagation of electromagnetic waves in nonlinear media has been given elsewhere.<sup>3</sup> Here only the outline for the quantum-mechanical calculation of these source terms is presented.

In many practical situations, e.g., in the case of a host lattice containing a dilute concentration of transition metal ions, it is of interest to exhibit more explicitly the various multipole moments that are present in a matrix element as given by Eq. (2.7). Fiutak<sup>29</sup> has shown in a general manner that the perturbation  $\mathcal{H}_{\text{coh}}$  given by Eq. (2.2) can be transformed canonically into the equivalent form,

$$\mathcal{H}_{\text{coh}}' = -\mathfrak{P} \cdot \mathbf{E} - \mathfrak{M} \cdot \mathbf{H} - \mathbf{Q} : \nabla \mathbf{E} + \dots \quad (2.13)$$

All expectation values of physical quantities derived from this equivalent Hamiltonian are the same as for the original one, to which it is related by a canonical transformation. The current density source term is now determined from

$$\langle \mathbf{j}(\mathbf{r}) \rangle = N \left[ \frac{\partial \langle \mathfrak{P} \rangle}{\partial t} + c \nabla \times \langle \mathfrak{M} \rangle - \frac{\partial}{\partial t} \nabla \cdot \langle \mathbf{Q} \rangle + \dots \right], \quad (2.14)$$

where  $N$  is the number of atomic systems per unit volume.

The expansions Eqs. (2.13) and (2.14) into multipole moments are not unique and depend on the choice of origin. Physical considerations often indicate a desirable choice, e.g., the center of a paramagnetic ion in a host lattice. If only dipole matrix elements are retained, the dipole source terms may be incorporated into Maxwell's

equations in the usual way,

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} - \frac{4\pi}{c} \frac{\partial \mathbf{M}}{\partial t}, \quad (2.15)$$

$$\nabla \times \mathbf{H} = -\frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \frac{\partial \mathbf{P}}{\partial t}, \quad (2.16)$$

$$\mathbf{P}(\mathbf{r}, t) = N \text{Tr}(\mathfrak{P}\rho(\mathbf{r}, t)), \quad (2.17)$$

$$\mathbf{M}(\mathbf{r}, t) = N \text{Tr}(\mathfrak{M}\rho(\mathbf{r}, t)). \quad (2.18)$$

Corrections for dense optical media have been discussed elsewhere.<sup>3</sup>

The advantage of the transformed Hamiltonian Eq. (2.13) is that noncommuting operators  $\mathbf{p}$  and  $\mathbf{r}$  do not occur in the same calculation. Quite a bit of care must be taken to calculate the linear electric susceptibility from the Hamiltonian with the momentum operators.<sup>30</sup> The complexity increases rapidly for the higher order nonlinear terms. The expectation value of the electric dipole moment  $\text{Tr}(\mathfrak{P}\rho)$  can readily be evaluated from the Hamiltonian Eq. (2.13). In a perturbation calculation a power series expansion in the electric and magnetic field amplitudes results.

The lowest order nonlinear term in a system that lacks inversion symmetry is the electric dipole moment proportional to a quadratic function of the electric field amplitudes. Consider explicitly the Fourier component of the dipole moment at the sum frequency  $\omega = \omega_1 + \omega_2$ , induced by an electric field with components at  $\omega_1$  and  $\omega_2$ . The Hamiltonian for this problem is

$$\begin{aligned}\mathcal{H}_{\text{coh}}' &= -\mathfrak{P} \cdot \frac{1}{2} (\mathbf{E}_1^* e^{i\omega_1 t} + \mathbf{E}_1 e^{-i\omega_1 t}) \\ &\quad - \mathfrak{P} \cdot \frac{1}{2} (\mathbf{E}_2^* e^{i\omega_2 t} + \mathbf{E}_2 e^{-i\omega_2 t}).\end{aligned}$$

It will be assumed that the electric dipole moment operator has only off-diagonal elements. (A case where diagonal elements are important will be discussed in the next section.) A typical off-diagonal element of the density matrix obeys the equation

$$\begin{aligned}i\hbar \dot{\rho}_{nn'} &= (+\omega_{nn'} - i\Gamma_{nn'}) \rho_{nn'} \\ &\quad + \sum_{n''} (\mathcal{H}_{nn''} \rho_{n''n'} - \rho_{nn''} \mathcal{H}_{n''n'}).\end{aligned}\quad (2.19)$$

The first or linear approximation to these off-diagonal elements is

$$\begin{aligned}\{\rho_{n''n'}^{(1)}\}^{(\omega_1)} &= \frac{\frac{1}{2} \mathfrak{P}_{n''n'} \cdot \mathbf{E}_1}{\omega_1 - \omega_{n''n'} + i\Gamma_{n''n'}} (+\rho_{n''n'}^{(0)} - \rho_{n'n''}^{(0)}), \quad (2.20)\end{aligned}$$

and similar expressions for frequency components at  $-\omega_1$  and  $\pm\omega_2$ .

<sup>29</sup> J. Fiutak, Can. J. Phys. **41**, 12 (1963). The build-up of diamagnetic energy is not correctly represented by Eq. (2.13). The terms of the  $A^2$ -type in Eq. (2.2) give the correct diamagnetic energy. This discrepancy is of no importance for the nonlinearities discussed in this paper.

<sup>30</sup> P. A. M. Dirac, Proc. Roy. Soc. (London) **A114**, 143, 720 (1927). See also, H. A. Kramers, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1959), pp. 482 ff.

In second approximation one finds

$$\begin{aligned}
 & \{\rho_{nn'}^{(2)}\}^{(\omega_1+\omega_2)} \\
 &= \sum_{n'' \neq n, n'} \frac{\frac{1}{4}\hbar^{-2}(\mathfrak{P}_{nn''} \cdot \mathbf{E}_2)(\mathfrak{P}_{n''n'} \cdot \mathbf{E}_1)}{\omega_1 + \omega_2 - \omega_{nn''} + i\Gamma_{nn''}} \\
 & \times \left[ \frac{\rho_{n'n''}^{(0)} - \rho_{n''n'}^{(0)}}{\omega_1 - \omega_{n'n''} + i\Gamma_{n'n''}} + \frac{\rho_{nn''}^{(0)} - \rho_{n''n'}^{(0)}}{\omega_2 - \omega_{nn''} + i\Gamma_{nn''}} \right] \\
 & + \sum_{n'' \neq n, n'} \frac{\frac{1}{4}\hbar^{-2}(\mathfrak{P}_{n''n'} \cdot \mathbf{E}_1)(\mathfrak{P}_{nn''} \cdot \mathbf{E}_2)}{\omega_1 + \omega_2 - \omega_{nn''} + i\Gamma_{nn''}} \\
 & \times \left[ \frac{\rho_{n'n''}^{(0)} - \rho_{n''n'}^{(0)}}{\omega_2 - \omega_{n'n''} + i\Gamma_{n'n''}} + \frac{\rho_{nn''}^{(0)} - \rho_{n''n'}^{(0)}}{\omega_1 - \omega_{nn''} + i\Gamma_{nn''}} \right]. \quad (2.21)
 \end{aligned}$$

The expectation value of the dipole moment at  $\omega_3$  proportional to the product of the field amplitudes at  $\omega_1$  and  $\omega_2$  may be calculated. A third-rank nonlinear polarizability tensor may be defined. Its component  $\beta_{ijk}$  is given by the following relationship:

$$\begin{aligned}
 \langle \mathcal{P}_i^{(2)}(\omega_3 = \omega_1 + \omega_2) \rangle &= \frac{1}{4}\beta_{ijk}\{E_j(\omega_1)E_k(\omega_2) + E_k(\omega_2)E_j(\omega_1)\} \\
 &= \sum_n \sum_{n'} (\mathcal{P}_i)_{nn'} \{\rho_{n'n}^{(2)}\}^{(\omega_1+\omega_2)}. \quad (2.22)
 \end{aligned}$$

The factor  $\frac{1}{4}$  is inserted so that for real  $\beta$  and real fields  $E_1 \cos\omega_1 t$  and  $E_2 \cos\omega_2 t$ , the real polarization is given by  $\mathfrak{P}_i \cos\omega_3 t$ . The expression is symmetrical in the component  $E_j(\omega_1)$  and  $E_k(\omega_2)$ . This follows immediately from the detailed form of Eq. (2.21).

If the damping is negligible, the terms  $i\Gamma_{nn'}$  in the denominators of Eq. (2.21) can be omitted. This situation is important in the harmonic generation of light, when all optical resonances are far removed. When the denominators are real and contain only frequency differences, the terms in Eq. (2.21) can be rearranged and relabeled. The  $ijk$  component of the third-rank polarizability tensor can be written in the absence of damping as,

$$\begin{aligned}
 \beta_{ijk} &= \sum_{g \neq n, n'} \sum \{ (\mathcal{P}_i)_{gn} (\mathcal{P}_j)_{n'g} (\mathcal{P}_k)_{nn'} A_{nn'} + (\mathcal{P}_i)_{gn} (\mathcal{P}_j)_{nn'} \\
 & \times (\mathcal{P}_k)_{n'g} A'_{nn'} + (\mathcal{P}_i)_{n'g} (\mathcal{P}_j)_{nn'} (\mathcal{P}_k)_{gn} B_{nn'} \\
 & + (\mathcal{P}_i)_{n'g} (\mathcal{P}_j)_{gn} (\mathcal{P}_k)_{nn'} B'_{nn'} \\
 & + (\mathcal{P}_i)_{n'n} (\mathcal{P}_j)_{gn'} (\mathcal{P}_k)_{ng} C_{nn'} \\
 & + (\mathcal{P}_i)_{n'n} (\mathcal{P}_j)_{ng} (\mathcal{P}_k)_{gn'} C'_{nn'} \} \rho_{gg}^{(0)}, \quad (2.23)
 \end{aligned}$$

with

$$\begin{aligned}
 A_{nn'} &= (2\hbar^2)^{-1} [(\omega_3 - \omega_{ng})^{-1} (\omega_1 - \omega_{n'g})^{-1}], \\
 A'_{nn'} &= (2\hbar^2)^{-1} [(\omega_3 - \omega_{ng})^{-1} (\omega_2 - \omega_{n'g})^{-1}], \\
 B_{nn'} &= (2\hbar^2)^{-1} [(\omega_3 + \omega_{n'g})^{-1} (\omega_2 + \omega_{ng})^{-1}], \\
 B'_{nn'} &= (2\hbar^2)^{-1} [(\omega_3 + \omega_{n'g})^{-1} (\omega_1 + \omega_{ng})^{-1}], \\
 C_{nn'} &= -(2\hbar^2)^{-1} [(\omega_1 + \omega_{n'g})^{-1} (\omega_2 - \omega_{ng})^{-1}], \\
 C'_{nn'} &= -(2\hbar^2)^{-1} [(\omega_2 + \omega_{n'g})^{-1} (\omega_1 - \omega_{ng})^{-1}].
 \end{aligned}$$

When the additional assumption is made that the matrix elements  $\mathcal{P}_{nn'}$  are real, the expression Eq. (2.23) is identical with Eqs. (2.13) and (2.14) of Armstrong<sup>3</sup> *et al.*

In a similar manner, higher order nonlinear electric and magnetic susceptibilities may be determined. Not only parametric effects, but also saturation, maser, and Raman maser action are described by these nonlinear complex susceptibilities. Far away from all resonance transitions the parametric effects dominate. In this case, the hierarchy in terms of ascending powers of the field amplitudes is especially useful. In case of resonance, one often wishes to retain all powers of the fields for the Fourier components of the density matrix at resonance to take complete cognizance of saturation effects. One decides in this case, *a priori*, which Fourier components in each of the matrix elements of  $\rho$  are to be retained and which are to be truncated off as small nonsecular terms. Sorting out the terms on the left and right with the same frequency dependence in the equations of motion (1.4) leads to a set of simultaneous linear algebraic equations. In principle, the Fourier components of the density matrix elements and, therefore, of expectation values of the dipole moments can be determined in a straightforward algebraic manner. In practice, the number of unknowns is large even in relatively simple situations with only two or three energy levels. Computer solutions are indicated, but they tend to obscure the basic physical processes in the high-order interference of parametric, maser, Raman maser and other multiple-photon processes.

The general methods outlined in this section will be applied and illustrated for a two-level and a three-level system. In these cases, the basic nonlinear mechanisms can be unraveled. The analysis will show when parametric and when maser effects are dominant and how they interfere.

If the applied electric or magnetic fields contain a dc component, i.e., if one of the applied frequencies is zero, this formalism contains, as special cases, the Pockels and quadratic electro-optic effect, as well as the Faraday and quadratic magnetic effects. In the case of applied dc fields, some care must be taken to correct the relaxation terms as well. The paramagnetic part of the Faraday effect<sup>27</sup> is, e.g., due to the change in population of states by the application of the dc magnetic field. The relaxation is towards thermal equilibrium for the instantaneous values of the applied fields as mentioned earlier.

### III. NONLINEAR SUSCEPTIBILITIES OF A TWO-LEVEL SYSTEM

Consider a system with two energy levels  $|a\rangle$  and  $|b\rangle$  with an energy separation,

$$\langle b | \mathcal{H}_A | b \rangle - \langle a | \mathcal{H}_A | a \rangle = \hbar\omega_{ba}. \quad (3.1)$$

### A. Two Rotating Fields

Two periodic perturbations at frequencies  $\omega_1$  and  $\omega_2$  are assumed to have only off-diagonal elements. In the language of magnetic resonance, the system is subjected to two rotating high-frequency fields. If  $\omega_2 = -\omega_1$ , the problem of a linear polarized high-frequency field results. A notation suggestive of magnetic dipole transitions will be used, although the results are valid for any two-level system.<sup>10,22</sup>

With

$$\mathcal{H}C_{ba}^{\text{coh}} = -\mu_{ba}(H_1 e^{-i\omega_1 t} + H_2 e^{-i\omega_2 t}) = \mathcal{H}C_{ab}^{\text{coh}*}$$

the equations of motion are in this case, with  $\Gamma_{ab}^{-1} = T_2$ ,

$$i\hbar\dot{\rho}_{ab} = -\hbar(\omega_{ba} + i/T_2)\rho_{ab} + \mathcal{H}C_{ab}^{\text{coh}}(\rho_{bb} - \rho_{aa}), \quad (3.2a)$$

$$i\hbar\dot{\rho}_{ba} = \hbar(\omega_{ba} - i/T_2)\rho_{ba} - \mathcal{H}C_{ba}^{\text{coh}}(\rho_{bb} - \rho_{aa}), \quad (3.2b)$$

$$i\hbar(\dot{\rho}_{bb} - \dot{\rho}_{aa}) = 2(\mathcal{H}C_{ba}^{\text{coh}}\rho_{ab} - \rho_{ba}\mathcal{H}C_{ab}^{\text{coh}}) - (i\hbar/T_1)(\rho_{bb} - \rho_{aa} - \rho_{bb}^0 + \rho_{aa}^0), \quad (3.2c)$$

$$\rho_{aa} + \rho_{bb} = 1. \quad (3.2d)$$

In first order, one finds the well-known linear approximation,

$$\rho_{ba}^{(1)}(\omega_1) = \frac{-\hbar^{-1}\mu_{ba}H_1}{+\omega_1 - \omega_{ba} + i/T_2}(\rho_{aa}^{(0)} - \rho_{bb}^{(0)}),$$

and a similar expression for  $\rho_{ba}^{(1)}(\omega_2)$ ,  $\rho_{ab}^{(1)}(\omega_1)$ , and  $\rho_{ab}^{(1)}(\omega_2)$ . Note that  $\rho_{ba}(\omega_1) = \rho_{ab}^*(\omega_1)$  in the case of damping. In second approximation the difference between the diagonal elements of the density matrix has Fourier components at  $\omega_1 - \omega_2$ ,  $\omega_2 - \omega_1$  and dc terms,

$$\begin{aligned} & (\rho_{bb}^{(2)} - \rho_{aa}^{(2)})^{(\omega_1 - \omega_2)} \\ &= \frac{2\hbar^{-2}|\mu_{ab}|^2 H_1 H_2^*}{\omega_1 - \omega_2 + i/T_1} \left\{ \frac{1}{-\omega_2 - \omega_{ab} + i/T_2} \right. \\ & \quad \left. + \frac{1}{\omega_1 - \omega_{ba} + i/T_2} \right\} (\rho_{bb}^{(0)} - \rho_{aa}^{(0)}) \\ & (\rho_{bb}^{(2)} - \rho_{aa}^{(2)})^{(\omega_2 - \omega_1)} = [(\rho_{bb}^{(2)} - \rho_{aa}^{(2)})^{(\omega_1 - \omega_2)}]^*. \end{aligned} \quad (3.3)$$

From Eq. (3.2d) we have in general,

$$\rho_{bb}(\omega) + \rho_{aa}(\omega) = 0 \quad \text{for } \omega \neq 0.$$

These terms are responsible for a longitudinal component of magnetization at this difference frequency.

$$\langle \mathfrak{M}_z \rangle_{(\omega_1 - \omega_2)} e^{-i(\omega_1 - \omega_2)t} = -\mu_0 \{ \rho_{bb}^{(2)} - \rho_{aa}^{(2)} \}^{(\omega_1 - \omega_2)} e^{-i(\omega_1 - \omega_2)t}, \quad (3.4)$$

where

$$-\langle b | \mathfrak{M}_z | b \rangle = \mu_0 = +\langle a | \mathfrak{M}_z | a \rangle.$$

With  $\omega_1 = -\omega_2$ , this term describes the source of second harmonic generation, if a magnetic resonance is driven by a linearly polarized high-frequency field.

The creation of a polarization at the difference frequency  $\pm(\omega_2 - \omega_1)$  is clearly a parametric process.

Note that the phase of the magnetization at this frequency depends on the difference of the phases of the applied fields at  $\omega_1$  and  $\omega_2$ . Whether positive or negative absorption will occur at  $\omega_2 - \omega_1$ , depends on the presence and relative phase of a longitudinal magnetic field at this frequency.

The dc term in second approximation describes the onset of saturation in the presence of two rotating fields,

$$\begin{aligned} \{ \rho_{bb}^{(2)} - \rho_{aa}^{(2)} \}^{\text{dc}} = & \left[ \frac{-2T_1 T_2 \hbar^{-2} |\mu_{ab}|^2 |H_1|^2}{(\omega_1 - \omega_{ba})^2 T_2^2 + 1} \right. \\ & \left. + \frac{-2T_1 T_2 \hbar^{-2} |\mu_{ab}|^2 |H_2|^2}{(\omega_2 - \omega_{ba})^2 T_2^2 + 1} \right] \times \{ \rho_{bb}^{(0)} - \rho_{aa}^{(0)} \}. \end{aligned} \quad (3.5)$$

It is clearly only a first approximation to the saturation effect, obtainable if the usual saturation denominator is expanded in a power series.

If  $\rho_{bb} - \rho_{aa}$  in Eq. (3.2a) is replaced by the expression for  $\rho_{bb}^{(2)} - \rho_{aa}^{(2)}$ , the third approximation  $\rho_{ab}^{(3)}$  is obtained. There are new frequency components at  $2\omega_1 - \omega_2$  and  $2\omega_2 - \omega_1$ . These are parametric terms. For  $\omega_1 = -\omega_2$  they describe the generation of third harmonics.

In addition, one finds that the magnetization at  $\omega_1$  has terms proportional to  $|H_1|^2 H_1$  and  $|H_2|^2 H_1$ . The first always decreases the first-order absorption at  $\omega_1$ . It corresponds to an absorption and emission process at  $\hbar\omega_1$ , and describes incipient saturation of the signal at  $\omega_1$ . The second term corresponds to the absorption of a quantum at  $\hbar\omega_1$ , and emission of a quantum at  $\hbar\omega_2$  or vice versa. The energy balance  $\pm\hbar(\omega_2 - \omega_1)$  is taken up by the damping mechanism. This term corresponds to a Raman process and may either increase or decrease the absorption at  $\omega_1$ . The process could be continued indefinitely;  $\rho_{bb}^{(4)} - \rho_{aa}^{(4)}$  may be found from  $\rho_{ba}^{(3)}$  and  $\rho_{ab}^{(3)}$ , etc. This gives successive approximations in ascending powers of both  $H_1$  and  $H_2$ .

It is also possible to obtain a solution correct to all powers of  $H_1$ , but ascending powers of  $H_2$  alone. This solution was already discussed by Bloch<sup>7</sup> in terms of a reference frame rotating at  $\omega_1$ , in which the large perturbation  $H_1$  is time-independent. With the present method the density matrix is solved in the laboratory coordinate system. The steady-state solution correct to terms independent of  $H_2$ , is of course nothing but the well-known saturation solution of the Bloch equations,

$$\begin{aligned} \rho_{bb}^{\text{dc}} - \rho_{aa}^{\text{dc}} = & (\rho_{bb}^{(0)} - \rho_{aa}^{(0)}) \\ & \times \frac{1 + (-\omega_1 + \omega_{ba})^2 T^2}{1 + (-\omega_1 + \omega_{ba})^2 T_2^2 + |\mu_{ab}|^2 |H_1|^2 T_1 T_2} \\ & - \frac{\hbar^{-1}\mu_{ba}H_1}{\omega_1 - \omega_{ba} + i/T_2} (\rho_{aa}^{\text{dc}} - \rho_{bb}^{\text{dc}}). \end{aligned} \quad (3.6)$$

Next, the terms of the density matrix elements linear

in  $H_2$  are sought. Equation (3.6) is still correct to this order of approximation. The equations for

$$\{\rho_{bb}-\rho_{aa}\}^{(\omega_2-\omega_1)}, \rho_{ba}^{(\omega_2)}, \text{ and } \rho_{ab}^{(\omega_2-2\omega_1)}$$

are considered simultaneously,

$$\begin{aligned} & (\omega_2-\omega_{ba}+i/T_2)\rho_{ba}^{(\omega_2)} \\ &= -\hbar^{-1}\mu_{ba}H_2(\rho_{aa}^{\text{dc}}-\rho_{bb}^{\text{dc}}) \\ & \quad +\hbar^{-1}\mu_{ba}H_1\{\rho_{bb}-\rho_{aa}\}^{(\omega_2-\omega_1)}, \quad (3.7) \end{aligned}$$

$$\rho_{ba}^{(\omega_2)}$$

$$= -\hbar^{-1}\mu_{ba}H_2(\rho_{aa}-\rho_{bb})^{\text{dc}} / \left( \omega_2-\omega_{ba}+i/T_2 - \frac{2\hbar^{-2}|\mu_{ab}|^2|H_1|^2}{\omega_2-\omega_1+i/T_1-2\hbar^{-2}|\mu_{ab}|^2|H_1|^2/(\omega_2-2\omega_1-\omega_{ab}+i/T_2)} \right). \quad (3.10)$$

Assume that the two applied frequencies are sufficiently different so that they can indeed be distinguished physically,  $|\omega_2-\omega_1| \gg T_1^{-1}$ . The expression may then be recast in the form,

$$\begin{aligned} \rho_{ba}^{(\omega_2)} &= -(1/D)\hbar^{-1}\mu_{ab}H_2[(\omega_2-\omega_1) \\ & \quad \times (\omega_2-2\omega_1-\omega_{ab}+i/T_2) \\ & \quad - 2\hbar^{-2}|\mu_{ab}|^2|H_1|^2](\rho_{aa}-\rho_{bb})^{\text{dc}}, \quad (3.11) \end{aligned}$$

$$\begin{aligned} D &= (\omega_2-\omega_1)[(\omega_2-\omega_1)^2 - (\omega_{ba}-\omega_1)^2 \\ & \quad - 4\hbar^{-2}|\mu_{ab}|^2|H_1|^2 - T_2^{-2}] \\ & \quad + i[2(\omega_2-\omega_1)^2 - 4\hbar^{-2}|\mu_{ab}|^2|H_1|^2]T_2^{-1}. \end{aligned}$$

Inspection of the denominator shows that the real part vanishes when

$$\omega_2-\omega_1 = \pm \{ (\omega_1-\omega_{ba})^2 + 4\hbar^{-2}|\mu_{ab}|^2H_1^2 + T_2^{-2} \}^{+1/2}. \quad (3.12)$$

This describes the resonance with respect to the effective field in the rotating coordinate system. The last term in the numerator corresponds to Raman processes; the first term gives the linear dispersion. Both effects are modified by the denominator, which takes account of the absorption and re-emission of an arbitrary number of quanta  $\hbar\omega_1$ , because  $|H_1|^2$  is retained to all powers of the power series expansion. The parametric processes occur in the corresponding expressions for  $\rho_{bb}-\rho_{aa}$ , which may be obtained by substitution of Eq. (3.10) or (3.11) back into Eq. (3.8).

In higher approximation the terms in  $H_2^2$  and  $|H_2|^2$  could be calculated in an analogous manner. The algebraic labor increases rapidly and basic physical processes cannot be easily separated in higher approximations, when many different quantum processes interfere.

### B. One Rotating Field and One Longitudinal Oscillating Field

In this example the negative absorption associated with Raman processes will be exhibited very clearly. The Hamiltonian of the coherent perturbations has

$$\begin{aligned} & (\omega_2-\omega_1+i/T_1)\{\rho_{bb}-\rho_{aa}\}^{(\omega_2-\omega_1)} \\ &= +2\hbar^{-1}\mu_{ab}H_1^*\rho_{ba}^{(\omega_2)} - 2\hbar^{-1}\mu_{ba}H_1\rho_{ab}^{(\omega_2-2\omega_1)}, \quad (3.8) \end{aligned}$$

$$\begin{aligned} & (\omega_2-2\omega_1-\omega_{ab}+i/T_2)\rho_{ab}^{(\omega_2-2\omega_1)} \\ &= -\hbar^{-1}\mu_{ab}H_1^*\{\rho_{bb}-\rho_{aa}\}^{(\omega_2-\omega_1)}. \quad (3.9) \end{aligned}$$

The explicit solution for this set of three simultaneous equations may readily be given a physical interpretation in the coordinate system rotating at the frequency  $\omega_1$ . The analytic expression for  $\rho_{ba}^{(\omega_2)}$  is

the form

$$\begin{aligned} \mathcal{H}\mathcal{C}_{ba}^{\text{coh}} &= -\mu_{ba}H_1e^{-i\omega_1t} = \mathcal{H}\mathcal{C}_{ab}^{\text{coh}*} \\ \mathcal{H}\mathcal{C}_{aa}^{\text{coh}} &= -\mathcal{H}\mathcal{C}_{bb}^{\text{coh}} = -\frac{1}{2}\mu_0(H_3e^{-i\omega_3t} + H_3^*e^{+i\omega_3t}). \end{aligned}$$

The equations of motion are now

$$\begin{aligned} i\hbar\dot{\rho}_{ba} &= -\mu_{ba}H_1e^{-i\omega_1t}(\rho_{aa}-\rho_{bb}) - \hbar(\omega+i/T_2)\rho_{ba} \\ & \quad - \mu_0(H_3e^{-i\omega_3t} + H_3^*e^{+i\omega_3t})\rho_{ba} \quad (3.13) \end{aligned}$$

$$\dot{\rho}_{bb} - \dot{\rho}_{aa}$$

$$\begin{aligned} &= -2i\hbar^{-1}(\mu_{ba}H_1e^{-i\omega_1t}\rho_{ab} - \mu_{ab}H_1^*e^{+i\omega_1t}\rho_{ba}) \\ & \quad - (\rho_{bb}-\rho_{aa}-\rho_{bb}^0+\rho_{aa}^0)T_1^{-1} + \frac{\hbar\omega_{ba}/kT}{\sinh(\hbar\omega_{ba}/kT)} \\ & \quad \times \frac{\mu_0(H_3e^{-i\omega_3t} + H_3^*e^{+i\omega_3t})}{\hbar\omega_{ba}}(\rho_{bb}^0-\rho_{aa}^0)T_1^{-1}. \quad (3.14) \end{aligned}$$

The assumption  $kT > \mu_0H_3$ , always valid in practice, has been made. The last term should be ignored within the approximations on the damping mechanism set forth at the beginning of this report. It takes account of the fact that the system relaxes toward the thermal equilibrium for the instantaneous Hamiltonian  $\mathcal{H}_A + \mathcal{H}^{\text{coh}}(t)$  rather than  $\mathcal{H}_A$  alone. It gives rise to a small linear longitudinal susceptibility.

$$\begin{aligned} & \{\rho_{bb}^{(1)} - \rho_{aa}^{(1)}\}^{(-\omega_3)} \\ &= \frac{(\hbar\omega_{ba}/kT)\mu_0H_3^*}{\sinh(\hbar\omega_{ba}/kT)\hbar\omega_{ba}} \frac{1}{i\omega_3T_1+1} (\rho_{bb}^0 - \rho_{aa}^0). \quad (3.15) \end{aligned}$$

This term is carried along into the next approximation only to show explicitly that its contribution is negligibly small.

The lowest order nonlinear response consists of the usual saturation correction  $\{\rho_{bb}^{(2)} - \rho_{aa}^{(2)}\}^{\text{dc}}$  proportional to  $|H_1|^2$ , and a parametric beat for the transverse components of magnetization at the frequencies  $\omega_1 \pm \omega_3$ . This may be derived from off-diagonal Fourier

components such as

$$\begin{aligned} & \{\rho_{ba}^{(2)}\}^{(\omega_1-\omega_3)} \\ &= \frac{-\hbar^{-2}\mu_0\mu_{ba}H_1H_3^*}{(\omega_1-\omega_{ba}+i/T_2)(\omega_1-\omega_3-\omega_{ba}+i/T_2)} \\ & \times (\rho_{aa}^{(0)}-\rho_{bb}^{(0)}) + \frac{\hbar\omega_{ba}/kT}{\sinh(\hbar\omega_{ba}/kT)} \\ & \times \frac{\mu_0\mu_{ba}H_1H_3^*}{(+i\omega_3T_1+1)\hbar\omega_{ba}(\omega_1-\omega_3-\omega_{ba}+i/T_2)} \\ & \times (\rho_{bb}^{(0)}-\rho_{aa}^{(0)}). \quad (3.16) \end{aligned}$$

The last term arises from the first term on the right-hand side of Eq. (3.13), when the expression Eq. (3.15) is substituted. It is clearly smaller by a factor

$$\frac{\hbar\omega_{ba}/kT}{\sinh(\hbar\omega_{ba}/kT)} |i\omega_3T_1+1|^{-1} < |i\omega_3T_1+1|^{-1} \ll 1$$

than the first term and will, henceforth, be ignored.

In the next higher nonlinear approximation the components at the original frequencies  $\omega_1$  and  $\pm\omega_3$  receive corrections proportional to the intensity of the applied fields.

$$\begin{aligned} & \{\rho_{ba}^{(3)}\}^{(\omega_1)} \\ &= -\frac{\hbar^{-3}\mu_0^2\mu_{ba}H_1|H_3|^2(\rho_{aa}^{(0)}-\rho_{bb}^{(0)})}{(\omega_1-\omega_{ba}+i/T_2)^2} \\ & \times \left[ \frac{1}{\omega_1-\omega_3-\omega_{ba}+i/T_2} + \frac{1}{\omega_1+\omega_3-\omega_{ba}+i/T_2} \right] \\ & + \text{terms proportional to } H_1|H_1|^2 \quad (3.17) \end{aligned}$$

$$\begin{aligned} & \{\rho_{bb}^{(3)}-\rho_{aa}^{(3)}\}^{(\omega_3)} \\ &= -\frac{2\hbar^{-3}|\mu_{ab}|^2\mu_0H_3|H_1|^2(\rho_{bb}^{(0)}-\rho_{aa}^{(0)})}{(\omega_3+i/T_1)(\omega_1-\omega_{ba}-i/T_2)(\omega_1-\omega_3-\omega_{ba}-i/T_2)} \\ & + \frac{2\hbar^{-3}|\mu_{ab}|^2\mu_0H_3|H_1|^2(\rho_{bb}^{(0)}-\rho_{aa}^{(0)})}{(\omega_3+i/T_1)(\omega_1-\omega_{ba}+i/T_2)(\omega_1+\omega_3-\omega_{ba}+i/T_2)}. \quad (3.18) \end{aligned}$$

Consider the case  $\omega_1-\omega_3=\omega_{ba}$ . A two-quantum Raman transition is possible between levels  $|a\rangle$  and  $|b\rangle$ , as indicated in Fig. 1(A). Exclude single quantum transitions,  $|\omega_1+\omega_{ba}| \gg T_2^{-1}$ . This implies  $\omega_3 \gg T_2^{-1} \geq T_1^{-1}$ . Under these circumstances the first terms on the right-hand side of Eqs. (3.17) and (3.18) are dominant and the nonlinear susceptibilities become pure imaginary

$$\{\rho_{ba}^{(3)}\}^{(\omega_1)}/H_1 = +2iT_2\hbar^{-3}\omega_3^{-2}\mu_0^2\mu_{ba}|H_3|^2 \times (\rho_{aa}^{(0)}-\rho_{bb}^{(0)}), \quad (3.19)$$

$$\{\rho_{aa}^{(3)}-\rho_{bb}^{(3)}\}^{(\omega_3)}/H_3 = -2iT_2\hbar^{-3}\omega_3^{-2}\mu_0|\mu_{ab}|^2 \times |H_1|^2(\rho_{aa}^{(0)}-\rho_{bb}^{(0)}). \quad (3.20)$$

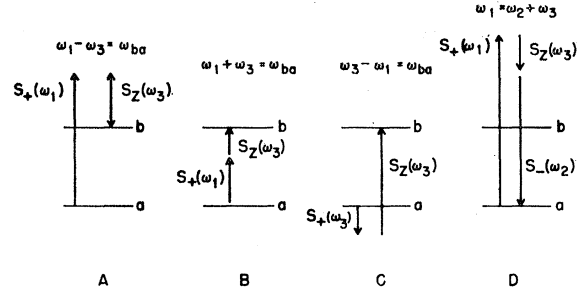


FIG. 1. Nonlinear processes in a two-level system. A Raman process, in which a "transverse" quantum is emitted and a "longitudinal" quantum absorbed. B Two-quanta absorption. C Raman process, in which a "transverse" quantum is absorbed and a "longitudinal" quantum emitted. D Illustration of a parametric process. It should not be interpreted literally as a three-photon scattering process, as explained in the text.

For normal populations  $\rho_{aa}^{(0)}-\rho_{bb}^{(0)}>0$ , the sign of the susceptibility is such, that there is a positive absorption at  $\omega_1$  proportional to the intensity  $|H_3|^2$ , but there is negative absorption at  $\omega_3$ , proportional to the intensity  $|H_1|^2$ . This is just what could be expected for the Raman effect.

If one takes  $\omega_1+\omega_3=\omega_{ba}$ , the last terms in Eqs. (3.17) and Eq. (3.18) dominate. In this case, Eq. (3.19) keeps the same sign, but the sign in Eq. (3.20) is reversed. There is now positive absorption at both frequencies, corresponding to a two-quantum absorption process shown in Fig. 1(B).

Figure 1(C) illustrates the case that  $\omega_1<0$ ,  $\omega_3=\omega_{ba}-\omega_1$ . Although the sign of the imaginary susceptibility in Eq. (3.19) remains formally unchanged, it now corresponds to a negative absorption at  $|\omega_1|$ , because the sign of  $\omega_1$  is negative. The transition from level  $|a\rangle$  to  $|b\rangle$  is accomplished by emission of  $\hbar\omega_1$ , and absorption of a larger quantum  $\hbar\omega_3$ . If the initial populations were inverted,  $\rho_{bb}^{(0)}-\rho_{aa}^{(0)}>0$ , all signs would be inverted and all processes would proceed in the opposite direction.

This problem could also be solved with all powers of  $H_1$  taken into account. Again, basic physical processes, such as parametric and Raman processes, can be identified. In the semiclassical theory the Raman processes are described by nonlinear complex susceptibilities, which are clearly distinguishable from the susceptibilities for parametric processes. The quantum process associated with the parametric susceptibility of Eq. (3.16) is shown in Fig. 1(D). The atomic system is purely reactive, and makes no real transition to a state with different energy. Although the parametric process is illustrated as a three-photon scattering, yet it appears in the perturbation calculation in lower order than the Raman process. The reason is that it is a coherent dispersive effect, rather than an incoherent scattering process with a transition probability proportional to the square of the matrix element, in which all phase information is lost. In a similar manner, the linear dispersion corresponds to a coherent scattering. Al-



though it is often visualized as a scattering in which the incoming and outgoing photon have the same frequency, it appears in the same order of the density matrix perturbation as the single-photon absorption process. It is, strictly speaking, not correct to visualize the linear dispersive and nonlinear parametric polarization by photon scattering processes in which phase information is not involved. The phase of the induced polarization at the frequencies  $\omega_1 \pm \omega_3$  is determined by the phases of the applied fields at  $\omega_1$  and  $\omega_3$ , and the number of quanta is not precisely known. One cannot decide whether there is absorption at the combination frequencies, until the phase of the field at these frequencies is known. It is, of course, inconsistent to assume that the field at  $\omega_1 \pm \omega_3$  vanishes. Even if originally no field is applied at these combination frequencies, such a field will be generated by the parametric polarization. To obtain a self-consistent description, the reaction of the polarization on the electromagnetic modes must be taken into account. This will be done in the final section of this paper.

### C. Two Rotating Fields and One Longitudinal Field

The two rotating fields have frequencies  $\omega_1$  and  $\omega_2$ , and the longitudinal field has the frequency  $\pm\omega_3 = \pm(\omega_1 - \omega_2)$ . If the method of ascending powers in the field amplitudes is used, a straightforward combination of cases A and B results. This is the best systematic approach to this problem. There is no satisfactory truncation procedure if  $\omega_1$  and  $\omega_2$  are both close to resonance and  $|\omega_1 - \omega_2|$  is small. The following diagonal Fourier components should be retained,  $(\rho_{bb} - \rho_{aa})^{\text{dc}}$ ,  $(\rho_{bb} - \rho_{aa})^{(\pm\omega_3)}$ ,  $(\rho_{bb} - \rho_{aa})^{(\pm 2\omega_3)}$ , etc. The following off-diagonal components are in the "near-resonance" category,  $\rho_{ba}^{(\omega_1)}$ ,  $\rho_{ba}^{(\omega_2)}$ ,  $\rho_{ba}^{(\omega_1 - \omega_2)}$ ,  $\rho_{ba}^{(2\omega_1 - \omega_2)}$ ,  $\rho_{ba}^{(2\omega_2 - \omega_1)}$ ,  $\rho_{ba}^{(3\omega_1 - 2\omega_2)}$ ,  $\rho_{ba}^{(3\omega_2 - 2\omega_1)}$ , etc.

If three fields at the frequencies  $\omega_1$ ,  $\omega_2$  and  $\omega_3 = \omega_1 + \omega_2$  are applied to a three-level system, a finite number of "near resonance" terms can be identified in an unambiguous fashion. This case is of considerable practical interest and will be discussed next.

### IV. NONLINEAR SUSCEPTIBILITY OF A THREE-LEVEL SYSTEM

The steady-state response of a system with a lower energy state  $|a\rangle$ , a middle state  $|b\rangle$ , and an upper state

$|c\rangle$  to three applied fields at the frequencies  $\omega_1$ ,  $\omega_2$ , and  $\omega_3 = \omega_1 + \omega_2$  can be calculated with the general Fourier power series expansion method. If the three applied frequencies are close to the resonant frequencies, i.e.,  $|\omega_1 - \omega_{ba}| \ll \omega_{ba}$ ,  $|\omega_2 - \omega_{cb}| \ll \omega_{cb}$ , and, consequently,  $|\omega_3 - \omega_{ca}| \ll \omega_{ca}$ , the Fourier series can be truncated in an unambiguous fashion. Only the following matrix elements of the periodic perturbations are retained, so that the truncated Hamiltonian becomes,

$$\mathcal{H}_{\text{coh}} = \begin{Bmatrix} 0 & V_{ab}e^{i\omega_1 t} & V_{ac}e^{i\omega_3 t} \\ V_{ba}e^{-i\omega_1 t} & 0 & V_{bc}e^{i\omega_2 t} \\ V_{ca}e^{-i\omega_3 t} & V_{cb}e^{-i\omega_2 t} & 0 \end{Bmatrix}. \quad (4.1)$$

For electric dipole transitions, one has, for example,  $V_{ab} = -\hbar^{-1} \mathbf{p}_{ab} \cdot \mathbf{E}_1$ , etc. Note that this truncated Hamiltonian can be made time-independent by a diagonal unitary transformation  $\mathcal{H}' = U^\dagger \mathcal{H} U$ ,

$$U = \begin{Bmatrix} e^{i\omega_1 t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_2 t} \end{Bmatrix}. \quad (4.2)$$

Wilcox and Lamb<sup>22</sup> have solved the three-level problem with two applied fields in the transformed representation. The steady-state solution is, however, more directly obtained in the laboratory frame. The fact that the problem can be reduced to a time-independent problem in which each matrix element in the steady state is time-independent, suggests that only one Fourier component for each element of the density matrix will occur in the laboratory frame. This is, indeed, the case. Only dc components of the diagonal elements of the density matrix are retained, together with the following six off-diagonal Fourier components:  $\rho_{ba}^{(\omega_1)}$  and  $\rho_{ab}^{(-\omega_1)}$ ,  $\rho_{ca}^{(\omega_3)}$  and  $\rho_{ac}^{(-\omega_3)}$ ,  $\rho_{cb}^{(\omega_2)}$  and  $\rho_{bc}^{(-\omega_2)}$ . The equations of motion reduce to nine algebraic linear equations with nine unknowns. One of these equations is the inhomogeneous normalization condition  $\rho_{aa}^{\text{dc}} + \rho_{bb}^{\text{dc}} + \rho_{cc}^{\text{dc}} = 1$ . With the abbreviations

$$\begin{aligned} \Delta_{ba} &= \omega_1 - \omega_{ba} + i\Gamma_{ba} = -\Delta_{ab}^*, \\ \Delta_{cb} &= \omega_2 - \omega_{cb} + i\Gamma_{cb} = -\Delta_{bc}^*, \\ \Delta_{ca} &= \omega_3 - \omega_{ca} + i\Gamma_{ca} = -\Delta_{ac}^*, \end{aligned} \quad (4.3)$$

the equations of motion are expressed in matrix form

$$\begin{Bmatrix} 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ w_{ba} & -w_{ab} - w_{cb} & w_{bc} & V_{ba} & -V_{ab} & -V_{cb} & V_{bc} & 0 & 0 \\ w_{ca} & w_{cb} & -w_{ac} - w_{bc} & 0 & 0 & V_{cb} & -V_{bc} & V_{ca} & -V_{ac} \\ -V_{ab} & V_{ab} & 0 & \Delta_{ab} & 0 & 0 & V_{ac} & -V_{cb} & 0 \\ V_{ba} & -V_{ba} & 0 & 0 & \Delta_{ba} & -V_{ca} & 0 & 0 & V_{bc} \\ 0 & -V_{bc} & V_{bc} & 0 & -V_{ac} & \Delta_{bc} & 0 & V_{ba} & 0 \\ 0 & V_{cb} & -V_{cb} & V_{ca} & 0 & 0 & \Delta_{cb} & 0 & -V_{ab} \\ -V_{ac} & 0 & V_{ac} & -V_{bc} & 0 & V_{ab} & 0 & \Delta_{ac} & 0 \\ V_{ca} & 0 & -V_{ca} & 0 & V_{cb} & 0 & -V_{ba} & 0 & \Delta_{ca} \end{Bmatrix} \begin{Bmatrix} \rho_{aa}^{\text{dc}} \\ \rho_{bb}^{\text{dc}} \\ \rho_{cc}^{\text{dc}} \\ \rho_{ab}^{(-\omega_1)} \\ \rho_{ba}^{(\omega_1)} \\ \rho_{bc}^{(-\omega_2)} \\ \rho_{cb}^{(\omega_2)} \\ \rho_{ac}^{(-\omega_3)} \\ \rho_{ca}^{(\omega_3)} \end{Bmatrix} = \begin{Bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{Bmatrix}. \quad (4.4)$$

The solution for the density matrix elements from this array of linear equations gives them as functions of all powers of the amplitudes of the three applied fields. The solution contains, therefore, all possible interference effects between single and multiple quantum absorption and emission processes and parametric scattering processes, as well as all saturation effects of successive absorption and re-emission of quanta.

There are schemes to unravel the complexity of the  $9 \times 10$  matrix problem. It is helpful to eliminate first  $\rho_{ab}$ ,  $\rho_{bc}$ , and  $\rho_{ca}$ , and write the remaining six variables as two vectors,  $\boldsymbol{\rho} = (\rho_{aa}, \rho_{bb}, \rho_{cc})$  and  $\boldsymbol{u} = (\rho_{ba}, \rho_{cb}, \rho_{ac})$ . The remaining six equations can then be expressed as two-vector equations multiplied by  $3 \times 3$  matrices. This procedure was used by Wilcox and Lamb<sup>22</sup>, who solved the case of two large applied fields, as did Yatsiv.<sup>13</sup> It allows for the arrangement of the various terms according to the powers of the field amplitudes. The expressions are too complicated for reproduction here, and are not particularly useful or illuminating. If all three fields are very large  $|V/\Gamma| \gg 1$ , a "heat death" of the system results,  $\rho_{aa} = \rho_{bb} = \rho_{cc} = \frac{1}{3}$ . In the intermediate situation when several  $(V/\Gamma)$  and  $(\omega/\Gamma)$  are of the order of unity, peculiar inversions may occur, and even the possibility that  $\rho_{cc} - \rho_{aa} > 0$  cannot be excluded in a limited range of field values and relaxation parameters. It appears, however, that the price for generality of the system (4.4) is too high in terms of algebraic complexity.

It is more useful to consider the more specialized case in which all powers of one large field amplitude, say at  $\omega_3$ , are retained, but a power series expansion is used for the two smaller field amplitudes at  $\omega_1$  and  $\omega_2$ . This approach was already used by Clogston,<sup>15</sup> whose calculation we shall follow. We shall not make the unnecessary assumption  $\omega_3 = \omega_{ca}$ , and shall arrange the various terms so that a physical identification is possible. First consider the zero-order solution independent of the field amplitudes at  $\omega_1$  and  $\omega_2$ . Consider the first, second, third, and last row of the matrix equation (4.4) together, with the terms in  $V_{ab}$ ,  $V_{ba}$ ,  $V_{bc}$ , and  $V_{cb}$  omitted. One thus obtains the terms which are independent of the fields at  $\omega_1$  and  $\omega_2$ . The solution consists of the well-known populations for a pumped three-level maser,  $\rho_{aa}^{(0)}$ ,  $\rho_{bb}^{(0)}$ , and  $\rho_{cc}^{(0)}$ , and the response of the off-diagonal elements at the pump frequency,

$$\{\rho_{ca}^{(0)}\}^{(\omega_3)} = \{\rho_{ac}^{(0)}\}^{(-\omega_3)*} = \Delta_{ca}^{-1} V_{ca} (\rho_{aa}^{(0)} - \rho_{cc}^{(0)}).$$

Consider next the two simultaneous equations for  $\rho_{ba}$  and  $\rho_{bc}$ , i.e., the fifth and sixth rows of the matrix (4.4),

$$V_{ba}(\rho_{aa}^{(0)} - \rho_{bb}^{(0)}) + \Delta_{ba}\rho_{ba}^{(1)} - V_{ca}\rho_{bc}^{(1)} + V_{bc}\rho_{ca}^{(0)} = 0 \quad (4.4a)$$

$$V_{bc}(\rho_{cc}^{(0)} - \rho_{bb}^{(0)}) + \Delta_{bc}\rho_{bc}^{(1)} - V_{ac}\rho_{ba}^{(1)} + V_{ba}\rho_{ac}^{(0)} = 0. \quad (4.4b)$$

The solution gives the first approximation to  $\rho_{ba}$  and

$\rho_{bc}$ , correct to linear terms in the field amplitudes at  $\omega_1$  and  $\omega_2$ .

$$\begin{aligned} \{\rho_{ba}^{(1)}\}^{(\omega_1)} &= \left[ \Delta_{ba}^{-1} V_{ba} (\rho_{aa}^{(0)} - \rho_{bb}^{(0)}) + \frac{V_{ba} |V_{ca}|^2 (\rho_{aa}^{(0)} - \rho_{cc}^{(0)})}{\Delta_{ac} \Delta_{ba} \Delta_{bc}} \right. \\ &\quad \left. + \frac{V_{bc} V_{ca} (\rho_{aa}^{(0)} - \rho_{cc}^{(0)})}{\Delta_{ba} \Delta_{ca}} + \frac{V_{bc} V_{ca} (\rho_{bb}^{(0)} - \rho_{cc}^{(0)})}{\Delta_{ba} \Delta_{bc}} \right] \\ &\quad \times \frac{\Delta_{ba} \Delta_{bc}}{\Delta_{ba} \Delta_{bc} - |V_{ac}|^2}. \quad (4.5) \end{aligned}$$

This expression contains the same terms as Eq. (25) of Clogston's paper.<sup>15</sup> There is a similar equation for  $\rho_{cb}^{(1)} = \rho_{bc}^{(1)*}$ . The terms have been rearranged to facilitate their identification.

The factor outside the square bracket is always of the order unity, if the frequencies are adjusted to maximum response for a given value of the pump amplitude. If the pump field is small compared to linewidth  $|V_{ac}/\Gamma| \ll 1$ , it is obvious that the factor may be replaced by unity. If, however,  $|V_{ac}/\Gamma| \gg 1$ , the term has a dip at the resonant frequencies  $\omega_1 = \omega_{ba}$ ,  $\omega_2 = \omega_{bc}$ . It causes a characteristic splitting of the response. This behavior is well known from the resonance condition (3.12) in the rotating coordinate system. If the frequency is adjusted, outside the dip at the center, for maximum response, the factor has again a magnitude of about unity.

The first term inside the square bracket of Eq. (4.5) has the appearance of a linear response term. The population difference  $\rho_{aa}^{(0)} - \rho_{bb}^{(0)}$  does not have the thermal equilibrium value, but is a function of the pump power  $|V_{ac}|^2$ . This term represents the maser action, when  $\rho_{bb}^{(0)} - \rho_{aa}^{(0)} > 0$ .

The second term has the appearance of a Raman maser effect. A transition from level  $|b\rangle$  to  $|c\rangle$ , while a quantum  $\hbar\omega_3$  is absorbed and a quantum  $\hbar\omega_1$  is emitted, would be proportional to  $\rho_{bb} - \rho_{cc}$ . The second term includes also the process proportional to  $\rho_{aa} - \rho_{bb}$  which has to be added to the Raman transition. It represents the single-quantum absorption associated with a transition from  $|a\rangle$  to  $|b\rangle$  modified by the simultaneous scattering of one or more quanta  $\hbar\omega_3$ .

The third and fourth terms between the square bracket look like parametric terms. A polarization at  $\omega_1$  is created by fields applied at frequencies  $\omega_3$  and  $\omega_2$ . These terms, however, do not only represent scattering processes in which three quanta take part. They also describe interference terms between single-photon and Raman processes in the transition probability between levels  $|a\rangle$  and  $|b\rangle$  which are connected by a matrix element of the form  $cV_{ab} + c'V_{ac}V_{cb}$ . This gives rise to an absorption proportional to  $V_{ab}V_{bc}V_{ca}$ .

This interpretation in terms of elementary quantum

processes is already quite complex in this approximation. The illustrations in Fig. 2 should not be taken too literally. The macroscopic behavior is, however, described by complex susceptibilities of the parametric or the Raman type. The former describe a polarization induced at a combination frequency by fields applied at other frequencies. The complex value of the susceptibility determines the phase of the polarization with respect to these applied fields. One cannot decide whether or not absorption occurs, until the phase of a field at the combination frequency is known. The Raman-type susceptibility describes a complex change in the linear index of refraction proportional to the intensity of a field at another frequency. Its imaginary part corresponds to positive or negative absorption.

The solutions (4.5) for  $\rho_{ab}^{(1)} = \rho_{ba}^{(1)*}$  and  $\rho_{bc}^{(1)} = \rho_{cb}^{(1)*}$  can be substituted back into the equations for the populations and  $\rho_{ac} = \rho_{ca}^*$ . One finds in second approximation terms quadratic in the small fields,  $|V_{ab}|^2$ ,  $|V_{bc}|^2$ ,  $V_{ab}V_{bc}$ , and  $V_{cb}V_{ba}$ . In third approximation one may use the equations (4.4a) and (4.4b) to obtain a relationship between  $\rho_{ba}^{(3)}$  and  $\rho_{bb}^{(2)} - \rho_{aa}^{(2)}$  etc. The labor involved is large, and one might as well solve the complete matrix (4.4), if the fields at  $\omega_1$  and  $\omega_2$  become comparable to the damping parameters,  $|V_{ab,bc}/\Gamma_{ab,bc}| \sim 1$ .

The relative importance of the various terms in Eq. (4.5) will now be discussed in some detail. If the pumping field is small compared to the linewidth and all frequencies are near resonance, the first term is dominant. The well-known case of the solid state three-level maser results.

The second or Raman-type term will not necessarily be larger than the first term, if  $|V_{ac}|$  is chosen very large, because the population difference  $\rho_{aa}^{(0)} - \rho_{cc}^{(0)}$  itself approaches zero. It should be remembered that the superscript (0) refers to zero power in the small fields only. In fact, the optimum response, i.e., the largest value of  $\rho_{ba}^{(1)}$  is obtained for  $|V_{ac}^2/\Delta^2| \sim 1$ , as explained previously. In that case, the Raman term has the same order of magnitude as the maser term, and precise values for  $|V_{ca}/\Delta_{ac}|$  and  $|V_{ca}/\Delta_{bc}|$  must be known for a detailed comparison in this case.

There is, however, a situation in which the Raman term will always dominate. This occurs when only the frequency  $\omega_2 = \omega_{cb}$  is at resonance and the applied field at this frequency is very small,  $V_{bc} = 0$ . Because of this last condition, the parametric terms vanish. Since the frequency  $\omega_1$  is off resonance,  $|\omega_1 - \omega_{ba}| > \Gamma_{ba}$ , and so is the pump field at  $\omega_3$ ,  $|\omega_1 - \omega_{ba}| = |\omega_3 - \omega_{ca}| > |V_{ca}| > \Gamma_{ca}$ , the imaginary part of the first term, corresponding to linear absorption, is  $\Gamma_{ba}|\Delta_{ba}|^{-2}V_{ba}(\rho_{aa}^{(0)} - \rho_{bb}^{(0)})$ . The ratio of the Raman-type term to the linear absorption can easily be made larger than unity,

$$\frac{|V_{ca}|^2(\rho_{aa}^{(0)} - \rho_{cc}^{(0)})}{\Gamma_{bc}\Gamma_{ba}(\rho_{aa}^{(0)} - \rho_{bb}^{(0)})} > 1.$$

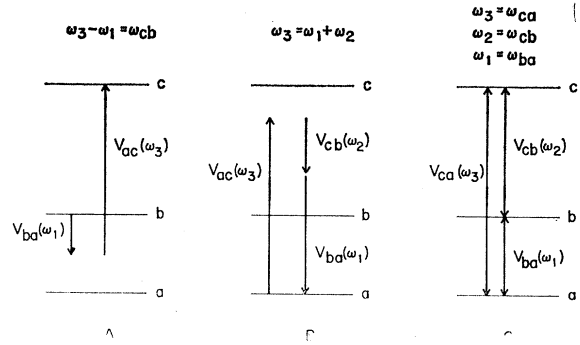


FIG. 2. Nonlinear processes in a three-level system. The text should be consulted for a correct interpretation of these illustrations. A Illustration of a Raman process. B Illustration of a parametric process. C Combination of saturation, maser, Raman maser, and parametric processes.

Since the pump field is off resonance, the populations have essentially their thermal equilibrium value. If the applied pump field is larger than the natural widths  $\Gamma_{bc}$  and  $\Gamma_{ba}$ , the Raman process is dominant. This situation is shown schematically in Fig. 2(A). The conditions set forth are, of course, precisely those under which optical Raman laser action has been observed.<sup>31</sup>

The parametric terms in Eq. (4.5) can always be made dominant, if all three frequencies are well removed from resonance. The ratios of the parametric term to the linear absorption is, in that case, larger than unity, if

$$\left| \frac{V_{bc}V_{ca}\Delta_{ba}}{V_{ba}\Gamma_{ba}\Delta_{bc}} \right| > 1.$$

This can be achieved, even if the pump amplitude is smaller than the linewidth. If the amplitude  $V_{ba}$  is initially very small, a polarization at the frequency  $\omega_1$  will be created by the larger applied fields at  $\omega_3$  and  $\omega_2$ . This “pure parametric” case is illustrated as a three-photon scattering process in Fig. 2(B), although important reservations about this pictorial representation must be made, as discussed previously. If the applied frequencies are far removed from resonance, the truncation procedure which led to Eq. (4.5) becomes invalid. Eventually, one should return to the general Fourier expansion method of Sec. II.

Thus far, the field amplitudes are assumed to be applied externally as given fixed quantities. This is the proper procedure in calculating macroscopic susceptibilities. If the applied field at  $\omega_1$  vanishes,  $V_{ab} = 0$ , the parametric terms in Eq. (4.5) are the only ones left. They create a polarization at  $\omega_1$ , which, in turn, will generate a field at  $\omega_1$ . The assumption  $V_{ab} = 0$  is not self-consistent. This extreme example clearly shows that the question should be considered, how the magnitude of the fields is in turn determined by the reaction of the material system on the fields.

<sup>31</sup> G. Eckard, R. W. Hellwarth, F. J. McClung, J. E. Schwarz, D. Weiner, and E. J. Woodbury, Phys. Rev. Letters 9, 455 (1962).

### V. COUPLING BETWEEN THE NONLINEAR MEDIUM AND THE ELECTROMAGNETIC MODES

The question of the reaction of the material system back on the electromagnetic modes was treated very early by Bloembergen and Pound.<sup>32</sup> They considered the precessing magnetization in a magnetic resonance experiment in turn as a source for the electromagnetic mode. This scheme has been further developed by many authors.<sup>14-16,33,34</sup> Mathematically, the equations of motion for the classical harmonic oscillator(s), representing the electromagnetic mode(s) is (are) added to the equations of motion for density matrix elements. We restrict ourselves to the electric dipole case and expand the electric field in terms of normal modes with dynamical variables  $p_\lambda(t)$ ,

$$\mathbf{E}(\mathbf{r}, t) = - (4\pi)^{1/2} \sum_{\lambda} p_\lambda(t) \mathbf{E}_\lambda(\mathbf{r}), \quad (5.1)$$

where the real mode functions constitute a normalized orthogonal set,

$$\int \mathbf{E}_\lambda(\mathbf{r}) \cdot \mathbf{E}_\mu(\mathbf{r}) d\mathbf{r} = \delta_{\lambda\mu}. \quad (5.2)$$

Jaynes<sup>33</sup> has given an elegant discussion how the semi-classical approach is related to the exact theory with quantized harmonic oscillators. The classical equation of motion for the  $\lambda$ th harmonic oscillator may be written in the form

$$\ddot{p}_\lambda(t) + \frac{\omega_\lambda}{Q_\lambda} \dot{p}_\lambda(t) + \omega_\lambda^2 p_\lambda(t) = - \frac{(4\pi)^{1/2}}{\epsilon\mu} \int \frac{\partial^2 \langle \mathbf{P}(\mathbf{r}, t) \rangle}{\partial t^2} \cdot \mathbf{E}_\lambda(\mathbf{r}) d\mathbf{r} + \frac{1}{2} (F_{\text{ext}} e^{-i\omega t} + F_{\text{ext}}^* e^{+i\omega t}). \quad (5.3)$$

The damping of the mode due to eddy current losses and coupling losses is described by the phenomenological term with the quality factor  $Q_\lambda$ ;  $\epsilon$  and  $\mu$  are the linear electric and magnetic susceptibility of the medium, exclusive of the terms considered explicitly in the expectation value of the polarization

$$\langle \mathbf{P}(\mathbf{r}, t) \rangle = N \sum_{nn'} \mathfrak{P}_{nn'} \rho_{n'n}(\mathbf{r}, t). \quad (5.4)$$

The last term in Eq. (5.3) represents an external driving source, which consists, for example, of coherent signal input or power supplied by an external pump oscillator.

The equations (5.3), after the substitution of Eq. (5.4), have to be solved simultaneously with the equations of motion (2.1) for the elements of the density matrix. Note that  $\mathfrak{C}_{\text{coh}}$  is a linear function of the dynamical variable  $p_\lambda(t)$ . It is still possible to find a steady-state solution by expanding all elements  $\rho_{nn'}(t)$  and all variables  $p_\lambda(t)$  into Fourier series. The pro-

cedure, which rapidly becomes very cumbersome, will be illustrated with a few examples.

The case of a microwave or optical maser pumped by an incoherent process consists of a two-level atomic system and one electromagnetic mode which produces an oscillating field at the position of the active particles with a density  $N \text{ cm}^{-3}$ . There are four simultaneous equations to be considered: equations for the dc component of the population difference  $\rho_{bb}^{\text{dc}} - \rho_{aa}^{\text{dc}}$ , two off-diagonal Fourier components of the density,  $\rho_{ba}^{(\omega)} = \rho_{ab}^{(-\omega)*}$  and  $\rho_{ab}^{(\omega)} = \rho_{ba}^{(-\omega)*}$ , and the Fourier component at  $\omega$  of the dynamical variable  $p_\lambda^{(\omega)}$ , belonging to the one mode with resonant frequency  $\omega_\lambda$  close to  $\omega$ . The equation (5.3) for this steady-state component can be written explicitly as

$$p_\lambda^{(\omega)} = p_\lambda^{(-\omega)*} = \frac{(4\pi)^{1/2} N \omega^2}{\epsilon\mu(-\omega^2 + \omega_\lambda^2 - i\omega\omega_\lambda/Q_\lambda)} \left[ \int \{\mathfrak{P}_{ba} \cdot \mathbf{E}_1(\mathbf{r})\} \times \rho_{ab}^{(\omega)}(\mathbf{r}) d\mathbf{r} + \int \mathfrak{P}_{ab} \cdot \mathbf{E}_1(\mathbf{r}) \rho_{ba}^{(\omega)}(\mathbf{r}) d\mathbf{r} \right]. \quad (5.5)$$

The orthonormal properties of the real mode functions have been used. The solution of Eq. (5.5) coupled with equations for the density matrix elements has been described in detail by Fain<sup>17</sup> and Davis.<sup>34</sup> The oscillation condition for a maser is obtained.

As the next example, we consider the lowest order parametric case, treated in Sec. II. We shall assume that there are three electromagnetic cavity modes with resonant frequencies  $\omega_{\lambda_1}$  close to  $\omega_1$ ,  $\omega_{\lambda_2}$  close to  $\omega_2$ , and  $\omega_{\lambda_3}$  close to  $\omega_3 = \omega_1 + \omega_2$ , respectively. When the density matrix element equations are solved and expressed in terms of the dynamical field variables  $p_{\lambda_1}$ ,  $p_{\lambda_2}$ , and  $p_{\lambda_3}$ , one obtains from Eqs. (2.22) and (5.1) the expectation value of polarization as a function of these field variables. They may be expressed in terms of the linear and nonlinear susceptibilities,

$$\begin{aligned} \langle \mathbf{P}^{(\omega_1)}(\mathbf{r}) \rangle &= -\chi(\omega_1) (4\pi)^{3/2} \cdot \mathbf{E}_{\lambda_1}(\mathbf{r}) p_{\lambda_1}^{(\omega_1)} \\ &\quad + (4\pi)^2 \chi^{\text{NL}}(\omega_1 = \omega_3 - \omega_2) : \mathbf{E}_{\lambda_3}(\mathbf{r}) \mathbf{E}_{\lambda_2}(\mathbf{r}) p_{\lambda_2}^{(-\omega_2)} p_{\lambda_3}^{(\omega_3)} \\ \langle \mathbf{P}^{(\omega_2)}(\mathbf{r}) \rangle &= -\chi(\omega_2) (4\pi)^{3/2} \cdot \mathbf{E}_{\lambda_2}(\mathbf{r}) p_{\lambda_2}^{(\omega_2)} \\ &\quad + (4\pi)^2 \chi^{\text{NL}}(\omega_2 = \omega_3 - \omega_1) : \mathbf{E}_{\lambda_3}(\mathbf{r}) \mathbf{E}_{\lambda_1}(\mathbf{r}) p_{\lambda_1}^{(-\omega_1)} p_{\lambda_3}^{(\omega_3)} \\ \langle \mathbf{P}^{(\omega_3)}(\mathbf{r}) \rangle &= -\chi(\omega_3) (4\pi)^{3/2} \cdot \mathbf{E}_{\lambda_3}(\mathbf{r}) p_{\lambda_3}^{(\omega_3)} \\ &\quad + (4\pi)^2 \chi^{\text{NL}}(\omega_3 = \omega_1 + \omega_2) : \mathbf{E}_{\lambda_1}(\mathbf{r}) \mathbf{E}_{\lambda_2}(\mathbf{r}) p_{\lambda_1}^{(\omega_1)} p_{\lambda_2}^{(\omega_2)}. \end{aligned} \quad (5.6)$$

These expressions are substituted into Eqs. (5.3) for Fourier components of the dynamical variables,  $p_{\lambda_1}^{(\omega_1)} = p_{\lambda_1}^{(-\omega_1)*}$ ,  $p_{\lambda_2}^{(\omega_2)} = p_{\lambda_2}^{(-\omega_2)*}$ ,  $p_{\lambda_3}^{(\omega_3)} = p_{\lambda_3}^{(-\omega_3)*}$ , which are retained. All other Fourier components are considered off resonance and are truncated off. One thus obtains a set of equations that describe the lowest order

<sup>32</sup> N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).

<sup>33</sup> E. T. Jaynes and F. W. Cummings, Proc. IEEE **51**, 89 (1963).

<sup>34</sup> L. W. Davis, Proc. IEEE **51**, 76 (1963).

nonlinear coupling between the electromagnetic modes,

$$\begin{aligned}
 & (-\omega_1^2 + \omega_\lambda^2 - i\omega_1\omega_\lambda/Q_{\lambda_1})p_{\lambda_1}^{(\omega_1)} \\
 &= -\frac{(4\pi)^2}{\epsilon\mu}\omega_1^2 p_{\lambda_1}^{(\omega_1)} \int \mathbf{E}_{\lambda_1}(\mathbf{r}) \cdot \boldsymbol{\chi}(\omega_1) \cdot \mathbf{E}_{\lambda_1}(\mathbf{r}) d\mathbf{r} \\
 &+ \frac{(4\pi)^{5/2}}{\epsilon\mu}\omega_1^2 p_{\lambda_3}^{(\omega_3)} p_{\lambda_2}^{(-\omega_2)} \int \mathbf{E}_{\lambda_1}(\mathbf{r}) \\
 &\cdot \boldsymbol{\chi}^{NL}(\omega_1 = \omega_3 - \omega_2) : \mathbf{E}_{\lambda_3}(\mathbf{r}) \mathbf{E}_{\lambda_2}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} F_{\text{ext}}. \quad (5.7)
 \end{aligned}$$

and two similar equations for  $p_{\lambda_2}^{(\omega_2)}$  and  $p_{\lambda_3}^{(\omega_3)}$ . The integral in the first term on the right-hand side is extended over the volume of the cavity mode. It is equal to the product of a "filling factor" times the linear part of the susceptibility which is not included in  $\epsilon$ . The second term represents the lowest order nonlinear coupling. Lamb<sup>35</sup> has considered nonlinear coupling between modes in a gaseous optical maser using similar methods.

The equations (5.7) are, of course, quite similar to the coupled amplitude equations in the paper of Armstrong<sup>3</sup> *et al.* [compare in particular their Eq. (4.9)]. They are algebraic, rather than differential equations, because they describe the steady-state response of the system to periodic driving forces, and are adapted to nonlinear effects in resonator modes, rather than traveling waves. They are more general than the corresponding expressions of Armstrong *et al.*, in the sense that they include damping mechanisms, both in the nonlinear medium and in the cavity walls. The integrals over the volume of the sample in the nonlinear term corresponds to the condition of momentum conservation or matching of the phase velocities for the case of an infinite homogeneous lossless medium with homogeneous plane waves. If one chooses  $\omega_1 = \omega_2$ , Eqs. (5.7) are well adapted to describe the microwave second harmonic generation in ferrites, or the harmonic generation in laser resonators.

The procedure is, of course, readily generalized to include higher order nonlinear effects, including Raman-type terms. If the driving terms  $\mathbf{F}$  are put equal to zero, the resulting set of nonlinear homogeneous equations may have a nonvanishing solution, provided a random pump field maintains some inversion of the populations. If a large input is present at one frequency, say  $\omega_3$ , one may have oscillation at both smaller frequencies simultaneously, due to parametric terms, mixed with maser and Raman maser terms. To show how all nonlinearities are, in principle, incorporated in this formalism, the example of the three-level system

in Sec. IV is re-examined. The three fields at  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are assumed to arise from the excitation of three different electromagnetic modes with resonant frequencies  $\omega_{\lambda_1}$  close to  $\omega_1$ ,  $\omega_{\lambda_2}$  close to  $\omega_2$ , and  $\omega_{\lambda_3}$  close to  $\omega_3$ . Only near-resonant Fourier components of the mode dynamical variables are retained. The reaction of the material system on the fields is, therefore, taken into account, if the following three mode equations are added to the nine density matrix element equations (4.4).

$$\begin{aligned}
 p_{\lambda_1}^{(\omega_1)} &= \frac{(4\pi)^{1/2}(\epsilon\mu)^{-1}\omega_1^2 N}{-\omega_1^2 + \omega_{\lambda_1}^2 - i\omega_1\omega_{\lambda_1}/Q_{\lambda_1}} \int (\mathfrak{P}_{ab} \cdot \mathbf{E}_{\lambda_1}(\mathbf{r})) \\
 &\quad \times \rho_{ba}^{(\omega_1)}(\mathbf{r}) d\mathbf{r} + \mathbf{F}^{(\omega_1)} \\
 p_{\lambda_2}^{(\omega_2)} &= \frac{(4\pi)^{1/2}(\epsilon\mu)^{-1}\omega_2^2 N}{-\omega_2^2 + \omega_{\lambda_2}^2 - i\omega_2\omega_{\lambda_2}/Q_{\lambda_2}} \int (\mathfrak{P}_{bc} \cdot \mathbf{E}_{\lambda_2}(\mathbf{r})) \\
 &\quad \times \rho_{cb}^{(\omega_2)}(\mathbf{r}) d\mathbf{r} + \mathbf{F}^{(\omega_2)} \\
 p_{\lambda_3}^{(\omega_3)} &= \frac{(4\pi)^{1/2}(\epsilon\mu)^{-1}\omega_3^2 N}{-\omega_3^2 + \omega_{\lambda_3}^2 - i\omega_3\omega_{\lambda_3}/Q_{\lambda_3}} \int (\mathfrak{P}_{ac} \cdot \mathbf{E}_{\lambda_3}(\mathbf{r})) \\
 &\quad \times \rho_{ca}^{(\omega_3)}(\mathbf{r}) d\mathbf{r} + \mathbf{F}^{(\omega_3)}. \quad (5.7)
 \end{aligned}$$

The off-diagonal matrix elements, solved from Eqs. (4.4) as a function of all powers of  $p_{\lambda_1}^{(\pm\omega_1)}$ ,  $p_{\lambda_2}^{(\pm\omega_2)}$ , and  $p_{\lambda_3}^{(\pm\omega_3)}$ , may be substituted into Eq. (5.7). This type of description is appropriate for Kellington's experiment.<sup>36</sup> The algebraic equations that result can, in principle, be solved for the components  $p_{\lambda}^{(\pm\omega)}$ . Because of the formidable nonlinearities on the right-hand side, approximate procedures have to be invoked. We do not believe, however, that Clogston's procedure,<sup>15</sup> in which only linear terms in  $p_{\lambda_1}^{(\omega_1)}$  and  $p_{\lambda_2}^{(\omega_2)}$  are retained in the reaction field, can be a satisfactory description of maser oscillators.

## VI. CONCLUSION

General expressions for complex nonlinear susceptibilities in the presence of damping have been derived which describe simultaneously parametric, maser, and Raman maser effects. If the applied fields are near resonances of the atomic system and have a magnitude equal to or larger than the linewidths, the different effects become inextricably mixed. It is still possible to consider the total polarization, which is a mixture of all linear and nonlinear effects, as a source term reacting with the electromagnetic fields. Joint equations of the dynamical variables of the modes and the density matrix elements of the general nonlinear medium can be written down, although explicit steady-state solutions require the retention of only a few terms in a Fourier series expansion, truncation of nonresonant terms, and other approximations.

<sup>36</sup> C. M. Kellington, Phys. Rev. Letters **9**, 57 (1962).

<sup>35</sup> W. E. Lamb, Paper presented at the Third International Conference on Quantum Electronics, Paris, 1963 (unpublished). See Phys. Rev. (to be published). See also, H. Haken and H. Sauerman, Z. Physik **173**, 261 (1963).