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(6) NONLINEAR QUANTUM EFFECTS,

By

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ABSTRACT

The purpose of this research WAS to study the phenomena of multiple quantum processes and to consider possible applications. These processes involve the interaction of more than a single quantum of radiation with an atomic system and are nonlinear in character. An equation of motion approach is used in the solution of the quantum mechanical problem, allowing the calculation of the observable quantities important for the radiation processes considered.

Three specific cases have been considered. In the first case, third harmonic generation is predicted for a two-level quantum system. The magnitude of the nonlinearity and the magnitude of the third harmonic power generated are evaluated in terms of known parameters of the quantum system and its surroundings. A shift of the natural transition frequency of the quantum system is also predicted. In the second case, the same two-level system is found to give rise to a form of parametric effect, suitable for amplification. The threshold conditions for parametric oscillation are found in terms of the known properties of the system. The third case considered was that of a three-level system. Its properties as a frequency converter were pointed out and a detailed study of second harmonic generation was performed, with the nonlinearity and second harmonic power evaluated in terms of the known properties of the system. Of particular interest was the prediction that the optimum harmonic generation occurred when two of the three transitions involved differed from degeneracy by one linewidth.

Two experiments were performed. In the first, the third harmonic generation phenomenon predicted by the theory was observed. The results of the experiment were in fair agreement with the theory. In the second experiment the second harmonic generation phenomenon predicted by the theory was observed and was found to be in general agreement with theory within the experimental uncertainty.

From the results of this research it is thus concluded that a quantum mechanical system possesses nonlinear as well as linear properties and that these nonlinear properties may find application, especially in the sub-millimeter and optical regions where suitable nonlinear elements do not presently exist.

ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

A. BACKGROUND

In 1955 Gordon, Zeiger and Townes[1] announced the successful operation of the ammonia beam maser. With this pioneering breakthrough the field of quantum electronics had its beginning. The achievements in this field have been many, starting with this first ammonia maser and including the solid state microwave maser, proposed by Bloembergen[2] and successfully operated by Scovil, Feher, and Seidel,[3] the optical maser proposed by Schawlow and Townes[4] and operated by Maiman[5] in a solid, and by Javan[6] in a gas, and most recently, the successful operation of a semiconductor junction laser.[7-9]

The field of quantum electronics differs from its predecessor, classical electronics, in that it makes use of the internal, quantized energy states of an atom or molecule rather than the translational states of electrons.[(1)] In general, efforts to date in the application of these properties have been concerned with producing amplification and oscillation using the phenomenon of stimulated emission from an atomic system which is in an inverted population state.

A study of the interaction of radiation with matter forms the basis for the analysis of these quantum electronic systems. Such a study must be quantum mechanical in nature in order to account for the discrete nature of the atomic system. The phenomenon of amplification by such a quantum system is a linear process and can be described as a preponderance of stimulated emission over absorption. Such a linear process is microscopically describable as the interaction of a single photon with the atomic system while macroscopically, a complex susceptibility, independent of the field strength, may be used. The latter description gives a complex polarization or magnetization proportional to the applied field.

[(1)] The words atom or atomic system are used to mean atom or molecule.

CHAPTER I

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Nonlinear Effects

In addition to the linear, single quantum processes important for maser theory, there exist higher order processes involving, on a microscopic scale, the interaction of more than a single quantum of radiation with the atomic system. Macroscopically these interactions are found to be described by a polarization or magnetization which is dependent on quadratic or higher powers of the applied radiation field. This nonlinear dependence on the field makes possible such phenomena as harmonic generation, parametric amplification, limiting, modulation, demodulation, and other frequency mixing effects.

The research described in this report is concerned with a study of these nonlinear phenomena. Because of their nonlinear character and quantum mechanical aspects they will be called nonlinear quantum effects. They may be further classified as bulk nonlinear effects since the phenomena are not connected with either a surface or a junction as, for example, in a semiconductor diode.

Although nonlinear phenomena have found general application in various fields of science and engineering, little, if any, use has been made of the bulk nonlinear phenomena considered here. In the region of the spectrum from dc to microwaves the nonlinear properties of diodes, varactors, and electron beams have had the most applications. This results both from the fact that such systems have strong, relatively frequency-insensitive nonlinearities and that these nonlinearities are easily describable in terms of familiar concepts.

The bulk nonlinearities of the type considered here, on the other hand, are generally smaller in magnitude, frequency-sensitive, and are described in a less familiar manner than their classical counterparts.

With the host of presently available, strong, nonlinear elements, the question might be asked as to the purpose of studying these nonlinear phenomena. Two main reasons can be offered. First of all, such a study would contribute to a further understanding of phenomena associated with the interaction of radiation with matter. Of particular interest is the study of radiation processes where atomic coherence effects, imposed by strong fields, become important. A second reason comes from the point of view of applications. Although the nonlinear properties of the presently

used diode, etc., are relatively frequency-independent below the microwave range, their efficiencies do fall off with increasing frequency above this range. Thus applications in the submillimeter to optical frequency ranges are marginal, if possible at all.

The bulk nonlinear properties described in this report are found to depend on the natural transition frequencies of the atom. Since atoms exhibit resonances throughout the electromagnetic spectrum these nonlinear properties will also occur throughout the spectrum. Further, it is shown in this report that the magnitude of the nonlinearity is, among other things, dependent on the Boltzmann factor and increases in magnitude with increasing frequencies. Thus at high frequencies these nonlinear effects may be expected to play an important, if not dominant, role.

Scope of the Problem

The purpose of this research is to study these nonlinear effects and to consider possible applications.

The first task in a study of these nonlinear effects is to find a method of formulation of the problem. Such a formulation should be valid for the large field strengths encountered in exciting the nonlinearities and must be capable of predicting coherent emission as well as absorption for the higher order processes. For such an analysis the usual approach of time-proportional transition probabilities and instantaneous quantum jumps between unperturbed energy states, used in solving maser problems, is not applicable inasmuch as the assumptions implicit in the derivation of the method are not valid. In particular, the assumption of weak field strengths used in deriving the time-proportional transition probabilities is not valid.

From such an analysis we should like to be able to evaluate the magnitude of the nonlinear effect in terms of known or measurable properties of the system such as natural frequencies, linewidths, and matrix elements. The effects of temperature, concentration and population should also be considered.

Finally, possible applications of these nonlinear phenomena should be considered. Included among these considerations should be the effects of the material's surroundings, whether a cavity resonator, propagating circuit, or free space.

Results

The results of the research described in this report may be summarized as follows:

1. A study has been made of the interaction of a radiation field with an atomic system using an equation of motion formulation including the effects of relaxation. This approach directly relates macroscopic, observable quantities to their microscopic sources, predicting nonlinear effects as well as linear ones. The effects of atomic coherence are included, and the formulation is valid for large as well as small field strengths. From this analysis various nonlinear effects may be predicted and their magnitude may be calculated in terms of known parameters of the system.

2. Detailed theoretical analyses have been carried out for three specific cases.

a. Harmonic generation in a two-level system. From a consideration of the interaction of an applied radiation field with a two-level electric dipole system, third harmonic generation is predicted.[10] Two values of the frequency of the applied radiation field are found which result in a strong effect, namely when applied frequency or its third harmonic is near the natural transition frequency of the atom.

A shift of the natural transition frequency due to the strong rf fields is predicted from the theory. This shift is the electric dipole equivalent of the Bloch-Siegert shift predicted by Bloch[11] for the case of magnetic resonance.

The magnitude of the induced third order polarization is calculated in terms of the known parameters of the system and the power generated by such a means is calculated, assuming a resonant cavity structure. The magnitude of the nonlinearity is found to be independent of whether or not the system is in an inverted population state, although population inversion is found to alter the efficiency through a modification of the source impedance. The dependence of the nonlinear effect on other properties of the atomic system is also considered.

b. Parametric effects in a two-level system.[12] Parametric oscillation and amplification are considered for a two-level electric dipole system. The frequency conditions for such an effect are that the pump frequency be equal to one-half the sum of the signal plus the idler, where the idler may be either a cavity mode or the internal transition of the molecule.

An analysis is carried out for the latter case and the start-oscillation condition is evaluated in terms of the parameters of the atomic system and the surrounding cavity.

c. Harmonic generation in a three-level system. A three-level system in which two natural frequencies are nearly degenerate is found to present a nonlinearity suitable for second harmonic generation. Second harmonic generation is predicted and its magnitude is evaluated from the general theory. Of particular interest is the prediction that the effect will occur not when the transitions are degenerate but when their values differ by a frequency corresponding to one linewidth. This second harmonic generation effect predicted by the theory was subsequently observed by Kellington[13] and independently by the author.

3. Two experiments at microwave frequencies have been performed to verify various aspects of the phenomena predicted by the theory.

a. Third harmonic generation in a two-level electric dipole system was observed using ammonia gas.[14] The fundamental and harmonic frequencies were 8.5 kMc and 25.5 kMc, respectively, and the inversion transition at 24 kMc was the two-level system. This experiment provided a direct confirmation of the effect predicted by the theory and gave results in general agreement with the theory.

b. The phenomenon of second harmonic generation in a three-level system was observed using the paramagnetic resonance levels in the ground state of ruby. This effect was independently observed and reported by Kellington,[13] who also used ruby under approximately the same operating conditions.

B. BRIEF HISTORY OF THE STUDY OF MULTIPLE QUANTUM EFFECTS

Until recently, interest in the phenomenon of multiple quantum transitions has centered on the study of these effects arising in various types of absorption spectra. The first published reports on the observation of this effect came from the work of Kastler's[15,16] group, resulting from their study of the hyperfine spectrum of sodium. In their experiments they observed the appearance of additional spectral lines not predicted by the theory. These lines were present in the spectrum at high rf power levels but were not present at low powers, while the frequencies of these

new lines corresponded to the algebraic mean of adjacent predicted lines. An example of the type of spectrum observed is shown in Fig. 1.1. In this case the selection rule for the hyperfine transition is $\Delta m = \pm 1$, where m is the magnetic quantum number. With further study they found that the phenomenon responsible for these additional lines was a double quantum absorption for which $\Delta m = 2$. This absorption process occurred when the applied frequency was equal to one-half of the frequency difference between levels differing in m by two units. Physically this process corresponded to an absorption of two photons with the system going directly from a level m to a level $m + 2$. Winter[17] showed that the absorbed power for this two-quantum process was proportional to the square of the applied power, explaining the absence of the effect at low power levels.

In subsequent reports, Margerie, Brossel and Winter[17,18] reported three and four quantum absorptions as well as multiple quantum absorptions involving combinations of two applied frequencies.

Other experimental results of absorption studies where multiple quantum phenomena were observed have been described by Kush,[19] Hughes and Geiger,[20] Wolga[21] and others. Sorokin, et al.,[22] found both double and triple quantum absorptions in some of their paramagnetic resonance work on solids. In all these studies the additional lines, due to multiple quantum processes, were present only at high rf field strengths and in absorption rather than emission spectra.

Theoretical studies of these multiple quantum absorption processes have been done by Salwen,[23] Hughes and Grabner,[24] and Winter.[25,26] These studies involve the use of time-dependent perturbation theory carried to higher order and predict multiple quantum absorptions. None of these analyses, however, considers nor predicts any form of emission related to or resulting from these higher order absorptions. It is precisely this latter effect which is responsible for such phenomena as harmonic generation.

Following the proposal and successful operation of the solid state maser, detailed theoretical studies of maser action were made by Javan,[27] Clogston[28] and Yatsiv.[29] These discussions pointed out that the rate equation approach, used in earlier analyses of the maser, failed to describe some of the quantum mechanical aspects of the radiation process. In particular they found that under some circumstances double-quantum processes could play an important role in maser operation. Yajima and

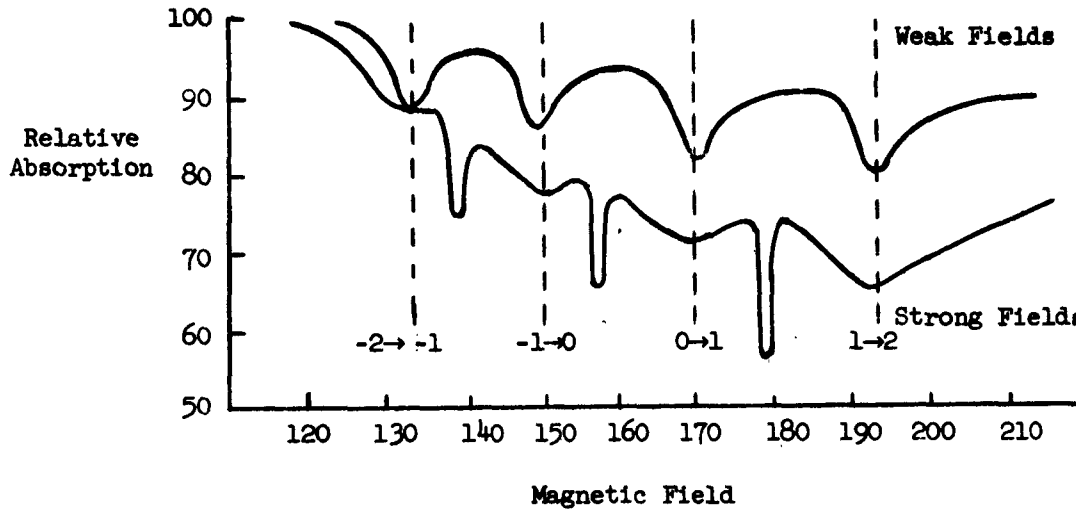

FIG. 1.1--Resonance curves obtained by Gagnac et al. In the upper curve, for low power levels, the four expected $\Delta m = \pm 1$ transitions are observed. In the lower curve, for high power levels, the three $\Delta m = \pm 2$, two-quantum transitions appear as the very sharp resonances.

Shimoda[30-32] observed maser operation where these double quantum processes play the dominant role. Anderson[33] and Suhl[34,35] at the same time analyzed the operation of two new forms of quantum mechanical amplifier, the reaction field amplifier and the ferromagnetic amplifier, both of which operated without the need for population inversion.[(1)] Along this same line a proposal for a Raman maser was made by Javan[36] and was experimentally verified by Winter.[37] The operation and analysis of these last three devices is closely related to the subjects discussed in this report.

Recently there has been renewed interest in the phenomenon of multiple quantum processes, this time in the optical frequency range. Franken, et al.,[38] generated optical harmonics by focusing the output of an optical maser on a piece of quartz. Giordmaine,[39] Maker, et al.,[40] and Terhune, et al.,[41] followed with other experimental results of harmonic generation. Kaiser and Garrett,[42] and recently Abella,[43] have observed optical double-photon absorption processes. Another form of nonlinear process, coherent Raman scattering at optical frequencies, has been observed by research groups at Hughes.[44,45] The microwave modulation of light has been accomplished by Kaminow,[46] and others, using the electro-optic effect which is another form of bulk nonlinear effect.

Theoretical treatments of some of these nonlinear optical phenomena have been given by Braunstein,[47] Bloembergen[48,49] and Kleinman.[50,51] Of these, the paper by Bloembergen[48] is perhaps the most thorough, discussing these higher order effects from a point of view that shows the coherent nature of the phenomena. The approach used by Bloembergen is, in many respects, similar to that used by the author. The details will be considered in following chapters.

The original suggestion for the use of these multiple quantum effects to produce harmonic generation is due to E. T. Jaynes.[52] Jaynes pointed out the generality and importance of multiple quantum effects and suggested subharmonic pumping of a two-level system as a means of generating high power levels at high frequencies. This suggestion of Jaynes provided the initial incentive for the research described in this report.

---

(1) Although these devices have sometimes been included under the broad heading of mascrs, their operation is essentially parametric in nature.

CHAPTER II

THE INTERACTION OF RADIATION WITH MATTER

In this chapter we shall study the interaction of a radiation field with an atom or molecule. A study of this type will form a basis for analyzing multiple quantum or nonlinear phenomena as well as linear, single quantum phenomena. Two approaches are presented. The first, using the concept of transition probabilities, is developed to include both single and double quantum absorption. The second is a macroscopic approach relating the macroscopic properties of a material to its microscopic properties.

A. RADIATION FIELD

In order to be rigorously correct the radiation field should be quantized. However, if we are interested in large field strengths, corresponding to large photon occupation numbers for the radiation fields, we may consider the fields classically. In such an approach the field is described by $\underset{\sim}{E}$ and $\underset{\sim}{H}$, its electric and magnetic fields, or by its vector and scalar potentials $\underset{\sim}{A}$ and ϕ. Use of this approach neglects the effect of spontaneous emission, which will not be important for the microwave frequency range but may play a role in optical phenomena.

B. ATOMIC SYSTEM

The atomic system must be considered quantum-mechanically. The equation governing the behavior of the quantum system is Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \mathcal{H} |\psi\rangle \quad , \qquad (2.1)$$

where $|\psi\rangle$ is the wave function of the system and $\mathcal{H}$ is the Hamiltonian. If there are no applied radiation fields present, then the Hamiltonian consists of the sum of the kinetic and potential energies of the atom.

We shall, for the time being, neglect the interactions between atoms themselves (spin-spin) and between the atoms and the lattice (spin-lattice). This Hamiltonian is denoted $\mathcal{H}_0$ and has stationary eigensolutions $|n\rangle$ and corresponding energies E_n satisfying the equation

$$\mathcal{H}_0 \, |n\rangle = E_n \, |n\rangle \qquad . \qquad (2.2)$$

We shall assume that these energies and their corresponding functions or kets are known. The functions $\{|n\rangle\}$ are assumed to be a complete set.

If we turn on the radiation field, then it will interact with the atom and cause a change in the Hamiltonian of the system. The new Hamiltonian may be written in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \qquad , \qquad (2.3)$$

where $\mathcal{H}'$ is the term due to the interaction of the atom with the radiation field. We shall be interested in the case where the perturbation results from a time harmonic field or sum of such fields and hence we may write it

$$\mathcal{H}' = \sum_{\ell} (\mathcal{H}^{\ell} e^{i\omega_{\ell} t} + \mathcal{H}^{\ell *} e^{-i\omega_{\ell} t}) \qquad . \qquad (2.4)$$

The quantity $\mathcal{H}'$ is real and the superscript ℓ refers to the particular frequency present. For a given applied field, $\mathcal{H}'$ is proportional to the field.

The matrix element of an operator Q in the energy representation is defined as

$$Q_{nm} = \langle n|Q|m\rangle \qquad . \qquad (2.5)$$

C. TRANSITION PROBABILITY METHOD OF SOLUTION

1. First Order Processes

In solving the radiation problem we assume that the total wave function is a superposition of the unperturbed eigenstates

$$|\psi\rangle = \sum_n a_n(t)\, e^{-i\, E_n t/\hbar} |n\rangle \qquad , \qquad (2.6)$$

where $a_n(t)$ is the coefficient of state n . Substituting (2.6) and (2.3) into (2.1) gives

$$i\,\hbar\,\dot{a}_k = \sum_n a_n \mathcal{H}'_{nk}\, e^{i(E_k - E_n)t/\hbar} \qquad . \qquad (2.7)$$

The general approach to the solution of this set of equations is to assume that the frequency of the applied signal satisfies the condition $\hbar\omega \approx E_k - E_m$ and that the system is initially in the state m , $a_m(0) = 1$. If it is further assumed that we consider the solution for times small enough that the approximation $a_m = 1$, $a_n \approx 0$, $n \neq m$, is valid, then we have from (2.4) and (2.7)

$$i\,\hbar\,\dot{a}_k = \mathcal{H}'_{mk}\, e^{i(\Omega_{km} - \omega)t} \qquad , \qquad (2.8)$$

where $\Omega_{km} = (E_k - E_m)/\hbar$ and the nonresonant term, involving the sum frequency $(\Omega_{km} + \omega)$, has been dropped. Upon integrating (2.8) subject to the initial condition $a_k(0) = 0$, we have

$$a_k(t) = \frac{-\mathcal{H}'_{mk}}{\hbar} \cdot \frac{e^{i(\Omega_{km} - \omega)t} - 1}{(\Omega_{km} - \omega)} \qquad . \qquad (2.9)$$

The probability of occupancy of state k is then given by

$$|a_k|^2 = \frac{4\,|\mathcal{H}'_{mk}|^2}{\hbar^2} \; \frac{\sin^2 (\Omega_{km} - \omega)t/2}{(\Omega_{km} - \omega)^2} \quad . \qquad (2.10)$$

If we assume that the final state is not well defined but rather is given by a density of final states, then in order to find the probability of a transition to one of these states we must integrate over the density of final states. We shall assume that the final state is not sharp on account of line broadening and that the density of final states is given by a line shape function $g(\nu)$, where

$$\int_0^\infty g(\nu)\, d\nu = 1 \quad . \qquad (2.11)$$

For a Lorentzian line we have

$$g(\nu) = \frac{2\, T_2}{1 + 4\pi^2\, T_2^{\,2}\, (\nu - \nu_0)^2} \quad , \qquad (2.12)$$

where T_2 is the spin-spin relaxation time.[53] The probability of finding the system in one of these states is given by

$$\text{Prob.} = \int_0^\infty |a_k(\nu)|^2\, g(\nu)\, d\nu \quad . \qquad (2.13)$$

If we further assume that the strength of the perturbation is small, then we can find a time t large enough that

$$\frac{\sin^2 (\Omega - \omega)t/2}{(\Omega - \omega)^2} \approx \frac{\pi t}{2}\, \delta(\Omega - \omega) \quad , \qquad (2.14)$$

consistent with the assumption that at the time t , $|a_m(t)| \approx 1$. By combining (2.10), (2.12), (2.13), and (2.14) and integrating, we have

$$\text{Prob.} = \frac{|\mathcal{H}_{mk}|^2 t}{\hbar^2} \frac{2 T_2}{1 + T_2^2 (\Omega_{km} - \omega)^2} \quad . \qquad (2.15)$$

The transition probability per unit time is given by

$$W_{mk} = \frac{|\mathcal{H}'_{mk}|^2}{\hbar^2} \cdot \frac{2 T_2}{1 + T_2^2(\Omega_{km} - \omega)^2} \quad . \qquad (2.16)$$

Since $\mathcal{H}$ is a Hermitian matrix, we have $\mathcal{H}_{mk} = \mathcal{H}^*_{km}$, and

$$W_{mk} = W_{km} \quad , \qquad (2.17)$$

thus stating that the probability of the system going from k to m is the same as its going from m to k . If we assume that $E_k > E_m$ and the number of atomic systems in levels k and m are n_k and n_m , respectively, then the power absorbed by such a system is given by the product (transition probability)(energy per photon)(net difference in population)

$$P_{abs} = (n_m - n_k)\hbar\omega \, W_{mk}$$

$$= (n_m - n_k)\hbar\omega \cdot \frac{|\mathcal{H}'_{mk}|^2}{\hbar^2} \cdot \frac{2 T_2}{1 + T_2^2(\Omega_{km} - \omega)^2} \quad . \qquad (2.18)$$

If the macrosystem is in a normal population state, $n_m - n_k > 0$, then the power absorbed is positive. Maser action occurs when an inverted population is achieved, $(n_k - n_m) > 0$, and the power absorbed is negative, implying emission. This single quantum process is linear in the sense that the power absorbed or emitted is proportional to the square of the field and hence to the incident power.

The assumption leading to the derivation of this relation are that $t \ll T_2$ in order that (2.14) be consistent with (2.12) and that $\mathcal{H}'_{mk}\, t/\hbar \ll 1$ in order that $|a_k| \ll 1$. Combining these gives the relation

$$\frac{\mathcal{H}' T_2}{\hbar} \ll 1 \qquad . \qquad (2.19)$$

If we look upon T_2 as the coherence time of the atom (coherence being disturbed by "collisions" occurring with a mean time T_2) then (2.19) states that $(\mathcal{H}'/\hbar)^{-1}$, which is a measure of the time it takes to cause a transition, must be greater than the coherence time. In other words the assumptions leading to (2.16) and (2.18) are satisfied only if the perturbation is weak enough so as not to introduce coherence effects in the atomic system.

2. <u>Higher Order Processes</u>

The equations derived in the preceding section assumed energy conservation, $\omega \cong \Omega_{km}$, and the absorption or emission of a single quantum of radiation. These results may be extended to processes involving more than a single quantum by carrying the calculation to higher order. These higher order processes may involve quanta from different radiation fields or more than one quantum from a single radiation field. In order to be definite we shall consider the latter and calculate a double-quantum absorption process. The important aspects of multiple quantum processes will be evident from this specific calculation.

Let us assume, as before, that the system is initially in state m, $a_m(0) = 1$. Then the equations for the a_k, to first order, are given by (2.9):

$$a_k(t) = -\frac{\mathcal{H}'_{mk}}{\hbar}\,\frac{e^{i(\Omega_{km} - \omega)t} - 1}{(\Omega_{km} - \omega)} \qquad . \qquad (2.9)$$

Substituting these first order solutions into (2.7) gives, for $\dot{a}_k$ to second order,

$$i\hbar\dot{a}_k = \sum_n \frac{\mathcal{H}'_{mn}\mathcal{H}'_{nk}}{\hbar(\Omega_{nm} - \omega)} e^{i(\Omega_{km} - 2\omega)t} \quad , \qquad (2.20)$$

where we have assumed that now $2\omega \cong \Omega_{km}$ and that the frequency ω is not near any of the natural resonances, Ω_{kn} and Ω_{mn}. Upon integrating (2.20) under the above assumption and finding the quantity $|a_k|^2$, we have

$$|a_k|^2 = \frac{4}{\hbar^2}\left[\sum_n \frac{\mathcal{H}'_{mn}\mathcal{H}'_{nk}}{\hbar(\Omega_{nm} - \omega)}\right]^2 \frac{\sin^2(\Omega_{km} - 2\omega)t/2}{(\Omega_{km} - 2\omega)^2} \quad . \qquad (2.21)$$

After comparing with the first order case, (2.10), we see that the expressions are similar, with $(\Omega_{km} - \omega)$ being replaced by $(\Omega_{km} - 2\omega)$ and the matrix element $\mathcal{H}'_{mk}$ being replaced by the sum

$$\sum_n \frac{\mathcal{H}'_{mn}\mathcal{H}'_{nk}}{\hbar(\Omega_{nm} - \omega)} \quad . \qquad (2.22)$$

By performing the integration over final states, we have for the transition probability

$$W_{mk} = \frac{1}{\hbar^2}\left[\sum_n \frac{\mathcal{H}'_{mn}\mathcal{H}'_{nk}}{\hbar(\Omega_{nm} - \omega)}\right]^2 \frac{2\,T_2}{1 + T_2^2(\Omega_{km} - 2\omega)^2} \quad , \qquad (2.23)$$

and for the power absorbed

$$P_{abs} = (n_m - n_k)\, 2\hbar\omega\, W_{mk} \quad . \qquad (2.24)$$

The important aspects of this double photon absorption, quantitatively described by (2.23) and (2.24), may be seen by considering a single term from the sum appearing in these expressions. This term describes the coupling of levels m and k with the level n acting as an intermediate or "virtual" state. The term virtual is used because the intermediate state (quantum system in level n , radiation field with N - 1 photons) does not conserve energy with the initial state (quantum system in level m , radiation field with N photons). The amount by which energy is not conserved is given by the energy denominator, $\hbar(\Omega_{nm} - \omega)$. The total probability of a transition from state m to k involves a summation over all possible virtual levels, taking into account the lack of conservation of energy through the energy denominator.

The following conclusions can thus be reached regarding these two-photon processes:

(1) There must be some intermediate quantum state n which is connected both to the initial and to the final state. This state may be a third level or either the initial or final state itself. In the latter case a term of the form $\mathcal{H}'_{mm}$ or $\mathcal{H}'_{kk}$ would be involved.

(2) The strength of the effect will depend on how close the virtual states come to conserving energy; the closer they are to conserving energy, the stronger the effect. The second order effect will be of the order of $(\mathcal{H}'/\hbar(\Omega_{nm} - \omega))^2$ times the first order effect.

(3) The power absorbed depends on the fourth power of $\mathcal{H}'$ and, since $\mathcal{H}'$ is proportional to the applied radiation field, the power absorbed is proportional to the fourth power of the field or to the square of the applied power.

Second order processes involving two different frequencies and higher order processes involving more than two quanta are considered in a similar manner. The third order process, for example, will involve two virtual states.

3. <u>Example</u>

As an example consider a three-level system with unequally spaced levels, (Fig. 2.1). Let the energy eigenvalues be E_1 , E_2 , E_3 , and define the natural frequencies $\Omega_{31} = (E_3 - E_1)/\hbar$, etc. Let us further suppose that there are matrix elements of the perturbation connecting

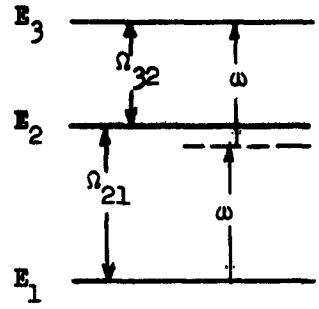

FIG. 2.1--Energy level diagram of a three-level system. First order absorptions occur at Ω_{21} and Ω_{32}. Second order absorption for $2\omega = \Omega_{31}$ is shown with a "virtual" level depicted by the dotted line.

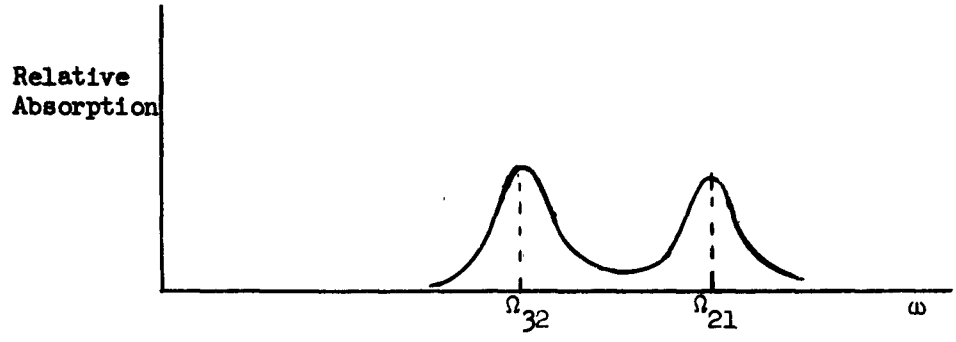

FIG. 2.2--Theoretical absorption spectrum at low rf power levels.

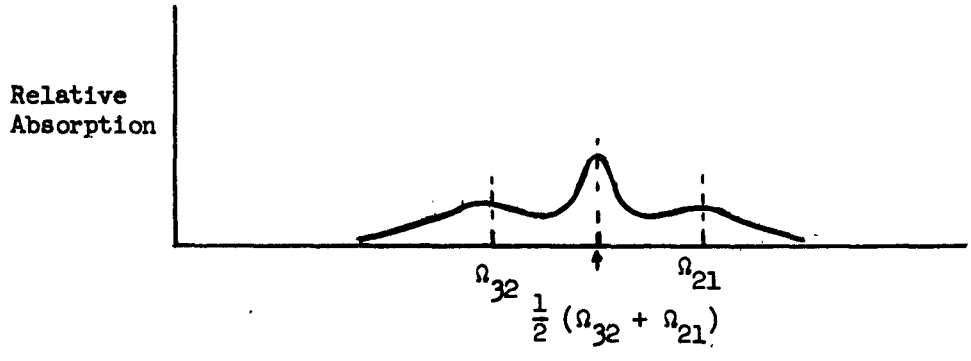

FIG. 2.3--Theoretical absorption spectrum at high rf power levels. The double quantum absorption appears midway between the two first order absorptions, here shown saturated.

levels 1 and 2, and 2 and 3, but levels 1 and 3 are not directly connected in first order. An observation of the spectrum of this system would, to first order, give two lines centered at Ω_{21} and Ω_{32} as shown in Fig. 2.2. Levels 3 and 1, although not connected in first order, are connected in second order via level 2. The power absorbed in this case, from (2.24), is

$$P_{abs} = (n_1 - n_3) \frac{\Omega_{31}}{\hbar} \left| \frac{\mathcal{H}'_{12} \mathcal{H}'_{23}}{\hbar(\Omega_{21} - \omega)} \right|^2 \frac{2\, T_2}{1 + T_2^2(\Omega_{31} - 2\omega)^2} \quad , \quad (2.25)$$

which shows a peak at $2\omega = \Omega_{31} = (\Omega_{32} + \Omega_{21})$, or the algebraic mean of the two first-order lines. This is shown in Fig. 2.3. From (2.25) we see that although the double quantum absorption line always occurs at the frequency $\omega = \Omega_{31}/2$, its strength will depend upon how close to degeneracy Ω_{32} and Ω_{21} are. Upon comparing this example with Kastler's original work,[1] we see that this is precisely the effect he saw.

We may summarize this approach by the following observations: First of all, for the field strengths usually encountered in experimental conditions the transition probability method correctly predicts single quantum absorption and emission processes as verified by experimentation. When carried to higher order, the theory predicts multiple quantum absorption processes which have been experimentally observed. The assumption on which the derivation is based, Eq. (2.10), does, however, limit the general validity of the theory to field strengths satisfying this condition. Further, it is not clear from this point of view how a process such as the absorption of two photons at frequency ω and the coherent emission of a single photon at the frequency 2ω would be handled. Rather than pursue this approach further, we shall turn to the macroscopic approach, which avoids many of the problems inherent in the use of transition probabilities and which is used through the rest of this paper.

D. MACROSCOPIC APPROACH

We may begin a study of the macroscopic approach by writing down

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[1] See Chapter I.

Maxwell's equations in the presence of matter:

$$\nabla \times \underset{\sim}{E} = -\frac{1}{c}\frac{\partial}{\partial t}\underset{\sim}{B} \quad , \quad \nabla \times \underset{\sim}{H} = \frac{1}{c}\frac{\partial}{\partial t}\underset{\sim}{D} + \frac{4\pi}{c}\underset{\sim}{J} \quad , \tag{2.26}$$

$$\nabla \cdot \underset{\sim}{D} = 4\pi\rho \quad , \quad \nabla \cdot \underset{\sim}{B} = 0 \quad , \tag{2.27}$$

along with the constitutive relations

$$\underset{\sim}{D} = \underset{\sim}{E} + 4\pi\underset{\sim}{P} \quad , \quad \underset{\sim}{B} = \underset{\sim}{H} + 4\pi\underset{\sim}{M} \quad . \tag{2.28}$$

The characteristics of the matter are embodied in the quantities $\underset{\sim}{P}$ and $\underset{\sim}{M}$, the polarization and magnetization, respectively. In particular, the relations

$$\underset{\sim}{P} = \underset{\sim}{P}(\underset{\sim}{E}) \quad , \quad \underset{\sim}{M} = \underset{\sim}{M}(\underset{\sim}{H}) \quad , \tag{2.29}$$

define the response of the material to the applied fields.[1] If the dependence is known, then a solution to Maxwell's equations may in principle be found. It is generally assumed that $\underset{\sim}{P}$ is proportional to $\underset{\sim}{E}$, and $\underset{\sim}{M}$ to $\underset{\sim}{H}$, giving the tensor susceptibilities, χ_e and χ_m :

$$\underset{\sim}{P} = \chi_e\underset{\sim}{E} \quad , \quad \underset{\sim}{M} = \chi_m\underset{\sim}{H} \quad . \tag{2.30}$$

From these susceptibilities the familiar dielectric constant and permeability are defined as

$$\epsilon = 1 + 4\pi\chi_e \quad , \quad \mu = 1 + 4\pi\chi_m \quad , \tag{2.31}$$

where now

$$\underset{\sim}{D} = \epsilon\underset{\sim}{E} \quad , \quad \underset{\sim}{B} = \mu\underset{\sim}{H} \quad . \tag{2.32}$$

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[1] A more general relation would be $\underset{\sim}{P} = \underset{\sim}{P}(\underset{\sim}{E}, \underset{\sim}{H})$ and $\underset{\sim}{M} = \underset{\sim}{M}(\underset{\sim}{E}, \underset{\sim}{H})$. We shall for simplicity assume the simpler relations, (2.29), where the polarization depends only on the electric field and the magnetization depends only on the magnetic field.

The above relations form the basis for the solutions to Maxwell's equations for the linear case.

It is more generally true, at least we may assume so, that the polarization depends not only linearly on $\mathbf{E}$ but on higher powers as well. By using a similar argument for the magnetization we may write these more general dependences as

$$\underset{\sim}{P} = \chi_e^{(1)} \underset{\sim}{E} + \chi_e^{(2)} \underset{\sim}{E}\,\underset{\sim}{E} + \chi_e^{(3)} \underset{\sim}{E}\,\underset{\sim}{E}\,\underset{\sim}{E} + \cdots$$

$$\underset{\sim}{M} = \chi_m^{(1)} \underset{\sim}{H} + \chi_m^{(2)} \underset{\sim}{H}\,\underset{\sim}{H} + \chi_m^{(3)} \underset{\sim}{H}\,\underset{\sim}{H}\,\underset{\sim}{H} + \cdots \quad , \tag{2.33}$$

where the new tensors are of higher order.[1] This more general constitutive relation is seen to give rise to nonlinear effects. For example, if $\mathbf{E}$ varies as $\cos \omega t$, the term $\underset{\sim}{E}\,\underset{\sim}{E}$ will have a component at the frequency 2ω and through (2.28) and (2.26) radiation fields will be set up at the frequency 2ω.

Equations (2.26) through (2.33) constitute a description of the macroscopic electromagnetic field for both the linear and nonlinear cases. It remains, however, to determine the response of the medium to the applied fields, Eqs. (2.29) or (2.33). In particular we should like to determine this response analytically from the microscopic properties of the atomic systems making up the medium. The basis for such a calculation follows from the relations

$$\underset{\sim}{P} = N\underset{\sim}{\bar{\bar{p}}}\,,\ M = N\underset{\sim}{\bar{\bar{m}}} \quad , \tag{2.34}$$

where $\underset{\sim}{P}$ and $\underset{\sim}{M}$ as before are the macroscopic polarization and magnetization, N is the number of atoms per unit volume and $\underset{\sim}{\bar{\bar{p}}}$ and $\underset{\sim}{\bar{\bar{m}}}$ are the average or expectation values of the polarization and magnetization per atom.[2] The average implied by the double bar constitutes both a statistical

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[1] For example, the second term in the expansion for P would be $P_i^{(2)} = \chi_{ijk} E_j E_k$ and the third term would be $P_i^{(3)} = \chi_{ijk\ell} E_j E_k E_\ell$.

[2] See J. H. Van Vleck, reference 54, for a proof of this relation.

average and a quantum mechanical average, the latter coming as a result of the inherent statistical nature of quantum phenomena. The problem thus is reduced to a quantum statistical evaluation of $\bar{\bar{\underset{\sim}{p}}}$ and $\bar{\bar{\underset{\sim}{m}}}$ in response to the radiation fields present.

E. EVALUATION OF THE MACROSCOPIC PROPERTIES: THE DENSITY MATRIX APPROACH[1]

The density matrix formulation provides a direct means for formulating quantum statistical problems. The density matrix may be characterized by its equation of motion,

$$i\hbar\dot{\rho} = [\mathcal{H}, \rho] + \frac{i\hbar}{\tau}(\rho - \rho^e) \quad , \qquad (2.35)$$

and the prescription for finding the expectation value of an observable,[2]

$$\langle Q \rangle = \text{Trace}\ (\rho Q) \quad . \qquad (2.36)$$

In these expressions ρ is the density operator, $\mathcal{H}$ is the total Hamiltonian, ρ^e is the value of ρ at equilibrium, and τ is the relaxation time associated with the return to equilibrium. The value of τ will depend on the particular element of the density matrix considered. In general, when using the energy representation, τ may be divided into longitudinal or spin-lattice relaxation times associated with the diagonal components of ρ and transverse or spin-spin relaxation times associated with the off-diagonal components of ρ. The longitudinal relaxation times, usually denoted by T_1, describe the characteristic time in which the spin system and the lattice reach equilibrium with each other. This process involves the exchange of energy between the spin system and the lattice. The transverse relaxation times, usually denoted by T_2, describe the characteristic time in which the spin system reaches equilibrium within itself. This relaxation process is important in determining

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(1) For an alternative approach to this calculation see Slater,[55] Chapter 6, pp. 154-157, Kramers,[56] Chapter 8, pp. 480, and Bloembergen.[48] Briefly, this method involves a calculation of the perturbed wave function due to the applied fields and the evaluation of the polarization and magnetization from these wave functions. This method assumes, however, that the frequency of the radiation field is not near any natural transition frequency and hence the field causes no transitions. The method used here is not limited by this assumption.

(2) These relations are derived in Appendix A.

the effects of coherence in the atomic system. In Eq. (2.36) the trace is taken of the product of the matrices defined as

$$\rho_{nm} = \langle n|\rho|m\rangle \tag{2.37}$$

$$Q_{nm} = \langle n|Q|m\rangle \quad , \tag{2.38}$$

where $|n\rangle$ is any complete set of functions. It is usually found convenient to define this set of functions as eigenfunctions of the unperturbed Hamiltonian, $\mathcal{H}_0$, where

$$\mathcal{H}_0|n\rangle = E_n|n\rangle \quad . \tag{2.2}$$

In this representation the time average value of the diagonal terms, ρ_{nn} , when normalized such that $\sum_n \rho_{nn} = 1$, may be interpreted as the probability of occupancy of level n . The off-diagonal elements, ρ_{nm} , are interpreted as giving a measure of the amount of coupling between levels m and n , where the coupling is proportional to the magnitude of the element. The procedure for finding the values of the observables is first to solve the density matrix Eqs. (2.35) under the particular conditions of the problem. From this we have a knowledge of all the elements ρ_{nm} . The magnitude and phase of an observable quantity is dependent on the elements of ρ through (2.36) and is generally dependent on both the diagonal and off-diagonal components of ρ :

$$\begin{aligned} \langle Q\rangle &= \sum_{m,n} \rho_{nm} Q_{mn} \\ &= \sum_n \rho_{nn} Q_{nn} + \sum_{\substack{n \\ m\neq n}} \rho_{nm} Q_{mn} \quad . \end{aligned} \tag{2.39}$$

The matrices of the observables are assumed to be constants, independent of time, and hence the time dependence of the observable is found from the

time dependence of ρ . By examining the equations of motion for ρ , we can see what the time dependence is, and in particular we can see how linear and nonlinear processes arise.

Let us write Eq. (2.35) in matrix form in the following way:

$n = m$

$$i\hbar\dot{\rho}_{nn} + \frac{i\hbar}{\tau}(\rho_{nn} - \rho^{e}_{nn}) = \sum_{\ell} (\mathcal{H}'_{n\ell}\,\rho_{\ell n} - \rho_{n\ell}\,\mathcal{H}'_{\ell n}) \tag{2.40}$$

$n \neq m$

$$\begin{aligned} i\hbar\dot{\rho}_{nm} + (E_m - E_n)\rho_{nm} + \frac{i\hbar\rho_{nm}}{\tau} &= \mathcal{H}'_{nm}\,(\rho_{mm} - \rho_{nn}) \\ &+ \rho_{nm}\,(\mathcal{H}'_{nn} - \mathcal{H}'_{mm}) + \sum_{\ell \neq n,m} (\mathcal{H}'_{n\ell}\,\rho_{\ell m} - \rho_{n\ell}\,\mathcal{H}'_{\ell m}) \,. \end{aligned} \tag{2.41}$$

From these equations we can see first of all that the "natural frequency" of the diagonal components is zero while for the off-diagonal term ρ_{nm} it is $(E_m - E_n)/\hbar$. Clearly a given component will be most strongly driven when the frequency of the driving term is near its natural frequency.

1. <u>Linear Effects</u>

Direct coupling of levels n and m occurs via the term $\mathcal{H}'_{nm}(\rho_{mm} - \rho_{nn})$ and is strongest when $\mathcal{H}'_{nm}$ varies with time as $\exp i(E_m - E_n)t/\hbar$. As a result of the direct coupling term, ρ_{nm} is proportional to $\mathcal{H}'_{nm}$ and hence to the applied field. Evaluation of an observable through Eq. (2.39) also gives a linear dependence on the applied field. Hence the direct coupling terms are seen to give rise to linear effects, among which are those described in Eqs. (2.32).

2. <u>Nonlinear Effects</u>

In addition to these direct coupling terms there are additional terms of the form $\mathcal{H}'_{n\ell}\,\rho_{\ell m}$ which describe the indirect coupling of levels n and m via level ℓ . These terms include the right hand side (rhs) of (2.40) and the last two terms on the rhs of (2.41). A term of this

form describes the fact that if levels ℓ and m are coupled, $\rho_{\ell m} \neq 0$, and if ℓ is also coupled to n, $\mathcal{H}'_{n\ell} \neq 0$, then n and m will also be coupled. If $\rho_{\ell m}$ is proportional to $\mathcal{H}'_{\ell m}$, then ρ_{nm} is proportional $\mathcal{H}'_{\ell m}$, and hence an observable dependent on ρ_{nm} will be quadratic in the applied fields. A term of this form thus gives rise to a nonlinear dependence on the field and accounts for the second term in Eq. (2.33). If $\rho_{\ell m}$ is nonzero because of indirect coupling to some level q, then ρ_{nm} is proportional to $\mathcal{H}'_{n\ell}\mathcal{H}_{\ell q}\mathcal{H}_{qm}$ and is thus a third order quantity in the radiation field. An observable dependent on $\rho_{\ell m}$ would thus be proportional to the cube of the field and would give rise to third order nonlinearities.

We thus see that, in this particular formalism, nonlinear effects are handled by means of a consideration of indirect coupling mechanisms. Processes of any order may be handled by this means.

The usual method of solution of such a problem may be summarized as follows:

(1) For the particular problem at hand allow for all the radiation fields which are present by including appropriate terms in the Hamiltonian.

(2) Assume solutions for the components of the density matrix of the form of harmonic series of the frequencies present.

(3) Find a steady state solution by equating terms with the same time dependence. This results in a set of algebraic equations which are then soluble by standard methods. In practice, simplifications can usually be made which will make these solutions easy to obtain.

Once the density matrix is found, then through (2.34) and (2.36) the macroscopic properties are known and Maxwell's equations (2.26) through (2.29) may be solved under the particular conditions of the problem. These equations then form a self-consistent means of solving the general radiation problem.

3. Examples

Let us briefly consider two examples using the density matrix approach.

a. Spin 1/2 System

Assume that a spin 1/2 system is in a dc magnetic field and that the natural frequency of the transition is given by $(E_2 - E_1)/\hbar = \Omega$. Choose the representation to be the one in which S^2 and S_z are diagonal,

where the matrices of the x and z components of the magnetic dipole operator are

$$\mu_x = \mu \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \mu_z = \mu \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad . \tag{2.42}$$

If an rf magnetic field $H_1 \cos \omega t$ is applied in the x-direction, then the interaction Hamiltonian is

$$\mathcal{H}' = - \mu_x H_1 \cos \omega t \quad , \tag{2.43}$$

and hence the nonzero matrix elements of $\mathcal{H}'$ are

$$\mathcal{H}'_{12} = \mathcal{H}'_{21} = - \mu H_1 \cos \omega t \quad . \tag{2.44}$$

Substituting (2.44) into (2.40) and (2.41), using the longitudinal and transverse relaxation times, T_1 and T_2, defined in Appendix A, and employing harmonic balance gives the following solutions for ρ :

$$\rho_{12} = \frac{-i\, T_2\, \mu\, H_1\, (\rho^o_{11} - \rho^o_{22})\, e^{i\omega t}}{2\hbar\, (1 - iT_2\delta)} \tag{2.45}$$

$$\rho_{21} = \rho^*_{12} \tag{2.46}$$

$$\rho_{11} = \rho^o_{11} - \frac{(\rho^o_{11} - \rho^o_{22})\, \mu^2\, H_1^2\, T_2\, [\sin 2\omega t + T_2\delta \cos 2\omega t]}{4\hbar^2\omega(1 + T_2^2\, \delta^2)} \tag{2.47}$$

$$\rho_{22} = 1 - \rho_{11} \tag{2.48}$$

and

$$\rho_{11}^{o} - \rho_{22}^{o} = \frac{\rho_{11}^{e} - \rho_{22}^{e}}{1 + \dfrac{T_1 T_2 \mu^2 H_1^2}{\hbar^2 (1 + T_2^2 \delta^2)}} \quad , \qquad (2.49)$$

where

$$\delta = \Omega - \omega \quad . \qquad (2.50)$$

The quantities ρ_{11}^{e} and ρ_{22}^{e} are the thermal equilibrium values of ρ while ρ_{11}^{o} and ρ_{22}^{o} are the dynamic equilibrium values or the average values with the rf fields present. Equation (2.49) thus describes the effects of saturation. From (2.39), (2.42), (2.45) and (2.46) we find the expectation value of the x component of the magnetic dipole moment

$$\langle \mu_x \rangle = \mu \, (\rho_{12} + \rho_{21})$$

$$= \frac{\mu^2 H_1 T_2 (\rho_{11}^{o} - \rho_{22}^{o})}{\hbar (1 + T_2^2 \delta^2)} (\sin \omega t + T_2 \delta \cos \omega t) \; . \qquad (2.51)$$

The power absorbed is given by

$$P_{abs} = \left\{ \langle \dot{\mu}_x \rangle H_1 \cos \omega t \right\}_{\text{time average}}$$

$$= (\rho_{11}^{o} - \rho_{22}^{o}) \hbar \omega \left(\frac{\mu H_1}{2\hbar} \right)^2 \frac{2 T_2}{1 + T_2^2 (\Omega - \omega)^2} \; . \qquad (2.52)$$

By multiplying by the number of particles N and noting that $N(\rho_{11}^{o} - \rho_{22}^{o}) = n_1 - n_2$, we see that (2.52) is the same as (2.18), calculated by transition probabilities, where $\mathcal{H}'_{12} = \mu H_1 / 2$.

If we now evaluate $\langle \mu_z \rangle$, the expectation value of the z-component of the dipole moment, we find from (2.39), (2.42), (2.47) and (2.48)

$$\mu_z = \mu(\rho_{11} - \rho_{22})$$

$$= \mu(\rho_{11}^{o} - \rho_{22}^{o}) - \frac{2(\rho_{11}^{o} - \rho_{22}^{o})\mu^3 H_1^2 T_2}{\hbar^2 \omega(1 + T_2^2 \delta^2)} (\sin 2\omega t + T_2 \delta \cos 2\omega t) \quad , \tag{2.53}$$

which shows a dc component as well as a component at the frequency 2ω . This component at 2ω comes as a result of the indirect coupling of level 1 to itself in second order via level 2, and similarly for level 2 via 1. When this latter component of μ_z is introduced into Maxwell's equations it will give rise to radiation fields at the frequency 2ω , an effect not predicted by the method used to derive Eq. (2.18). Hence we see that the density matrix formulation gives a more general approach, giving more information than do transition probabilities.

b. <u>Three-level System</u>

For the second example let us consider the three-level system previously discussed in section C.2, this time using the density matrix approach. To be definite, let us assume magnetic dipole transitions and an applied field $H_1 \cos \omega t$. The nonzero perturbation terms are

$$\begin{aligned} \mathcal{H}'_{12} &= - \mu_{12} H_1 \cos \omega t \\ \mathcal{H}'_{21} &= - \mu_{21} H \cos \omega t \\ \mathcal{H}'_{23} &= - \mu_{23} H \cos \omega t \\ \mathcal{H}'_{32} &= - \mu_{32} H \cos \omega t \end{aligned} \tag{2.54}$$

By assuming that $\rho_{12} = \lambda_{12}\, e^{i\omega t}$, $\rho_{23} = \lambda_{23}\, e^{i\omega t}$, $\rho_{13} = \lambda_{13}\, e^{i2\omega t}$, then to first order we have the solutions[1]

$$\lambda_{12} = \frac{(\rho_{11}^{o} - \rho_{22}^{o})\, \mu_{12}\, H_1}{2\hbar\, [(\Omega_{21} - \omega) + i/T_2]} \tag{2.55}$$

$$\lambda_{23} = \frac{(\rho_{22}^{o} - \rho_{33}^{o})\, \mu_{23}\, H_1}{2\hbar\, [(\Omega_{32} - \omega) + i/T_2]} \tag{2.56}$$

and

$$\lambda_{13} = 0 \quad \text{, to first order} \quad . \tag{2.57}$$

A calculation of the magnetic moment using these values would predict first order absorption at $\omega = \Omega_{21}$ and $\omega = \Omega_{32}$. By keeping second order terms we find that levels 1 and 3 are coupled since level 2 is coupled to both 1 and 3 in first order. Simplifying the exact expression somewhat by assuming that $(\Omega_{12} - \omega) \gg 1/T_2$ and $2\omega = \Omega_{31}$ gives

$$\lambda_{13} = \frac{i\, T_2\, \mu_{12}\, \mu_{23}\, H_1^2}{4\hbar^2\, \delta} (\rho_{33}^{o} - \rho_{11}^{o}) \quad , \tag{2.58}$$

where $\delta = \Omega_{21} - \omega$. Finally, using this value for λ_{13} , we find that λ_{12} and λ_{23} take on nonzero third order terms. In the case of λ_{12} this occurs as a result of the fact that levels 1 and 3 are connected (in second order) and 3 is in turn connected to 2. A similar argument applies for λ_{23} . These third order terms are

$$\lambda_{12}^{(3)} = \frac{i T_2\, \mu_{12}\, \mu_{32}\, \mu_{23}\, H_1^3}{8\hbar^3\, \delta^2} (\rho_{33}^{o} - \rho_{11}^{o}) \tag{2.59}$$

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[1] See Chapter V for a derivation of these equations and for a more detailed explanation of this problem.

and

$$\lambda_{23}^{(3)} = \frac{i\, T_2\, \mu_{12}\, \mu_{21}\, \mu_{23}\, H_1^3}{8\hbar^3\, \delta^2} (\rho_{33}^o - \rho_{11}^o) \quad , \qquad (2.60)$$

where the time dependence is still $e^{i\omega t}$. Calculation of the magnetic moment from the relation

$$\langle\mu\rangle = (\mu_{12}\, \rho_{21} + \mu_{21}\, \rho_{12}) + (\mu_{23}\, \rho_{32} + \mu_{32}\, \rho_{23}) \quad , \qquad (2.61)$$

and subsequently evaluating the power absorbed, gives Eq. (2.25) where we have set $2\omega = \Omega_{31}$. Thus not too unexpectedly we arrive at the same answer as was given by the transition probability method. One important point can be made, however. If the selection rules for the transitions were such that μ_{13} was not zero, then from (2.39) and (2.58) we immediately find a nonzero component of magnetization at 2ω and, as mentioned before, this will generate radiation fields at the new frequency. A more detailed analysis of this particular case is given in Chapter V.

F. GENERAL ASPECTS OF NONLINEAR QUANTUM EFFECTS

From the formulation of the problem presented above we can draw some general conclusions about the various nonlinear effects which are possible.

a. The strength of the nonlinear effect measured by the magnitude of the nonlinear polarization or magnetization will be proportional to the magnitude of the higher order components of the density matrix. These, in turn, will involve combinations of first order terms in the density matrix. Hence the higher order effects will, in general, be large when the corresponding linear effects are large. The latter are found to be largest when the matrix elements connecting the various levels are large and when energy is nearly conserved, i.e., when the applied frequency is near a natural transition frequency (if the applied signal is resonant with a natural frequency then the strength of the transition is inversely proportional to the linewidth of the transition). We then see that

nonlinear effects will be strongest when the frequencies of the radiation fields are near the natural frequencies of the transitions involved and when these transitions are strong. The dependence on the proximity to natural resonant frequencies points out the fact that for a given material the nonlinear effects will be frequency-sensitive. This is in contrast to a diode, for example, where the nonlinearity is relatively frequency insensitive.

b. In general, the higher the order of the effect (the larger the number of photons involved), the smaller is the magnitude of the effect. In practice second and third order nonlinear effects will probably find the most application.

c. The total energy of the field and atomic system must be conserved in the overall interaction. This may be achieved either by the radiation field and the molecule separately conserving energy, or by an increase in energy of one system being compensated by a corresponding decrease in the energy of the other. In the latter case the change in the energy of the quantum system must correspond to the difference between two of the eigenenergies E_n, defined in (2.2).

d. The type of nonlinearity, i.e., whether even or odd, and the number of photons involved, depends upon the number of levels involved and on the selection rules for the pertinent transitions. The selection rules are, in turn, determined by the symmetry properties of the atomic system and its surroundings. For example, if a crystal has a center of inversion, then only odd order effects due to electric dipole transitions are allowed.[38]

e. In any nonlinear effect there will in general be contributions to the effect from many combinations of levels. It may be the case, however, that the contribution of two or three of the levels dominates, in which case the essential properties may be found from a consideration of the simpler two- or three-level system.

G. EXAMPLES OF NONLINEAR EFFECTS

We may consider briefly some of the more important effects possible in two- and three-level systems. Some of these effects are considered in detail later in this report, some are considered by other authors, and some have not yet been investigated.

1. Two-level System

a. Harmonic Generation

From an examination of the density matrix Eqs. (2.40) and (2.41) for the specific case of a two-level system, it can easily be seen that the off-diagonal components contain only odd powers of the applied field, while the diagonal components contain even powers. From (2.39) we see then, that if a dipole moment, which may act as a source of radiation, has diagonal components, then generation of even harmonics is possible, whereas if it contains only off-diagonal components, then only odd harmonic generation is possible. The question of diagonal and off-diagonal components of the dipole is determined by the type of interaction (magnetic or electric dipole) and upon the symmetry of the Hamiltonian. Second harmonic generation is briefly discussed in part E.3 of this chapter and third harmonic generation is considered in detail in Chapter III.

b. Parametric Processes

There are several types of parametric processes possible in a two-level system. They may be separated into two classes depending on whether the dipole operator possesses a diagonal component (μ_{11} or μ_{22}), or not.

If the system possesses either a μ_{11} or a μ_{22} then the two processes shown in Figs. 2.4 and 2.5 are possible.

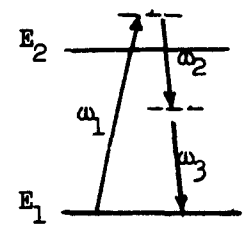

FIG. 2.4--Parametric process with three frequencies present; μ_{11} or μ_{22} nonzero.

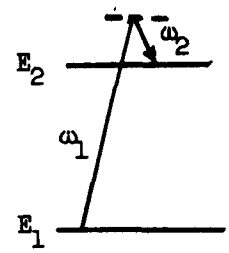

FIG. 2.5--Parametric process with two frequencies present; μ_{11} or μ_{22} nonzero.

In the first, shown in Fig. 2.4, a strong field is applied at the frequency ω_1, and two radiation fields at frequencies ω_2 and ω_3 are generated by the nonlinear action. This is a threshold effect and requires $\omega_1 = \omega_2 + \omega_3$ in order to conserve energy. Such a system is essentially considered by Suhl.[35] The second effect, shown in Fig. 2.5, involves only two radiation fields, at ω_1 and ω_2, and is usually referred to as a Raman effect. From section F above, we have $\omega_1 = \omega_2 + (E_2 - E_1)/\hbar$. Neglecting the effects of spontaneous emission, this is also a threshold effect. Javan has considered this as a form of Raman maser.[36]

For systems with a dipole moment containing off-diagonal components two parametric processes are also possible and are shown in Figs. 2.6 and 2.7.

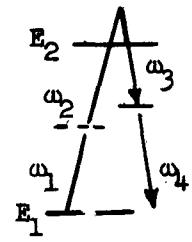

FIG. 2.6--Parametric process with four frequencies present.

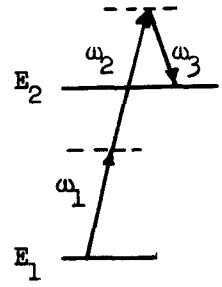

FIG. 2.7--Parametric process with three frequencies present.

In the first, Fig. 2.6, four radiation fields are present, their frequencies satisfying $\omega_1 + \omega_2 = \omega_3 + \omega_4$. Here, for example, fields applied at ω_1 and ω_2 will generate fields at ω_3 and ω_4 when the magnitude of the applied fields exceeds a threshold value determined by the parameters of the problem. In the second case the quantum system resonance replaces one of the radiation fields and the frequencies must satisfy $\omega_1 + \omega_2 = \omega_3 + (E_2 - E_1)/\hbar$. This is also a threshold effect with a field at ω_3 generated when the fields applied at ω_1 and ω_2 exceed a given threshold. In the last two cases considered it is possible for ω_1 to equal ω_2 , reducing the actual number of fields present. The second of these effects is considered in Chapter IV while the first has not been considered in the literature.

In the case of the two-level system we find that the presence of a diagonal component of the dipole operator allows processes involving one less radiation field than for systems with only off-diagonal matrix elements. This may be seen by comparing the processes described by Figs. 2.4 and 2.6 and those shown in Figs. 2.5 and 2.7.

There are several possible applications of these parametric effects. As in the case of classical parametric systems, these quantum systems may act as amplifiers when operated below threshold and as oscillators when operated above threshold. The two cases shown in Figs. 2.5 and 2.7 have a slightly different character than classical parametric effects. Here the quantum system acts as the "idler," removing the necessity for providing an electromagnetic field at this frequency.

2. Three-level System

The number of nonlinear effects possible in a three-level system exceeds those possible in a two-level system as a result of the additional number of combinations of levels possible. We shall thus point out only some of the important possible applications. The first is a three-frequency mixing process, shown in Fig. 2.8.

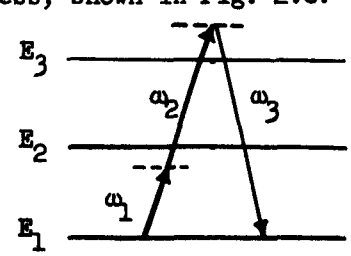

FIG. 2.8--Three-frequency mixing process; μ_{12} , μ_{23} , μ_{13} all nonzero.

Here, the application of any two frequencies, ω_1 , ω_2 or ω_3 , where $\omega_1 + \omega_2 = \omega_3$, will generate fields at the third frequency if all the transitions are allowed. A special example of this is the case in second harmonic generation where $\omega_1 = \omega_2$, considered in Chapter V. Such a mixing process could also act as an up- or down-converter.

The reverse of this process, namely where fields at ω_3 are applied and parametric oscillations at ω_2 and ω_1 occur above a given threshold, has been considered as a form of amplifier by Anderson.[33]

Javan,[27] and Shimoda and Yajima[30-32] have considered a process similar to that of Fig. 2.8, in which only two radiation fields are present. This is shown in Fig. 2.9 where now $\omega_1 = \omega_2 + (E_2 - E_1)/\hbar$ and only the 1-3 and 2-3 transitions need be allowed. This effect is very similar to that considered in Fig. 2.5 where now the coupling to the third level replaces the self-coupling (μ_{11} or μ_{22}) . This is also a type of Raman effect.

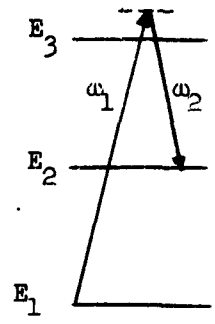

FIG. 2.9--Parametric oscillator; μ_{13} and μ_{23} nonzero.

Finally, let us consider the three-frequency process shown in Fig. 2.10.

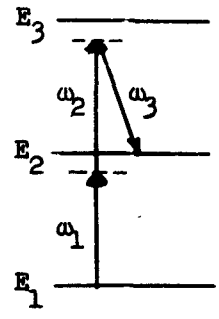

FIG. 2.10--Three-frequency parametric process; μ_{12} and μ_{23} nonzero.

Here it is assumed that there exist nonzero dipole moments connecting levels 1 and 2 and 2 and 3. The application of radiation fields at ω_1 and ω_2 will cause a field to be generated at the frequency ω_3, when the level of the applied fields exceeds a given threshold. If $\omega_1 = \omega_2$, then this process is seen to provide a form of parametric amplification where the pump frequency is near that of the signal. This has not been previously considered.

H. SUMMARY

In this chapter nonlinear as well as linear effects have been discussed and their analysis has been presented from the transition probability and density matrix points of view. The latter approach is the more general and is best suited for the types of problems where multiple quantum processes are involved. The nonlinearities encountered make possible harmonic generation and various forms of parametric processes which may be used for amplification and mixing.

Since the natural frequencies of atoms extend from radio frequencies to optical and above, these forms of nonlinear, multiple quantum effects will similarly occur throughout the spectrum. The transitions involved may include paramagnetic, rotational, vibrational, and electronic energy levels.

CHAPTER III

THEORY OF THIRD HARMONIC GENERATION IN A TWO-LEVEL QUANTUM MECHANICAL SYSTEM

In this chapter we shall consider the theory of third harmonic generation in a two-level quantum mechanical system. Such a system may consist of only two levels as in the case of a spin 1/2 magnetic dipole, or a particular pair of levels in the case of a more complicated atomic structure. The classical interpretation of the problem is presented briefly, followed by a detailed quantum mechanical analysis in which various aspects of the interaction are discussed. The results of the analysis will be applied to the specific case of third harmonic generation in a gas where the inversion transition in NH_3 is used as an example.

A comparison of these predictions with the experiment performed on NH_3 are presented in Chapter VI.

A. GENERAL CONSIDERATIONS

The problem to be examined is the interaction of an electromagnetic field of frequency $\omega = 2\pi\nu$ with a quantum mechanical system consisting of a pair of levels with energies E_1 and E_2 and a natural frequency $\Omega = (E_2 - E_1)/\hbar$. Such a process may take place via either an electric dipole or magnetic dipole interaction (electric quadrupole and higher order interactions will not be considered) and the order of the interaction, i.e., the number of photons involved, will be determined by the type of interaction involved. These may be summarized as follows:

1. Electric Dipole Transitions

a. Induced Electric Dipole

When the interaction is pure electric dipole in character, provided neither the upper nor lower state possesses a permanent dipole moment, then only odd order interactions may occur, i.e., only an odd number of photons may be absorbed or emitted. This type of interaction will occur when each state has either even or odd parity.

b. Permanent Electric Dipole

If either of the states possesses a permanent dipole moment or a dc electric field is applied (creating a permanent electric moment via a mixing of states)[1] then even order interactions are allowed as well as the odd order ones. Permanent moments may exist when a state has neither even nor odd parity.

2. Magnetic Dipole

If the transitions between states are due to pure magnetic dipole interactions, then three possible situations may be considered:

a. H_{rf} Perpendicular to H_{dc}

If the rf magnetic field is orthogonal to the dc field (assuming a free spin and no crystalline fields) then the only transitions which are allowed are of the form $\Delta m = \pm 1$, where m is the magnetic quantum number. In order to go from one level to the other, a net change in m of 1 is required. This is seen to occur only when an odd number of photons is involved.

b. H_{rf} Parallel to H_{dc}

When the rf magnetic field is parallel to the dc field, the photons carry no angular momentum. In this case, no transitions are allowed between states which have different m values.

c. H_{rf} Arbitrary Relative to H_{dc}

With the rf field in an arbitrary direction, it may be divided into components parallel to and perpendicular to H_{dc}; these photons carry 0 and ± 1 units of angular momentum, respectively. Transitions between states can then occur with any number of photons.

The phenomenon of second harmonic generation involves the absorption of two photons and the emission of a single photon at twice the frequency. From the discussion above, such a process is seen to occur in either a magnetic dipole system of type (2c) or in an electric dipole system possessing a permanent dipole moment (1b). Third harmonic generation may occur in magnetic cases (2a) and (2c) and for either electric dipole case.

For the two-level system, the electric dipole transitions have the distinct advantage over their magnetic counterparts in that the value of

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[1] In the absence of state mixing and for states of either even or odd parity, we have the quantity $\langle i|x|i\rangle = 0$, which means zero permanent electric dipole moment. If a dc field is applied or the state has neither even or odd parity, then we have $\langle i|x|i\rangle \neq 0$, and a permanent dipole exists.

the electric dipole moment, (in C.G.S. units where $E = H$) , is typically 100 times that of the magnetic dipole moment. Since the output power generated varies as some high power of the dipole moment, (eighth for third harmonic, sixth for second harmonic) magnetic dipole interactions are of little interest compared to their electric counterpart. In this chapter we shall consider third harmonic generation in an electric dipole system. Magnetic dipole transitions will be considered later in Chapter V, pertaining to three-level systems in which other factors are made to compensate for the smallness of the dipole moment.

B. PHYSICAL PICTURE OF THE PROBLEM

At this point, before launching into a detailed quantum mechanical study of the problem, it is perhaps appropriate to consider it from a physical point of view. Let us assume that we have an atom in which there is a single electron bound to the nucleus by some form of potential well. For simplicity, assume the electron to be a localized particle with coordinate x (rather than a smeared out wave function) and assume that the potential is expanded about its equilibrium position. From texts on classical mechanics[1] the potential (assumed one-dimensional) may be written

$$V = V(x_0) + \left(\frac{dV}{dx}\right)_{x_0} \cdot (x - x_0) + \frac{1}{2!}\left(\frac{d^2V}{dx^2}\right)_{x_0} (x - x_0)^2 + \frac{1}{3!}\left(\frac{d^3V}{dx^2}\right)_{x_0} (x - x_0)^3 + \ldots , \tag{3.1}$$

where the first term is an additive constant to the zero of energy which may be set equal to zero without loss of generality and $(dV/dx)x_0 = 0$

[1] For example, see Ref. 57, p. 319.

since the point x_0 is assumed to be a point of equilibrium. Taking $x_0 = 0$, we have

$$V(x) = \frac{1}{2} V_1 x^2 + \frac{1}{3} V_2 x^3 + \frac{1}{4} V_3 x^4 + \ldots \quad , \qquad (3.2)$$

where the constants V_1, V_2, V_3 may be derived from the coefficients in the Taylor expansion of $V(x)$. We shall be interested in the qualitative details of V and not in its quantitative nature since in practice such detailed knowledge is not usually available. In the usual case, for small excursions, the first term predominates in the expansion and one obtains simple periodic motion with a natural frequency given by the relation

$$\omega_0^2 = \frac{V_1}{m} \quad . \qquad (3.3)$$

If the particle has a charge e, then the application of an oscillating electric field $E \cos \omega t$ will cause the charge to oscillate at the frequency ω in response to this drive. The equation of motion for the particle, assuming only the first term in the expansion for V to be kept, is

$$\frac{d^2x}{dt^2} + \omega_0^2 x = \frac{eE}{m} \cos \omega t \quad . \qquad (3.4)$$

The solution is easily seen to be

$$x = \frac{\frac{eE}{m} \cos \omega t}{\omega_0^2 - \omega^2} \quad , \qquad (3.5)$$

where the particle oscillates at the frequency of the applied electric field and the strength of the oscillation is proportional to the applied

field and depends on the relation of the applied to natrual frequencies through the resonance denominator.[1]

The polarization or dipole moment induced by the motion of this charge is

$$p = ex = \frac{e^2 E \cos \omega t}{m(\omega_0^2 - \omega^2)} \quad , \qquad (3.6)$$

giving the susceptibility per atom

$$\chi = \frac{e^2}{m(\omega_0^2 - \omega^2)} \quad . \qquad (3.7)$$

If now the magnitude of the fundamental excitation, measured by x, Eq. (3.5), is increased, the higher order terms in the expansion of $V(x)$ become increasingly important and must be included. In order to be specific, let us assume that the potential function $V(x)$ is symmetric, $V_2 = 0$, and the next nonvanishing term in (3.2) is $V_3 x^4/4$. By including this in the equation of motion for the charge, Eq. (3.4), we have

$$\frac{d^2x}{dt^2} + \omega_0^2 x + \frac{V_3 x^3}{m} = \frac{eE}{m} \cos \omega t \quad . \qquad (3.8)$$

To first order in the perturbation E the solution is simply that given by Eq. (3.5). Upon substituting the first order solution into (3.8), expanding the term containing x^3, and using the trigonometric identity $\cos^3 \omega t = 1/4\ (3 \cos \omega t + \cos 3\omega t)$, we find that in order to satisfy the equation to the order of V_3 we must include in x a term

---

[1] For completeness there should be a term in the differential equation (3.4) which is proportional to $\dot{x}$ and which describes the damping, both dissipative and radiative. This term will remove the infinite response for x in Eq. (3.5) when $\omega = \omega_0$.

at 3ω . Harmonic balance yields

$$x_3 = \frac{1}{4}\,\frac{V_3}{m}\,\frac{\left(\frac{eE}{m}\right)^3 \cos 3\omega t}{(9\,\omega^2 - \omega_0^2)(\omega_0^2 - \omega^2)^3} \quad . \qquad (3.9)$$

This component of x gives rise to a term in the polarization at the frequency 3ω given by

$$p(3\omega) = e\,x_3 = \frac{V_3}{4}\left(\frac{e}{m}\right)^4 \frac{E^3 \cos 3\omega t}{(9\omega^2 - \omega_0^2)(\omega_0^2 - \omega^2)^3} \quad , \qquad (3.10)$$

which when incorporated into Maxwell's equations gives rise to third harmonic fields. We thus have a simple classical picture of the nonlinearity.

From a quantum mechanical point of view, the discrete charge located at the point x is replaced by the charge density $e\,\psi^*(x)\,\psi(x)$, where $\psi(x)$ is the wave function in the Schrödinger picture. In this picture the motion of the center of gravity of the charge density is equivalent to the motion of the particle. We may imagine the motion of this charge cloud oscillating in response to the applied fields as setting up a dipole moment of the form

$$p = \int \psi^* e\,x\,\psi\,dx \quad . \qquad (3.11)$$

The characteristics of this motion will determine the linear and nonlinear character of p . The exact motion of the charge cloud, and hence p , is determined by the time evolution of the wave function which in turn is governed by Schrödinger's equation.

C. QUANTUM THEORY OF THIRD HARMONIC GENERATION IN A TWO-LEVEL SYSTEM

The quantum system to be considered will be taken to consist of two levels with energies E_1 and E_2 in order of increasing energy where

the natural frequency Ω is defined by

$$\Omega = (E_2 - E_1)/\hbar \quad , \qquad (3.12)$$

as illustrated:

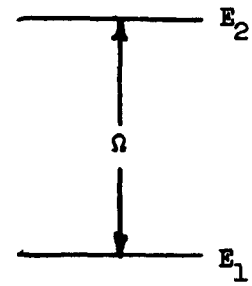

FIG. 3.1--Energy level diagram for two-level system.

The Hamiltonian of the system is assumed to consist of the unperturbed term $\mathcal{H}_0$ and an interaction term $\mathcal{H}'$, such that

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad , \qquad (3.13)$$

where the matrix elements of the two are given by

$$\langle 1|\mathcal{H}_0|1\rangle = E_1$$

$$\langle 2|\mathcal{H}_0|2\rangle = E_2 \qquad (3.14)$$

$$\langle 1|\mathcal{H}_0|2\rangle = \langle 2|\mathcal{H}_0|1\rangle = 0$$

and

$$\langle 1 | \mathcal{H}' | 2 \rangle = -\mu E$$
$$\langle 2 | \mathcal{H}' | 1 \rangle = -\mu E$$
$$\langle 1 | \mathcal{H}' | 1 \rangle = \langle 2 | \mathcal{H}' | 2 \rangle = 0 \quad , \tag{3.15}$$

where E is the total electric field present. The above matrix elements are taken in the energy representation in which $\mathcal{H}_0$ is diagonal and the phases of the unperturbed wave functions are taken so as to make the dipole matrix elements real. It is assumed that the type of interaction is induced electric dipole; hence we have the zero diagonal components of $\mathcal{H}'$. In order to make this apply to the magnetic case one would simply change E to H and restrict the rf magnetic field to lie in a plane normal to the dc field.

Equations of Motion

The equations of motion for the two-level system in the density matrix notation are

$$\dot{\rho}_{11} + \frac{(\rho_{11} - \rho_{11}^e)}{T_1} = \frac{1}{i\hbar} (\mathcal{H}'_{12} \rho_{21} - \mathcal{H}'_{21} \rho_{12}) \tag{3.16a}$$

$$\dot{\rho}_{22} + \frac{(\rho_{22} - \rho_{22}^e)}{T_1} = \frac{1}{i\hbar} (\mathcal{H}'_{21} \rho_{12} - \mathcal{H}'_{12} \rho_{21}) \tag{3.16b}$$

$$\dot{\rho}_{12} + \frac{\rho_{12}}{T_2} - i\Omega\rho_{12} = \frac{1}{i\hbar} (\rho_{22} - \rho_{11}) \mathcal{H}'_{12} \tag{3.16c}$$

$$\dot{\rho}_{21} + \frac{\rho_{21}}{T_2} + i\Omega\rho_{21} = \frac{1}{i\hbar} (\rho_{11} - \rho_{22}) \mathcal{H}'_{21} \quad , \tag{3.16d}$$

where T_1 is the longitudinal relaxation time, T_2 is the transverse relaxation time, and ρ_{11}^e and ρ_{22}^e are the values of the diagonal elements

of the density matrix in the absence of applied radiation fields.[1] In general, ρ_{11}^{e} and ρ_{22}^{e} will be given by the Boltzmann factor when the system is in thermal contact with a reservoir. If the system is at a temperature T, then we have

$$\rho_{22}^{e} = \rho_{11}^{e} \, e^{-\frac{\hbar\Omega}{kT}} \quad , \qquad (3.17)$$

where k is Boltzmann's constant.

Let us assume that there are present two electric fields: the first, $E_1 \cos \omega t$, is the applied fundamental field at the frequency ω and is assumed to be strong; the second, $E_3 \cos (3\omega t - \phi)$, is the third harmonic field which, for generality, may be arbitrary in origin but in the case ultimately considered, will be generated from the nonlinear properties of the molecular system. The total field E is then

$$E = E_1 \cos \omega t + E_3 \cos (3\omega t - \phi) \quad . \qquad (3.18)$$

The parameters β may be introduced in the following manner:

$$\beta_1 = \frac{\mu E_1}{2\hbar} \qquad (3.19a)$$

$$\beta_1^* = \frac{\mu E_1}{2\hbar} \qquad (3.19b)$$

$$\beta_3 = \frac{\mu E_3}{2\hbar} e^{-i\phi} \qquad (3.19c)$$

$$\beta_3^* = \frac{\mu E_3}{2\hbar} e^{i\phi} \quad , \qquad (3.19d)$$

---

[1] A brief explanation of the relaxation times T_1 and T_2 is given in Appendix A.

where now the strength of the interaction, μE , is measured in the units of angular frequency. The conjugate is left on β_1 (even though the quantity is real) in order to retain the symmetric form of the resulting equations. The interaction Hamiltonian is then

$$\mathcal{H}'_{12} = \mathcal{H}'_{21} = -\hbar\left(\beta_1 e^{i\omega t} + \beta_1^* e^{-i\omega t} + \beta_3 e^{i3\omega t} + \beta_3^* e^{-i3\omega t}\right) . \qquad (3.20)$$

Substituting (3.20) into (3.16) gives

$$\dot{\rho}_{11} + \frac{\rho_{11} - \rho_{11}^e}{T_1} = i(\rho_{21} - \rho_{12})(\beta_1 e^{i\omega t} + \beta_1^* e^{-i\omega t} + \beta_3 e^{i3\omega t} + \beta_3^* e^{-i3\omega t}) \qquad (3.21a)$$

$$\dot{\rho}_{22} + \frac{\rho_{22} - \rho_{22}^e}{T_1} = i(\rho_{12} - \rho_{21})(\beta_1 e^{i\omega t} + \beta_1^* e^{-i\omega t} + \beta_3 e^{i3\omega t} + \beta_3^* e^{-i3\omega t}) \qquad (3.21b)$$

$$\dot{\rho}_{12} + \frac{\rho_{12}}{T_2} - i\Omega\rho_{12} = i(\rho_{22} - \rho_{11})(\beta_1 e^{i\omega t} + \beta_1^* e^{-i\omega t} + \beta_3 e^{i3\omega t} + \beta_3^* e^{-i3\omega t}) \qquad (3.21c)$$

$$\dot{\rho}_{21} + \frac{\rho_{21}}{T_2} + i\Omega\rho_{21} = i(\rho_{11} - \rho_{22})(\beta_1 e^{i\omega t} + \beta_1^* e^{-i\omega t} + \beta_3 e^{i3\omega t} + \beta_3^* e^{-i3\omega t}) . \qquad (3.21d)$$

We now look for a steady state solution to the above set of equations. The usual procedure in solving these equations for the interaction of radiation with matter is to assume the diagonal components to be constants and the off-diagonal components to vary as $e^{\pm i\omega t}$. Such an assumption leads to the usual linear or single quantum interactions. In order to include the effect of higher order interactions involving more than a

single quantum, a more general solution is required. Thus, we assume the following:

$$\rho_{11} = \lambda_{11}^{0} + \lambda_{11}^{(2)} e^{i2\omega t} + \lambda_{11}^{(-2)} e^{-i2\omega t} + \lambda_{11}^{(4)} e^{i4\omega t} + \lambda_{11}^{(-4)} e^{-i4\omega t} \tag{3.22a}$$

$$\rho_{22} = \lambda_{22}^{0} + \lambda_{22}^{(2)} e^{i2\omega t} + \lambda_{22}^{(-2)} e^{-i2\omega t} + \lambda_{22}^{(4)} e^{i4\omega t} + \lambda_{22}^{(-4)} e^{-i4\omega t} \tag{3.22b}$$

$$\rho_{12} = \lambda_{12}^{(1)} e^{i\omega t} + \lambda_{12}^{(-1)} e^{-i\omega t} + \lambda_{12}^{(3)} e^{i3\omega t} + \lambda_{12}^{(-3)} e^{-i3\omega t} \tag{3.22c}$$

$$\rho_{21} = \lambda_{21}^{(1)} e^{i\omega t} + \lambda_{21}^{(-1)} e^{-i\omega t} + \lambda_{21}^{(3)} e^{i3\omega t} + \lambda_{21}^{(-3)} e^{-i3\omega t}, \tag{3.22d}$$

where the diagonal components contain only even harmonics and the off-diagonal components contain only odd harmonics. The superscripts denote the corresponding frequency dependence and the λ are complex constants. Terms up to third order are kept in ρ_{12} and ρ_{21} since these will be seen to give rise to the third harmonic generation (fifth order terms would give rise to fifth harmonics, etc., but only third harmonic generation is here considered). Although terms to second order in the diagonal components would be sufficient to show third harmonic generation, there is a frequency detuning effect, to be discussed later, whose correct magnitude requires the inclusion of the fourth order terms in ρ_{11} and ρ_{22}. It can be shown that even order terms in the off-diagonal components and odd order terms in the diagonal components are related and vanish identically.[1]

---

[1] All the coefficients of these terms could be linearly related to the average or dc component of the off-diagonal components λ_{12}^{e} and λ_{21}^{e}. From the random phase argument of statistical mechanics (see Appendix A for references) the off-diagonal components of ρ are identically zero in equilibrium; hence $\lambda_{12}^{e} = \lambda_{21}^{e} = 0$.

From the basic relations governing the density matrix for a two-level system,

$$\rho_{11} + \rho_{22} = 1 \quad ,$$

and (3.23)

$$\rho_{12} = \rho_{21}^{*} \quad ,$$

the following relationships between the constants λ may be derived:

$$\lambda_{11}^{0} + \lambda_{22}^{0} = 1 \tag{3.24a}$$

$$\lambda_{11}^{(\pm 2)} + \lambda_{22}^{(\pm 2)} = 0 \tag{3.24b}$$

$$\lambda_{11}^{(\pm 4)} + \lambda_{22}^{(\pm 4)} = 0 \tag{3.24c}$$

$$\lambda_{12}^{(\pm 1)} = \lambda_{21}^{(\mp 1)*} \tag{3.24d}$$

$$\lambda_{12}^{(\pm 3)} = \lambda_{21}^{(\mp 3)*} \quad . \tag{3.24e}$$

After substituting the assumed solutions (3.22) into the equations (3.21), using (3.24b) and (3.24c) and employing harmonic balance, the following algebraic equations are found for the diagonal components:

$$\frac{\lambda_{11}^{0} - \lambda_{11}^{e}}{i\, T_1} = (\lambda_{21}^{(1)} - \lambda_{12}^{(1)})\, \beta_1^{*} + (\lambda_{21}^{(-1)} - \lambda_{12}^{(-1)})\, \beta_1 + (\lambda_{21}^{(3)} - \lambda_{12}^{(3)})\, \beta_3^{*} + (\lambda_{21}^{(-3)} - \lambda_{12}^{(-3)})\, \beta_3 \tag{3.25a}$$

$$(2\omega - \frac{i}{T_1})\, \lambda_{11}^{(2)} = (\lambda_{21}^{(1)} - \lambda_{12}^{(1)})\beta_1 + (\lambda_{21}^{(-1)} - \lambda_{12}^{(-1)})\, \beta_3 + (\lambda_{21}^{(3)} - \lambda_{12}^{(3)})\, \beta_1^{*} \tag{3.25b}$$

and

$$(2\omega + \frac{i}{T_1})\, \lambda_{11}^{(-2)} = -\,(\lambda_{21}^{(1)} - \lambda_{12}^{(1)})\beta_3^* - (\lambda_{21}^{(-1)} - \lambda_{12}^{(-1)})\beta_1^* \tag{3.25c}$$

$$- (\lambda_{21}^{(-3)} - \lambda_{12}^{(-3)})\beta_1$$

$$(4\omega - \frac{i}{T_1})\, \lambda_{11}^{(4)} = (\lambda_{21}^{(1)} - \lambda_{12}^{(1)})\, \beta_3 + (\lambda_{21}^{(3)} - \lambda_{12}^{(3)})\beta_1 \tag{3.25d}$$

$$(4\omega + \frac{i}{T_1})\, \lambda_{11}^{(-4)} = -\,(\lambda_{21}^{(-1)} - \lambda_{12}^{(-1)})\beta_3^* - (\lambda_{21}^{(-3)} - \lambda_{12}^{(-3)})\beta_1^* \quad , \tag{3.25e}$$

and the off-diagonal components:

$$[(\Omega - \omega) + \frac{i}{T_2}]\, \lambda_{12}^{(1)} = \Delta\, \beta_1 + 2\lambda_{11}^{(2)}\, \beta_1^* + 2\lambda_{11}^{(4)}\, \beta_3^* + 2\lambda_{11}^{(-2)}\, \beta_3 \tag{3.25f}$$

$$[(\Omega + \omega) - \frac{i}{T_2}]\, \lambda_{21}^{(1)} = \Delta\, \beta_1 + 2\lambda_{11}^{(-2)}\, \beta_3 + 2\lambda_{11}^{(2)}\, \beta_1^* + 2\lambda_{11}^{4}\, \beta_3^* \tag{3.25g}$$

$$[(\Omega - 3\omega) + \frac{i}{T_2}]\, \lambda_{12}^{(3)} = \Delta\, \beta_3 + 2\lambda_{11}^{(2)}\, \beta_1 + 2\lambda_{11}^{(4)}\, \beta_1^* \tag{3.25h}$$

$$[(\Omega + 3\omega) - \frac{i}{T_2}]\, \lambda_{21}^{(3)} = \Delta\, \beta_3 + 2\lambda_{11}^{(2)}\, \beta_1 + 2\lambda_{11}^{4}\, \beta_1^* \quad , \tag{3.25i}$$

where

$$\Delta \equiv \lambda_{11}^{0} - \lambda_{22}^{0} \quad . \tag{3.26}$$

The quantity Δ represents the average difference between the diagonal components when the system is in equilibrium with the radiation fields.

The quantity Δ^e may be defined as the value when the system is in thermal equilibrium with its surroundings:

$$\Delta^e = \lambda_{11}^e - \lambda_{22}^e \quad . \tag{3.27}$$

When multiplied by the total number of particles, N, the quantity $N\Delta$ represents the average population difference $n_1 - n_2$ where n_1 and n_2 are the number of particles in the lower and upper states, respectively.

By using Eq. (3.25b) through (3.25e), the diagonal components may be eliminated from (3.25f) through (3.25i) to yield a set of equations involving only the off-diagonal terms. In order to simplify the algebra somewhat, it shall be assumed that

$$\omega \gg \frac{1}{T_2}, \frac{1}{T_1} \quad , \tag{3.28}$$

which physically is equivalent to saying that the linewidth of the transition is much less than the frequency of operation. For a gas, this implies that the operating pressure is not too high. Upon using (3.28) in the diagonal equations and assuming $\beta_3 \ll \beta_1$, the off-diagonal equations become:

$$\left[\Omega - \omega + \frac{\beta_1\beta_1^*}{\omega} + \frac{i}{T_2}\right]\lambda_{12}^{(1)} = \Delta\beta_1 + \frac{\beta_1\beta_1^*}{\omega}\lambda_{21}^{(1)} + \frac{\beta_1^*\beta_1^*}{\omega}(\lambda_{21}^{(3)} - \lambda_{12}^{(3)}) \tag{3.29a}$$

$$\left[\Omega + \omega - \frac{\beta_1\beta_1^*}{\omega} - \frac{i}{T_2}\right]\lambda_{21}^{(1)} = \Delta\beta_1 - \frac{\beta_1\beta_1^*}{\omega}\lambda_{12}^{(1)} + \frac{\beta_1^*\beta_1^*}{\omega}(\lambda_{21}^{(3)} - \lambda_{12}^{(3)}) \tag{3.29b}$$

$$\left[\Omega - 3\omega + \frac{3}{2\omega}\beta_1\beta_1^* + \frac{i}{T_2}\right]\lambda_{12}^{(3)} = \Delta\beta_3 + \frac{\beta_1\beta_1}{\omega}(\lambda_{21}^{(1)} - \lambda_{12}^{(1)}) \tag{3.29c}$$

$$\left[\Omega + 3\omega - \frac{3}{2\omega}\beta_1\beta_1^* - \frac{i}{T_2}\right]\lambda_{21}^{(3)} = \Delta\beta_3 + \frac{\beta_1\beta_1}{\omega}(\lambda_{21}^{(1)} - \lambda_{12}^{(1)}) \quad . \tag{3.29d}$$

It will be shown later that the harmonic polarization is directly proportional to $\lambda_{12}^{(3)}$ and $\lambda_{21}^{(3)}$. Since we are interested in those conditions giving rise to a large third harmonic polarization we may examine Eqs. (3.29) for conditions consistent with this goal. The maximization of the λ's will be consistent with the minimization of the determinant of the coefficients in (3.29). From an examination of this determinant we see that there are two frequency regions where such a maximization may occur, namely $\omega \approx \Omega$ and $\omega \approx \Omega/3$.

These two situations correspond to the fundamental frequency near the natural transition and to the case where the third harmonic is near the natural frequency. We shall consider these cases separately, thereby simplifying somewhat the mathematics.

D. SOLUTIONS TO THE QUANTUM MECHANICAL EQUATIONS

1. Solution for Case I: $\omega \approx \Omega/3$

Let us assume that the fundamental or pump frequency is approximately one-third of the natural transition frequency, $\omega \approx \Omega/3$, and that the fundamental fields, measured by β_1, are sufficiently strong to cause appreciable harmonic generation, yet not so strong that the assumption $\beta_1 < \omega$ is invalid. The upper limit on the fields imposed by the latter restriction is approximately

$$E \text{ (volts/cm)} < 3{,}500\ \nu(\text{kMc}) \qquad , \qquad (3.32)$$

for a system with a dipole moment equal to one debye (10^{-18} esu). Strictly speaking, the approximations involved in the solution will be valid to the order $(\beta_1/\Omega)^2$ which will be less than 0.1 if we satisfy the condition $(\beta_1/\omega) < 1$. This assumption is made in order to make the mathematics tractable.

By combining (3.29a) and (3.29b) and solving for $\lambda_{12}^{(1)}$ and $\lambda_{21}^{(1)}$

in terms of β_1 , $\lambda_{21}^{(3)}$ and $\lambda_{12}^{(3)}$, we have

$$\lambda_{12}^{(1)} = \frac{\left[\Omega + \omega - \frac{i}{T_2}\right]\left[\Delta\beta_1 + \frac{\beta_1^*\beta_1^*}{\omega}(\lambda_{21}^{(3)} - \lambda_{12}^{(3)})\right]}{\left[\Omega - \omega + \frac{\beta_1\beta_1^*}{\omega} + \frac{i}{T_2}\right]\left[\Omega + \omega - \frac{\beta_1\beta_1^*}{\omega} - \frac{i}{T_2}\right] + \left(\frac{\beta_1\beta_1^*}{\omega}\right)^2} \tag{3.33}$$

and

$$\lambda_{21}^{(1)} = \frac{\left[\Omega - \omega + \frac{i}{T_2}\right]\left[\Delta\beta_1 + \frac{\beta_1^*\beta_1^*}{\omega}(\lambda_{21}^{(3)} - \lambda_{12}^{(3)})\right]}{\left[\Omega - \omega + \frac{\beta_1\beta_1^*}{\omega} + \frac{i}{T_2}\right]\left[\Omega + \omega - \frac{\beta_1\beta_1^*}{\omega} - \frac{i}{T_2}\right] + \left(\frac{\beta_1\beta_1^*}{\omega}\right)^2} \quad . \tag{3.34}$$

It is to be noted that although $\lambda_{12}^{(1)}$ and $\lambda_{21}^{(1)}$ are nonvanishing to first order in β_1 , expressions (3.33) and (3.34) include terms up to fifth order in β_1 (the next nonvanishing term) and also retain the term $1/T_2$ compared to Ω , even though by assumption, $\Omega \gg 1/T_2$. It is necessary to retain these smaller quantities in order to evaluate expressions (3.25a) (which will be found to describe the phenomenon of saturation) as many of the first order terms cancel. For the evaluation of other quantities the higher order terms may be dropped. Simplifying (3.33) and (3.34) by dropping terms of the order of $1/T_2$ and keeping only first order terms in β_1 gives

$$\lambda_{12}^{(1)} = \frac{\Delta\beta_1}{\Omega - \omega} \tag{3.35}$$

$$\lambda_{21}^{(1)} = \frac{\Delta\beta_1}{\Omega + \omega} \quad , \tag{3.36}$$

and the derived quantity

$$\lambda_{21}^{(1)} - \lambda_{12}^{(1)} = \frac{-2\omega\,\Delta\,\beta_1}{\Omega^2 - \omega^2} \quad . \tag{3.37}$$

The third harmonic components of λ_{12} and λ_{21} may be found by substituting (3.37) into (3.29c) and (3.29d). These are

$$\lambda_{12}^{(3)} = \Delta \frac{\beta_3 - \dfrac{2\,\beta_1^3}{\Omega^2 - \omega^2}}{\Omega - 3\omega \dfrac{3\,\beta_1\beta_1^*}{2\omega} + \dfrac{i}{T_2}} \tag{3.38}$$

$$\lambda_{21}^{(3)} = \Delta \frac{\beta_3 - \dfrac{2\,\beta_1^3}{\Omega^2 - \omega^2}}{\Omega + 3\omega - \dfrac{3\,\beta_1\beta_1^*}{2\omega} - \dfrac{i}{T_2}} \quad . \tag{3.39}$$

We are interested in the case where $\omega \approx \Omega/3$. Examination of (3.38) and (3.39) shows that $\lambda_{12}^{(3)}$ will be larger than $\lambda_{21}^{(3)}$ by a factor of the order $(\Omega + 3\omega)/(\Omega - 3\omega)$, which for these conditions will be very large. We thus drop $\lambda_{21}^{(3)}$ in comparison to $\lambda_{12}^{(3)}$.

The condition for maximization of $\lambda_{12}^{(3)}$ will correspond approximately to the vanishing of the real part of the resonant denominator of (3.29) or

$$\Omega - 3\omega + \frac{3\,\beta_1\beta_1^*}{2\omega} = 0 \quad . \tag{3.40}$$

By solving for the frequency ω we obtain

$$\omega = \frac{\Omega}{3}\left(1 + \frac{9}{2\Omega^2}\,\beta_1\beta_1^*\right) \quad , \tag{3.41}$$

or after defining an effective natural frequency Ω' by

$$\Omega' = \Omega\left(1 + \frac{9\,\beta_1\beta_1^*}{2\Omega^2}\right) \quad , \qquad (3.42)$$

we have the condition for optimum interaction

$$\omega = \Omega'/3 \quad . \qquad (3.43)$$

The new frequency Ω' is the effective natural frequency under the conditions of a strong applied field at a frequency near $\Omega/3$. In terms of the quantity Ω' the components of the density matrix at 3ω are

$$\lambda_{12}^{(3)} = \Delta \frac{\beta_3 - \dfrac{2\,\beta_1^3}{\Omega^2 - \omega^2}}{\Omega' - 3\omega + \dfrac{i}{T_2}} \qquad (3.44a)$$

and

$$\lambda_{21}^{(3)} \approx 0 \quad . \qquad (3.44b)$$

From expressions (3.33), (3.34), (3.44) and the defining relations (3.24d) and (3.24e), the off-diagonal components of the density matrix are known. Next we must evaluate expression (3.25a) which, as will be seen, describes the phenomenon of saturation. Substituting (3.33), (3.34) and (3.44) into (3.25a) gives

$$\frac{\lambda_{11}^0 - \lambda_{11}^e}{i\,T_1} = i\,\Delta \left\{ \frac{4\beta_1\beta_1^*}{T_2(\Omega^2 - \omega^2)} + \frac{8T_2(\beta_1\beta_1^*)^3}{(\Omega^2 - \omega^2)^2[1 + T_2^2\,(\Omega' - 3\omega)^2]} \right.$$

$$\left. + \frac{2\,\beta_3\beta_3^*\,T_2}{1 + T_2^2(\Omega' - 3\omega)^2} - \frac{4T_2\,(\beta_1^3\beta_3^* + \beta_1^{*3}\beta_3)}{(\Omega^2 - \omega^2)[1 + T_2^2\,(\Omega' - 3\omega)^2]} \right\} . \qquad (3.45)$$

If we consider the limiting case where the harmonic fields generated are small, $\beta_3 \ll \beta_1^3 (\Omega^2 - \omega^2)^{-1}$, this expression becomes

$$\frac{\lambda_{11}^0 - \lambda_{11}^e}{i\, T_1} = i\, \Delta \left\{ \frac{4\beta_1\beta_1^*}{T_2(\Omega^2 - \omega^2)} + \frac{8T_2\, (\beta_1\beta_1^*)^3}{(\Omega^2 - \omega^2)^2 [1 + T_2^2\, (\Omega' - 3\omega)^2]} \right. \quad . \quad (3.46)$$

Now by using the fact that $\lambda_{11}^0 + \lambda_{22}^0 = 1$ and $\lambda_{11}^e + \lambda_{22}^e = 1$, we may show that

$$\lambda_{11}^0 - \lambda_{11}^e = \frac{1}{2} (\Delta - \Delta^e) \quad , \quad (3.47)$$

where

$$\Delta^e = \lambda_{11}^e - \lambda_{22}^e \quad , \quad (3.48)$$

with λ_{11}^e and λ_{22}^e being the thermal equilibrium values. Substituting (3.47) into (3.45) and solving for Δ yields

$$\Delta = \Delta^e \left\{ 1 + 2T_1 \left[\frac{4\, \beta_1\beta_1^*}{T_2(\Omega^2 - \omega^2)} + \frac{8\, T_2\, (\beta_1\beta_1^*)^3}{(\Omega^2 - \omega^2)^2\, [1 + T_2^2\, (\Omega' - 3\omega)^2]} \right. \right.$$

$$\left. \left. + \frac{2\, T_2\, \beta_3\beta_3^*}{1 + T_2^2\, (\Omega' - 3\omega)^2} - \frac{4\, T_2\, (\beta_1^3\, \beta_3^* + \beta_1^{*3}\beta_3}{(\Omega^2 - \omega^2)\, [1 + T_2^2\, (\Omega' - 3\omega)^2]} \right] \right\}^{-1} \quad . \quad (3.49)$$

Upon using the same assumptions leading to (3.46) we have

$$\Delta = \Delta^e \left\{ 1 + 2T_1 \left[\frac{4\, \beta_1\beta_1^*}{T_2(\Omega^2 - \omega^2)} + \frac{8\, T_2\, (\beta_1\beta_1^*)^3}{(\Omega^2 - \omega^2)^2\, [1 + T_2^2(\Omega' - 3\omega)^2]} \right] \right\}^{-1} \quad . \quad (3.50)$$

With the knowledge of Δ given by (3.49) or (3.50) and the off-diagonal elements (3.33), (3.34) and (3.44) we have sufficient knowledge of the quantum system to calculate its response to the fundamental fields and the extent to which it will generate the desired third harmonic fields, for the case $\omega \approx \Omega/3$.

2. Solution for Case II: $\omega \approx \Omega$

The second case of interest is one in which the frequency of the fundamental radiation is near the natural transition frequency, $\omega \approx \Omega$. Here the third harmonic fields will occur at approximately three times the natural frequency in contrast to the case previously considered where the output was near the natural resonant frequency. To find the response of the system under these conditions we shall solve Eqs. (3.29a) through (3.29d) under the new assumption that $\omega \approx \Omega$ along with those previously used, $\beta_1 \gg \beta_3$ and $\omega \gg 1/T_2$.

First of all consider Eqs. (3.29a) and (3.29b) for the fundamental components of λ_{12} and λ_{21} . Since we have chosen $\omega \approx \Omega$ it is clear that $\lambda_{12}^{(1)}$ will be much greater than $\lambda_{21}^{(1)}$ and hence we may neglect the latter quantity. Considering the solution to (3.29a) to first order only (neglecting the much smaller fifth order term) gives

$$\lambda_{12}^{(1)} = \frac{\Delta \beta_1}{\Omega - \omega + \frac{\beta_1 \beta_1^*}{\omega} + \frac{i}{T_2}} \quad . \tag{3.51}$$

By setting the real part of the denominator of (3.51) equal to zero and defining the solution to the resulting equation Ω'' one obtains

$$\lambda_{12}^{(1)} = \frac{\Delta \beta_1}{\Omega'' - \omega + \frac{i}{T_2}} \quad , \tag{3.52}$$

where

$$\Omega'' = \Omega\left(1 + \frac{\beta_1 \beta_1^*}{\Omega^2}\right) \quad . \tag{3.53}$$

The quantity Ω'' is the effective natural frequency of the system under the influence of the radiation fields applied near the natural frequency of the system.

Upon using expression (3.52) for $\lambda_{12}^{(1)}$, and $\lambda_{21}^{(1)} \approx 0$ in (3.29c) and (3.29d) we obtain

$$\lambda_{12}^{(3)} = -\Delta \frac{\beta_3 - \dfrac{\beta_1^3}{\Omega\left(\Omega'' - \omega + \dfrac{i}{T_2}\right)}}{2\,\Omega - \dfrac{i}{T_2}} \tag{3.54}$$

$$\lambda_{21}^{(3)} = \Delta \frac{\beta_3 - \dfrac{\beta_1^3}{\Omega\left(\Omega'' - \omega + \dfrac{i}{T_2}\right)}}{4\,\Omega - \dfrac{i}{T_2}} \quad , \tag{3.55}$$

where in all nonresonant terms we have set $\omega = \Omega$ and dropped terms of the order of β^2 compared to those of the order of Ω^2. Substituting (3.52), (3.54) and (3.55) into (3.25a) gives

$$\frac{\lambda_{11}^{0} - \lambda_{11}^{e}}{i\,T_1} = \frac{2\,i\,T_2\,\Delta\,\beta_1\beta_1^*}{1 + T_2^2(\Omega'' - \omega)^2} + \frac{3\,\Delta\,\beta_3\beta_1^{*3}}{4\,\Omega^2(\Omega'' - \omega - \frac{i}{T_2})} - \frac{3\,\Delta\,\beta_3^*\beta_1^3}{4\,\Omega^2(\Omega'' - \omega + \frac{i}{T_2}} \tag{3.56}$$

The first term on the right hand side will predominate, the last two being of the order of $(\beta_1/\Omega)^4$ smaller than the first. Using (3.47)

and keeping only the first term above gives

$$\Delta = \frac{\Delta^e}{1 + \dfrac{4\, T_1 T_2\, \beta_1 \beta_1^*}{1 + T_2^2(\Omega' - \omega)^2}} \quad , \qquad (3.57)$$

where Δ^e is defined by (3.48). With expressions (3.52), (3.54), (3.55) and (3.57) we have the density matrix for the case of pumping near the natural frequency.

With the knowledge of the density matrix in the two cases of interest we are now in a position to determine the reaction of the quantum system on its surroundings, namely a resonant cavity.

E. MACROSCOPIC POLARIZATION AND CAVITY REACTION

We turn now to the question of the dynamics of the electromagnetic (E-M) field and in particular to the reaction of the quantum system on it. From classical electricity and magnetism we know that the electromagnetic fields may be derived from Φ , and $\underset{\sim}{A}$, the scalar and vector potentials, or if the charge density is zero a gauge may be chosen where $\Phi = 0$ and both $\underset{\sim}{E}$ and $\underset{\sim}{H}$ may be determined from the relations

$$\underset{\sim}{E} = -\frac{1}{c}\frac{\partial}{\partial t}\underset{\sim}{A} \qquad \underset{\sim}{H} = \text{curl}\, \underset{\sim}{A} \quad . \qquad (3.58)$$

The vector potential $\underset{\sim}{A}$ is determined from the relation

$$\nabla^2 \underset{\sim}{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\underset{\sim}{A} = -\frac{4\pi}{c}\underset{\sim}{J} \quad , \qquad (3.59)$$

where $\underset{\sim}{J}$ is the total current density and is composed of several types of currents as follows:[1]

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[1] See Ref. 58, p. 117.

(a) **True currents:** identical with transportation of true charges.

(b) **Polarization currents:** currents that arise from the change of polarization with time.

(c) **Magnetization currents:** stationary currents that flow within regions which are inaccessible to observation but which might give rise to net boundary or volume currents, due to imperfect orbit cancellation on an atomic scale.

(d) Convective currents: currents due to the motion of a medium as a whole.

1. Macroscopic Polarization

Our interest will be in polarization currents, (b), since we are considering electric dipole effects in bound states of atoms and molecules, not free electrons, and bulk motions clearly will not be of interest. The polarization current which acts as a source for the E-M fields is given by

$$\underset{\sim}{J} = \frac{\partial}{\partial t} \underset{\sim}{P} \quad , \qquad (3.60)$$

where $\underset{\sim}{P}$ is the polarization or the macroscopic dipole moment per unit volume.

The macroscopic polarization, $\underset{\sim}{P}$, will be equal to the expectation value of the polarization for a single atom times the number of systems per unit volume, N :

$$\underset{\sim}{P} = N \bar{\bar{\underset{\sim}{p}}} = N \langle \underset{\sim}{\mu} \rangle \quad . \qquad (3.61)$$

The expectation value of a single dipole system $\langle \underset{\sim}{\mu} \rangle$ may be calculated from the density matrix ρ by the relation[1]

$$\langle \underset{\sim}{\mu} \rangle = \mathrm{Tr}\,(\rho \underset{\sim}{\mu}) \quad , \qquad (3.62)$$

where ρ and $\underset{\sim}{\mu}$ are the matrices of the density matrix and dipole moment

[1] See Appendix A for the derivation of this relation.

operators, respectively. The vector notation is to be interpreted as

$$\langle \mu_x \rangle = \mathrm{Tr}\ (\rho\ \mu_x) \qquad , \qquad (3.63)$$

with similar relations for μ_y and μ_z . In the representation used, the matrices are

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} , \quad \mu = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{21} & 0 \end{pmatrix} \qquad , \qquad (3.64)$$

and the trace of their product is

$$\mathrm{Tr}(\rho\mu) = \rho_{12}\ \mu_{21} + \rho_{21}\ \mu_{12} \qquad . \qquad (3.65)$$

By the previous choice of the phases of the wave functions we have $\mu_{12} = \mu_{21} = \mu$; hence (3.65) reduces to

$$\mu = \mu(\rho_{12} + \rho_{21}) \qquad , \qquad (3.66)$$

where now we assume that the direction of the quantity μ is that of the fundamental field E . Returning to the definitions of ρ_{12} and ρ_{21} in terms of the λ's and substituting into (3.61) gives

$$P = N\mu[(\lambda_{12}^{(1)} + \lambda_{21}^{(1)})\ e^{i\omega t} + (\lambda_{12}^{(-1)} + \lambda_{21}^{(-1)})\ e^{-i\omega t}$$

$$+ (\lambda_{12}^{(3)} + \lambda_{21}^{(3)})\ e^{i3\omega t} + (\lambda_{12}^{(-3)} + \lambda_{21}^{(-3)})\ e^{-i3\omega t}] \quad . \ (3.67)$$

By using the following definitions

$$P_1^{(+)} = N\mu(\lambda_{12}^{(1)} + \lambda_{21}^{(1)}) \tag{3.68a}$$

$$P_1^{(-)} = N\mu(\lambda_{12}^{(-1)} + \lambda_{21}^{(-1)}) \tag{3.68b}$$

$$P_3^{(+)} = N\mu(\lambda_{12}^{(3)} + \lambda_{21}^{(3)}) \tag{3.68c}$$

$$P_3^{(-)} = N\mu(\lambda_{12}^{(-3)} + \lambda_{21}^{(-3)}) \quad , \tag{3.68d}$$

the polarization becomes

$$P = P_1^{(+)} e^{i\omega t} + P_1^{(-)} e^{-i\omega t} + P_3^{(+)} e^{i3\omega t} + P_3^{(-)} e^{-3\omega t} \quad , \tag{3.69}$$

displaying components at both the fundamental and the third harmonic. The magnitudes of these components are related to the quantum mechanical properties by Eqs. (3.68).

2. Cavity Reaction

To be specific, in the problem at hand, it will be assumed that the quantum system is placed inside a cavity which is resonant at both the fundamental and third harmonic frequencies. The resonance at the fundamental is provided in order to achieve the required field strengths at reasonable applied power levels. Provision of a resonance at the harmonic matches the impedance of the source to that of the outside world, increasing the power generated by the nonlinear action of the sample.

In order to calculate the power generated by the component of the polarization at 3ω we must first determine the fields it sets up in the cavity. This may be formally expressed by the relation

$$E = \frac{1}{\epsilon} P \quad , \tag{3.70}$$

where $\chi_c = \chi_c' - i\chi_c''$ and the quantities E and P vary as $e^{i\omega t}$. The quantity χ_c is called the cavity susceptibility and relates the field in the cavity to its source, in this case a time-varying polarization.

Let us assume that the polarization in the cavity is a vector function of the coordinates of the cavity, $\underset{\sim}{P}(\underset{\sim}{r})$, and let the orthonormal eigenfunctions of the cavity be $\underset{\sim}{u}_n(\underset{\sim}{r})$. To simplify things somewhat let us further assume that there is just one resonance near the frequency ω, denoted ω_0, and the loaded Q of the cavity is given by Q_0. By letting the field $\underset{\sim}{E}(\underset{\sim}{r})$ be given by

$$\underset{\sim}{E}(\underset{\sim}{r}) = \bar{E}\, \underset{\sim}{u}_0(\underset{\sim}{r}) \qquad , \qquad (3.71)$$

it can be shown that

$$\bar{E} = \frac{4\pi\omega^2 f_0 P V^{1/2}}{\omega_0^2 - \omega^2 + \dfrac{i\omega\omega_0}{Q_0}} \qquad , \qquad (3.72)$$

where

$$\int_{\text{cavity}} \underset{\sim}{P}(\underset{\sim}{r}) \cdot \underset{\sim}{u}_0(\underset{\sim}{r})\, dV = P\, f_0\, V^{1/2} \qquad . \qquad (3.73)$$

The quantity f_0 is a filling factor and V is the volume of the cavity. In this case from (3.70) and (3.72) we have

$$\frac{1}{\chi_c} = \frac{4\pi\omega^2 f_0 V^{1/2}}{\omega_0^2 - \omega^2 + \dfrac{i\omega\omega_0}{Q_0}} \qquad . \qquad (3.74)$$

It should be pointed out that in all previous expressions involving the fields E_1 and E_3, these are the fields at a particular point in space and are not to be confused with the normalized quantity $\bar{E}_0$.

3. Output Power

The power coupled out of a cavity where the fields are generated from within is given by the relation

$$P_{out} = \frac{\omega_0 W}{Q_e} \quad , \qquad (3.75)$$

where ω_0 is the angular frequency of the output radiation, W is the energy stored in the cavity, and Q_e is the external Q (which for optimum coupling equals the Q of the source). The energy stored in the cavity is

$$W = \frac{1}{8\pi} \overline{\int_{cavity} (E^2 + H^2)\, dv} \quad , \qquad (3.76)$$

where the bar signifies a time average and we assume $\epsilon = 1$, $\mu = 1$, the same as for free space. At resonance we have $\overline{E^2} = \overline{H^2}$, so (3.76) becomes

$$W = \frac{1}{4\pi} \int_{cavity} \overline{E^2}\, dV \quad . \qquad (3.77)$$

If we assume that the third harmonic field is written as the product of a function of time (giving the amplitude) and a function of space (the normal mode function)

$$\underset{\sim}{E}_3 = [\bar{E}_3\, e^{i(3\omega t - \phi)} + \bar{E}_3^*\, e^{-i(3\omega t - \phi)}]\, \underset{\sim}{u}_3(r) \quad , \qquad (3.78)$$

where ϕ is an arbitrary phase factor, then we have

$$W_3 = \frac{1}{2\pi} \bar{E}_3 \bar{E}_3^* \quad . \qquad (3.79)$$

Combining (3.75) and (3.79) gives

$$P_{out}(3\omega) = \frac{(3\omega)\bar{E}_3 \bar{E}_3^*}{2\pi Q_e} \quad . \qquad (3.80)$$

By using the results derived so far we shall now calculate the harmonic power out in the two cases considered.

F. OUTPUT POWER AND REACTION AT THE FUNDAMENTAL

1. Case I: $\omega \approx \Omega/3$

a. Output Power

We shall now evaluate the harmonic power for the case where the applied fields are at a frequency approximately one-third the natural transition frequency. In this case combining (3.68a) with (3.33) and (3.34) and (3.68c) with (3.44) and (3.45) gives, for the dipole moments,

$$P_1^{(+)} = \frac{2N\mu\,\Omega\left[\Delta\,\beta_1 + \frac{\beta_1^*\beta_1^*}{\omega}(\lambda_{21}^{(3)} - \lambda_{12}^{(3)})\right]}{\Omega^2 - \omega^2} \quad , \qquad (3.81)$$

and

$$P_3^{(+)} = N\mu\Delta\,\frac{\beta_3 - \frac{2\,\beta_1^3}{\Omega^2 - \omega^2}}{\Omega' - 3\omega + \frac{1}{T_2}} \quad . \quad . \qquad (3.82)$$

The component of the polarization at 3ω , $P_3^{(+)}$, is seen to consist of two terms; the first is proportional to β_3 (or to E_3) and the second is proportional to β_1^3 (or E_1^3) . They have somewhat different characteristics.

The first term, proportional to β_3 , is the polarization induced in response to the harmonic field E_3 . It is the linear, first order response of the system to fields at the frequency 3ω such as would occur were a signal at this frequency applied to a system with a natural frequency Ω' . As such, this component of $P_3^{(+)}$ will have the same spatial distribution as the normal mode fields in the cavity.

The second component of $P_3^{(+)}$, proportional to β_1^3 , is the polarization generated by the nonlinear action of the media; it is this component of the polarization which acts as the source of the third harmonic fields in the cavity. The spatial distribution of this component will be equal to the cube of the spatial distribution of the fundamental fields ($P_{3x} \propto E_{1x}^3$, etc.). Since this spatial distribution is not the same as that of the other component of $P_3^{(+)}$ one must allow for a different filling factor. Let us denote the filling factor for the first component by f_1 and that of the second by f_2 . Then combining (3.72) and (3.82) gives

$$\bar{E}_3\, e^{-i\theta} = \frac{-4\pi\, i\, Q_3\, N\mu\Delta}{\left[1 + \frac{i2Q_3}{\omega_3}(3\omega - \omega_3)\right]\left[\Omega' - 3\omega + \frac{i}{T_2}\right]}\left[f_1\beta_3 - \frac{2f_2\, V^{1/2}\, \beta_1^3}{\Omega^2 - \omega^2}\right], \tag{3.83}$$

where ω_3 is the cavity resonant frequency near 3ω and Q_3 is its loaded Q . Upon moving the first term on the right to the left, using the definition of β_3 (3.19c) and rearranging the denominator slightly, we have

$$\bar{E}_3 e^{-i\phi}\left\{1 + \frac{4\pi\, \mu^2\, Q_3\, N\Delta\, T_2\, f_1}{\hbar\left[1 + \frac{i2Q_3}{\omega_3}(3\omega - \omega_3)\right]\left[1 - iT_2(\Omega' - 3\omega)\right]}\right\} =$$

$$\frac{8\pi\mu\, Q_3\, N\Delta\, T_2 f_2\, \beta_1^3\, V^{1/2}}{\left[1 + \frac{i2Q_3}{\omega_3}(3\omega - \omega_3)\right]\left[1 - iT_2(\Omega' - 3\omega)\right]\left[\Omega^2 - \omega^2\right]} \tag{3.84}$$

ring a quality factor for the
as

. (3.85)

ar absorption coefficient,
available. In Appendix D,

, (3.86)

. (3.87)

$$\frac{\sqrt{3}}{\frac{\quad}{(\Omega' - 3\omega)]}}$$

$$\frac{\quad}{S\, f_1}, \qquad (3.88)$$

$$\frac{\quad}{1 - i\, T_2\, (\Omega' - 3\omega)]}$$

ects of saturation and is defined

. (3.89)

From Eq. (3.50) we find

$$S = \frac{1}{1 + 2T_1\left[\dfrac{4\,\beta_1\beta_1^*}{T_2(\Omega^2 - \omega^2)} + \dfrac{8(\beta_1\beta_1^*)^3\,T_2}{(\Omega^2 - \omega^2)^2\,[1 + T_2^2(\Omega' - 3\omega)^2]}\right]} \quad . \tag{3.90}$$

As explained in section D.1, where it was derived, this expression is an approximation in the limit that β_3 is less than the theoretical maximum value, which will be the case in any practical situation. A more exact expression may be derived from Eq. (3.49). In section G a more detailed discussion of saturation will be given.

By using (3.80) and (3.88) we find that the power coupled out at the harmonic is

$$P_{out}(3\omega) = \frac{(3\omega)\,\dfrac{4\,\hbar^2\,s^2\,f_2^2\,\beta_1^6\,V}{\mu^2\,Q_s^2[1 + T_2^2(\Omega' - 3\omega)^2]\,(\Omega^2 - \omega^2)^2}}{2\pi Q_e\left|\dfrac{1 + i\,\dfrac{2Q_3}{\omega_3}(3\omega - \omega_3)}{Q_3} + \dfrac{S\,f_1}{Q_s[1 - i\,T_2(\Omega' - 3\omega)]}\right|^2} \quad . \tag{3.91}$$

The above expressions, along with the subsidiary defining conditions (3.19a), (3.42), (3.85), (3.87), (3.90) give the value of the harmonic power coupled out of the cavity in terms of the operating conditions, $(\omega\,,\,E_1)$, the properties of the cavity $(Q_e\,,\,Q_3\,,\,V\,,\,f_1\,,\,f_2\,,\,\omega_3)$ and of the quantum system $(\Omega\,,\,\mu\,,\,T_1\,,\,T_2\,,\,\gamma)$. It then completely defines the generation of harmonic power due to the nonlinearities in the quantum system in terms of the familiar linear properities of the system. Let us simplify this expression and put it in a form which is more easily understandable from a physical point of view.

If we examine the denominator of (3.91), using the definition of loaded Q, $1/Q_3 = 1/Q_0 + 1/Q_e$, where Q_0 is the unperturbed cavity Q, we see that it is of the form

$$Q_e\left[\frac{1}{Q_0} + \frac{1}{Q_e} + \frac{1}{Q_{sample}}\right]^2 \quad , \qquad (3.92)$$

which is that of a cavity (Q_0) coupled to the external world (Q_e) with an additional loss mechanism Q_{sample}. The value of Q_{sample} describes in effect the "source impedance" of the sample at the frequency 3ω. The exact form of these quantities in (3.91) shows that they are reactive as well as resistive. That arises from the fact that both the cavity and the atom are resonant and will have a reactive component if the frequency 3ω does not coincide with their resonance. Let us assume that the cavity is tuned by varying its resonant frequency ω_3 such that the reactive or imaginary components in the denominator cancel. Then the denominator becomes

$$Q_e\left[\frac{1}{Q_0} + \frac{1}{Q_e} + \frac{S\, f_1}{Q_s[1 + T_2^2(\Omega' - 3\omega)^2]}\right]^2 \quad . \qquad (3.93)$$

Taking for the moment $S = 1$, i.e., no saturation, unity filling factor, $f_1 = 1$, and $3\omega = \Omega'$, the effective source impedance of the sample is described by $1/Q_s$. This quantity is equivalent to the familiar "magnetic Q," of the standard maser terminology and may be defined in the usual manner as

$$\frac{1}{Q_{sample}} = \frac{(\text{power lost in sample})}{2\pi\ (\text{frequency})\ (\text{energy stored in cavity})}$$

$$= \frac{P_{lost}}{\omega_0 W} \quad . \qquad (3.94)$$

If the system's population distribution corresponds to positive temperatures (more in lower level than in upper), then $(\lambda_{11}^0 - \lambda_{22}^0) > 0$ implies $\Delta > 0$

implies $Q_s > 0$ and hence a net loss or attenuation of the signal at 3ω ; whereas if populations are inverted, Q_s is negative and the system acts as a negative resistance. The possibility then exists for oscillations to occur if $1/Q_s$ becomes sufficiently negative to cancel the losses, i.e.,

$$-\frac{1}{Q_s} = \frac{1}{Q_0} + \frac{1}{Q_e} \quad . \qquad (3.95)$$

This, of course, is the familiar condition for start oscillations in a maser oscillator.

Let us now combine the cavity Q and the sample Q into an effective source Q defined by

$$\frac{1}{Q_{source}} = \frac{1}{Q_0} + \frac{S\, f_1}{Q_s\,[1 + T_2^2(\Omega' - 3\omega)^2]} \quad . \qquad (3.96)$$

Expression (3.93) then becomes

$$Q_e \left[\frac{1}{Q_{source}} + \frac{1}{Q_e}\right]^2 \quad , \qquad (3.97)$$

which is maximized for $Q_e = Q_{source}$; under these conditions we have

$$\left\{\frac{1}{Q_e\left[\frac{1}{Q_{source}} + \frac{1}{Q_e}\right]^2}\right\}_{max} = \frac{Q_{source}}{4} \quad . \qquad (3.98)$$

Referring to (3.91) we see that the power out under matched conditions, $Q_{source} = Q_e$, is directly proportional to Q_{source} . If the sample Q is positive, indicating a normal population and hence loss, the source Q is reduced, lowering the power out. If the population is inverted, $Q_s < 0$, then the source Q will increase and the output power will increase proportionally. We thus see that the question of population

inversion is important in determining the magnitude of the emitted power through its effect on the source Q but is not required in order to achieve harmonic generation. From a qualitative point of view we see that the system behaves first as a nonlinear element, generating third harmonic fields, and second in a linear manner, either amplifying or attenuating the signal depending on whether it is in an inverted or normal population state. Clearly, the latter linear process, to be important, requires that an allowed transition be near the output frequency 3ω as demonstrated by the resonance denominator in the sample term. In the case herein considered where $3\omega \approx \Omega$ this is satisfied.

We shall not pursue the question of population inversion any further. It will be assumed that the system is in a normal population state, $Q_s > 0$, and that the external Q is matched to the source. Then using the definition of β_1, Eq. (3.91) for the power out becomes

$$P_{out}(3\omega) = \frac{(3\omega)\left(\frac{\mu}{\hbar}\right)^4 \left(\frac{S}{Q_s}\right)^2 f_2^2\, Q_{source}\, E_1^6\, V}{128\pi[1 + T_2^2(\Omega' - 3\omega)^2](\Omega^2 - \omega^2)^2} \quad . \qquad (3.99)$$

Finally, if we assume that conditions are satisfied such that $3\omega = \Omega'$, there is no saturation so $S = 1$; and that the unloaded Q of the cavity, Q_0, is much larger than the simple Q, Q_s, the expression for the power out simplifies to

$$P_{out}(3\omega) \cong \frac{\left(\frac{\mu}{\hbar}\right)^4 \frac{1}{Q_s} \frac{f_2^2}{f_1} E_1^6\, V}{128\pi\, \Omega^3} \quad . \qquad (3.100)$$

Before discussing in detail the expressions for output power we shall calculate the reaction of the sample to the fundamental fields and then perform the calculations for the case where $\omega \approx \Omega$, which will give similar results to the above.

b. Reaction at the Fundamental

The power supplied to the cavity at the fundamental may be dissipated via three main mechanisms. First, there is the cavity loss which is due to the finite conductivity of the walls and is represented by the unloaded quality factor of the cavity, Q_0 . Second, there may be a loss due to absorption of the fundamental by the atomic system when there is an atomic resonance nearby. For the case at hand, $\omega \approx \Omega/3$, this loss will be very small. Both of these loss mechanisms are first-order in nature, the power absorbed being proportional to the energy density E_1^2 . They may be lumped together in an effective first order Q , $Q^{(1)}$. The third source of loss is third-order in nature and is that power going via the nonlinearity into the third order process. This component of the power supplied by the fundamental generator goes into cavity losses, molecular absorption, and output power, all at a frequency 3ω . This form of loss, reflected by the nonlinearity, is familiar from the theory of parametric amplifiers.

To evaluate the effective Q of this coupling, we may proceed in a manner similar to that yielding the output power at 3ω . By using (3.72), (3.81) and allowing for an external source, we have

$$\frac{E_1}{2} = \frac{1}{X_c} \cdot \frac{2N\mu\Omega[\Delta\beta_1 + \frac{\beta_1^*\beta_1^*}{\omega}(\lambda_{21}^{(3)} - \lambda_{12}^{(3)})]}{\Omega^2 - \omega^2 + 2\beta_1\beta_1^*} + (\text{external source term}) \quad . \tag{3.101}$$

Upon substituting for $\lambda_{12}^{(3)}$ and $\lambda_{21}^{(3)}$, rearranging the expression, and dropping higher order terms, we obtain

$$E_1\left\{\frac{1}{Q^{(1)}} + \frac{4f\Omega s}{\omega Q_s}\left[\frac{\beta_1^4}{(\Omega^2 - \omega^2)^2} - \frac{\beta_1\beta_3}{2(\Omega^2 - \omega^2)}\right]\right\} = (\text{external source term}) \quad . \tag{3.102}$$

The effective Q of the third order losses, $Q^{(3)}$, is then seen to be

$$\frac{1}{Q^{(3)}} = \frac{4f\Omega s}{\omega Q_s}\left[\frac{\beta_1^4}{(\Omega^2 - \omega^2)^2} - \frac{\beta_1\beta_3}{2(\Omega^2 - \omega^2)}\right] \quad , \tag{3.103}$$

where f is the filling factor at the fundamental, Q_s is the sample Q, (3.85), and S is the saturation parameter. As expected, the magnitude of the reflected loss is dependent on the fundamental field strength (β_1) making the loss, E_1^2/Q, go as $(E_1)^6$. The maximum value of $1/Q^{(3)}$ will occur for $S = 1$, $f = 1$, and $\beta_3 \ll \beta_1^3/\Omega^2 - \omega^2$; it is

$$\left(\frac{1}{Q^{(3)}}\right)_{max} = \frac{12}{Q_s} \frac{\beta_1^4}{(\Omega^2 - \omega^2)^2} \quad . \qquad (3.104)$$

Since β_1 represents the strength of the perturbation $\mathcal{H}'$ and Ω is of the order of $\mathcal{H}_0$, the unperturbed Hamiltonian, we see that $1/Q^{(3)}$ is of the order $(\mathcal{H}^1/\mathcal{H}_0)^4$ times $1/Q_s$. For practical fields [see Eq. (3.32)] this factor will be small, demonstrating the necessity of either an extremely high cavity Q or a large value of $1/Q_s$ in order to obtain any sort of efficiency; otherwise most of the input power will be wasted in cavity losses. Such a consideration is seen to limit the usefulness of this as a traveling wave device where the field strengths will be quite low for reasonable power levels.

We shall now proceed to calculate the expected power in second case, where the fundamental fields are approximately resonant with the transition frequency $\omega \approx \Omega$.

2. <u>Case II: $\omega \approx \Omega$</u>

a. Output Power

Having gone through a similar calculation for the other case, we shall follow the same procedure, adding comments where there are differences.

From (3.68a) and (3.52) we have

$$P_1^{(+)} = \frac{N\mu \, \Delta \, \beta_1}{\Omega' - \omega + \frac{1}{T_2}} \quad , \qquad (3.105)$$

and from (3.68c), (3.54) and (3.55), we have

$$P_3^{(+)} = - N\mu\Delta \left[\frac{1}{4\Omega} + \frac{3i/T_2}{(4\Omega)^2}\right] \left[\beta_3 + \frac{i\, T_2\, \beta_1^3}{\Omega[1 - i\, T_2(\Omega'' - \omega)]}\right] . \quad (3.106)$$

By substituting this in the expression for the generation of cavity fields (3.72), assuming that $\Omega \gg 1/T_2$, and tuning the cavity so as to tune out the reactive component of M_3 , we have

$$E_3 e^{-i\phi} \left[\frac{1}{Q_3} + \frac{3\, f_1\, S}{Q_s(4\Omega T_2)^2}\right] = - \frac{S\, \hbar\, f_2\, \beta_1^3\, V^{\frac{1}{2}}}{4\mu\Omega^2\, Q_s[1 - i\, T_2(\Omega'' - \omega)]} \quad , (3.107)$$

where f_1 and f_2 are the filling factors, Q_s is defined in (3.85), Q_3 is the combination of unloaded cavity and external Q's , and S for this case may be derived from (3.57) and is

$$S = \frac{1}{1 + \dfrac{4\, T_1 T_2\, \beta_1 \beta_1^*}{1 + T_2^2(\Omega'' - \omega)^2}} \quad . \quad (3.108)$$

By using expression (3.80) for the power out, we obtain

$$P_{out}(3\omega) = \frac{3\Omega}{2\pi Q_e} \frac{\left(\dfrac{S}{Q_s}\right)^2 \left(\dfrac{\hbar}{\mu}\right)^2 \dfrac{f_2^2\, \beta_1^6\, V}{16\Omega^4[1 + T_2^2(\Omega'' - \omega)^2]}}{\left[\dfrac{1}{Q_3} + \dfrac{3\, f_1}{(4\Omega T_2)^2} \dfrac{S}{Q_s}\right]^2} \quad . \quad (3.109)$$

In this case, because of the factor $(1/4\Omega T_2)^2$, the contribution to the source Q from the sample will be very small and it may be neglected in comparison to the cavity Q , for reasonable values of the latter. Physically this is due to the fact that the output frequency

corresponds to three times the natural transition frequency and there will be negligible self-absorption, in contrast to the previous case where the output occurred near the natural transition and there was absorption. Optimizing the output by setting $Q_e = Q_0$, we have

$$P_{out}(3\omega) = \frac{(3\Omega)\left(\frac{\mu}{\hbar}\right)^4 \left(\frac{S}{Q_s}\right)^2 f_2^2\, Q_0\, E_1^6\, V}{\pi \cdot 2^{13}\, \Omega^4\, [1 + T_2^2(\Omega'' - \omega)^2]} \quad . \qquad (3.110)$$

Upon assuming $\Omega'' = \omega$, $S = 1$, we have the approximate expression

$$P_{out}(3\omega) = \frac{3\left(\frac{\mu}{\hbar}\right)^4 \left(\frac{1}{Q_s}\right)^2 f_2^2\, Q_0\, E_1^6\, V}{\pi \cdot 2^{13}\, \Omega^3} \quad . \qquad (3.111)$$

b. Reaction at the Fundamental

As before, there will be three main contributions to the loss at the fundamental: the cavity losses, the first order absorption, and the third order losses which are reflected by the nonlinearity. The cavity losses will be the same. For this case, however, the first order losses in the quantum system will be much larger than the third order losses, due to the proximity of the natural resonant frequency to the "pump" frequency. The value of the Q due to the first order losses in the quantum system is

$$\frac{1}{Q^{(1)}} = \frac{fS}{Q_s} \cdot \frac{1}{1 + T_2^2(\Omega'' - \omega)^2} \quad . \qquad (3.112)$$

As virtually all the third harmonic power is dissipated in the cavity and in the useful load, the third order Q will be such that it will give a loss equal to twice the output power;[1] its specific value will not interest us here.

[1] When the output is matched, $Q_e = Q_0$, the power dissipated in the cavity equals the output power and hence the total power dissipated at 3ω equals twice the output power.

Our interest in the values of the molecular Q's, both at the fundamental and at the harmonic, can be seen when one considers the problem of getting the most harmonic power out for a given input power level. The problem is different in the two cases.

For the first case considered, $\omega \approx \Omega/3$, the quantum system presents a large, first order loss at the harmonic, while at the fundamental there is only a much smaller third order loss. An increase in the cavity Q at 3ω is seen to be less valuable than a corresponding increase in the Q at ω since the effective maximum Q at 3ω is determined by the sample Q, Q_s. At the fundamental, however, the field in the cavity, E_1, will be determined primarily by the cavity Q, Q_0, as the third order losses of the quantum system will in general be less. In this limit, $E_1^6 \propto Q_0^3$, and the output power for a given input power will vary as the cube of the fundamental cavity Q.

On the other hand, when $\omega \approx \Omega$, the quantum system "loads" the fundamental, limiting the effective input Q to that presented by the sample; very little is gained by increasing the cavity Q beyond this value. Referring to Eq. (3.110) we see, however, that the output is proportional to the cavity Q at the third harmonic, and an increase in its value will bring a corresponding increase in the power out.

In other words, if we consider our system to be either "transparent" or "opaque," depending on whether it is nonabsorbing or absorbing, we find that if it is transparent at the fundamental, harmonic generation is enhanced by providing a high Q resonator at the fundamental, while if it is opaque at the fundamental, the best performance will occur for a high Q at the output. If the system were transparent at both frequencies, then improving the Q values at both fundamental and harmonic would result in improved operation.

It should be noted that in the case where $\omega \approx \Omega$ even though the system absorbs more power by virtue of its resonance near ω this power is first order in nature and does not help at all in contributing to the generation of harmonics. It is to be remembered that only the third order losses (at ω) contribute to the harmonic generation process. In fact, the first order losses may reduce the level of output power through the phenomenon of saturation to be discussed next.

G. SATURATION

In the preceding sections mention is made of the phenomenon of saturation. In the context of this problem it describes the tendency of the population density of the upper and lower levels to equalize under the influence of strong rf fields. A parameter S has been defined which describes this effect by relating the difference in population density under dynamic conditions, Δ, to the difference in population density under conditions of thermal equilibrium, Δ^e. When the population densities λ_{11}^0 and λ_{22}^0 have their equilibrium values, S takes its maximum value of unity. As the levels tend to equalize, Δ tends to zero and hence, S tends to zero.

In referring to the equations for the output power (3.99) and (3.110), we see that in both cases the power depends on the square of S. Thus, as the levels tend to equalize, and $S \to 0$, the power output falls below the nonsaturated value.

When a system tends to saturate, this implies that its internal energy has increased since the average energy of the system (due to this degree of freedom) is

$$E = \lambda_{11}^0 E_1 + \lambda_{22}^0 E_2$$

$$= \frac{E_1 + E_2}{2} - \frac{\hbar\Omega}{2}\Delta \qquad ,$$

where E_1 and E_2 are the energies of the two levels. This increase in the energy will occur as a result of the net absorption of radiation by the system.[1] In addition to its coupling to the radiation field the system is presumed to be in contact with a thermal bath, this mechanism tending to restore thermal equilibrium, with the system giving up energy to the bath at a rate given by the inverse of the quantity T_1.[2] When

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[1] It is implicitly assumed that we are considering a situation where the populations of the two levels are not inverted, corresponding to a positive temperature.

[2] The quantity T_1 is <u>defined</u> as the inverse of the rate at which the system thermalizes.

the net rate of energy input exceeds the rate at which the system can dispose of this energy (to lattice vibrations in a solid and kinetic energy or other degrees of freedom in a gas) then the system begins to saturate. We shall now investigate this effect in both cases considered and see how it limits the output power.

1. Saturation When $\omega \approx \Omega/3$

For this case the system may absorb power under two conditions. There will be a first order effect corresponding to the absorption of power at the fundamental in the tail of the absorption curve. For narrow lines one would expect this to be small since the applied frequency is approximately one-third of the natural or resonant frequency. The power absorbed in this case would be proportional to the incident fundamental power or E_1^2. The second term in the saturation is due to the absorption of the harmonic power by the system by virtue of the proximity of its resonance Ω' to the output frequency 3ω. This power will be proportional to E_3^2 or to E_1^6. We thus expect the saturation parameter to contain two terms, one proportional to E_1^2 (or β_1^2) and the other proportional to E_1^6 (or β_1^6). Referring to Eq. (3.90), we see this is so.

Let us now calculate the field strengths, β_1, at which the saturation takes the value $S = 1/2$. Assuming $3\omega = \Omega'$, the first order term would cause saturation when

$$\frac{8T_1 \beta_1^2}{T_2 \Omega} \approx 1$$

or

$$\beta_1^2 \approx \frac{T_2 \Omega^2}{8T_1} \quad , \qquad (3.113)$$

while the third order term would cause saturation for

$$\beta_1^6 \approx \frac{\Omega^4}{16\, T_1 T_2} \quad . \qquad (3.114)$$

For the assumption $T_1 \approx T_2$, valid for a gas at microwave frequencies, and the assumption $\Omega \gg 1/T_2$, the third-order term is seen to be the primary source of saturation.

At the onset of saturation the source Q , (3.96), tends to Q_0 and the expression (3.99) for power out varies as S^2 . For the predominant third order saturation, Eq. (3.99) tends asymptotically towards

$$P_{out}(3\omega) = \text{const.} \frac{E_1^6}{(1 + \text{const.}\ E_1^6)^2} \quad ,$$

which shows that the power out actually decreases in the limit of large E_1 .

2. <u>Saturation When $\omega \approx \Omega$</u>

In the second case, $\omega \approx \Omega$, the strong fundamental fields, near resonance and causing first order absorption, will dominate the saturation. From Eq. (3.108) the condition for saturation is

$$\beta_1^2 \approx \frac{1}{4\ T_1 T_2} \quad . \qquad (3.115)$$

In this case, under the conditions of saturation Eq. (3.110) becomes

$$P_{out}(3\omega) = \text{const.} \frac{E_1^6}{(1 + \text{const.}\ E_1^2)^2} \quad ,$$

which shows that even under these conditions the power out is proportional to the power in, and does not decrease as in the first case. In this limit the expression for the power out becomes

$$P_{out}(3\omega) = \frac{3\ Q_0\ f_2^2\ E_1^2\ V}{\pi \cdot 2^{13}\ Q_s^2\ \Omega^3\ T_1^2\ T_2^2} \quad . \qquad (3.116)$$

3. Comments on Saturation

By comparing the saturation levels for the two cases of interest, (3.114) and (3.115), we have

$$\frac{(\beta_1^6)_{\Omega/3}}{(\beta_1^6)_{\Omega}} = 4\Omega^4 T_1^2 T_2^2 \qquad . \qquad (3.117)$$

As ΩT_1 and ΩT_2 are usually much greater than unity, we see that the occurrence of saturation comes earlier in the case of pumping near resonance. In the above it has been implicitly assumed that $\omega = \Omega'$ or $\omega = \Omega''$. A further look at the exact expressions for saturation, (3.90) and (3.108), shows that by operation off resonance, Ω' , $\Omega'' \neq \omega$, the effects of saturation can be reduced. However, (3.99) and (3.110) show that corresponding to this reduction in saturation there is a reduction in the output power. In the operation of a device based on these principles the choice of ω relative to Ω'' or Ω' must be based on the various parameters of the problem, such as power available, the harmonic power desired and the properties of the circuit.

One comment which can be made, however, is that in all the expressions for saturation, (3.113), (3.114) and (3.115), a speeding-up of the relaxation process, i.e., a reduction in T_1 , will result in an increase in the value of β_1 at which saturation occurs; this will result in higher available output powers. Hence, in any material which is to be used for harmonic generation in this manner, we desire a short T_1 or spin-lattice relaxation time.

H. DISCUSSION

In the preceding sections of this chapter the mathematical theory of harmonic generation in a two-level system has been discussed. Two particular cases have been studied: the first, in which the frequency of the third harmonic output is near the natural resonant frequency; the second, where the applied fundamental frequency is near the natural transition. In both cases the quantum system behaves as a nonlinear element generating a component of the macroscopic polarization at a frequency three times that of the input. This time-varying polarization acts as a source for the

electromagnetic fields which may be calculated from Maxwell's equations. The magnitude of the polarization and the fields generated may be expressed entirely in terms of the known parameters of the quantum system and its surroundings; no phenomenological nonlinearity must be assumed. Thus it is seen that the nonlinearity is intrinsic to the quantum system and may be evaluated in terms of known quantities. Some of the aspects of the results obtained will now be discussed.

1. Resonant vs Nonresonant Behavior

Although only two particular cases have been considered, namely when the applied frequency is such that $\omega \approx \Omega/3$ or $\omega \approx \Omega$, it is more generally true that the existence of the nonlinearity is independent of the frequency ω. This may be seen from the fact that in the over-all interaction the total energy in the radiation field is constant (three fundamental photons being destroyed and one at three times the frequency being created) and hence the energy of the quantum system is conserved.[1] The fact that the system contains discrete natural frequencies (in this case only one) manifests itself in the theory by means of the resonant denominators, which in the two cases considered are $1 + T_2^2(\Omega' - 3\omega)^2$ and $1 + T_2^2(\Omega'' - \omega)^2$. A general theory would contain two such denominators, one for the fundamental and one for the harmonic, and would appear as the product of the two above. The two cases considered are thus only special cases of the more general result in which we have chosen the frequency to minimize one or the other of the resonant terms.

The important thing to note here is that the nonlinearity is intrinsic to the system and independent of the frequencies applied. The relation between the operating frequency and the natural transition frequency merely alters the magnitude of the effect through the resonance denominators. When the operating frequencies are all far from quantum transitions then the system looks similar to a nonlinear reactive element. When operating near a resonance, the system looks like a combination of nonlinear resistance

[1] If the quantum system's energy were increased or decreased, the change would have to correspond to the difference between its energy eigenvalues. Such a change would place restrictions on the radiation frequencies causing the transition, namely $\Sigma \pm \omega_i = (E_f - E_i)/\hbar$, where + indicates absorption, - indicates emission, and E_f and E_i are the final and initial energies of the system.

and reactance but of a larger magnitude due to the reduction of the resonance term. In the microwave region the maximum strenth of the nonlinearity will usually be small enough that resonant operation will be required. In general, the question of resonant vs nonresonant operation will depend on the particular aspects of the overall problem.

Another aspect of this problem is the question of saturation. Under resonant operation the system will absorb energy, thus causing saturation; for nonresonant operation the saturation is reduced along with the magnitude of the nonlinearity. The importance of saturation is again a function of the particular problem, being most severe for high power applications.

2. Dependence on the Parameters of the System

The dependence of the output power, Eqs. (3.99) and (3.109), on the various parameters of the system are summarized below:

(a) Dipole moment. The output power varies as μ^8, a factor of μ^4 coming from $1/Q_s^2$. From this it is clear that magnetic dipole transitions will give negligible effects compared to electric dipole transitions.[1]

(b) Linewidth and concentration. The concentration along with the linewidth enter through the factor Q_s or, alternatively, through the absorption coefficient γ. They occur as the product NT_2, which for a given transition is approximately constant. Thus increasing the concentration N, will leave Q_s constant while increasing the linewidth, and conversely.

The quantity T_2 also occurs in the resonance denominators as well as in the expressions for saturation (along with the longitudinal relaxation time T_1). Here a broader line (smaller T_2) will result in a broader frequency response as well as in a reduction in saturation.

(c) Population difference and the Boltzmann factor. In both cases the output power is proportional to the square of the population difference through its dependence on Q_s^{-2}. This squared dependence points out the important fact that the sign of Δ or, alternatively, normal vs inverted population, does not play a fundamental role in the nonlinear process. It

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[1] In the first case considered, when $S = 1$, $f_1 = 1$, and the cavity Q is large, the output varies as μ^6. This is a special case.

does, however, have a subsidiary effect through the first order loading of the cavity which is proportional to the first power of Δ . A normal population distribution, $\Delta > 0$, causes the system to present a positive loss to the cavity and lowers the Q ; an inverted population presents a negative loss and raises the Q .

There exists possibilities of using inverted populations to enhance the overall nonlinear effect but they will not be given here.

The magnitude of Δ may be found from Boltzmann statistics, which for no saturation is

$$\Delta = \Delta^e = \frac{\hbar\Omega}{2kT} \approx \frac{1}{40} \frac{\nu(\mathrm{kMc})}{T(^{\circ}\mathrm{K})} \quad . \qquad (3.118)$$

For room temperature and wavelengths around 1 cm, this is a factor of the order of 1/400 compared to a maximum value of unity. Operation at higher frequencies or lower temperatures will result in an increase in Δ , and hence an increase in the output power.

(d) Filling factor. The output varies as the square of the filling factor f_2 (3.73), which is to be compared to a linear dependence in first order processes. This places a strong importance on good circuit design by which f_2 may be increased. The other filling factor f_1 helps determine the source Q (for the first case), and should be minimized consistent with a maximization of f_2 . For a gas completely filling a structure, $f_1 = 1$.

3. Dynamic Shift of the Natural Resonant Frequency

One aspect of this problem which does not appear in usual formulations of the problem is the effective detuning of the natural frequency of the quantum system. In the two cases considered the new frequencies were denoted Ω' and Ω'' , and are given by (3.42) and (3.53). This detuning is of second order in the perturbation, $\mathcal{H}'$, and under the usual assumption of small perturbations is negligible. In the field of magnetic resonance this shift is known as the Bloch-Siegert shift. In terms of the dc

field H_0 and the rf field H_1, it is given by[1]

$$\Omega' = \Omega \left[1 + \left(\frac{\mu H_1}{4\hbar\Omega}\right)^2\right] = \Omega \left[1 + \frac{1}{16}\left(\frac{H_1}{H_0}\right)^2\right] \tag{3.119}$$

where Ω' is the effective frequency and Ω is the frequency corresponding to the unperturbed eigenstates. By using values of dc and rf fields typical to spectroscopy or maser applications this shift is of the order of one part in 10^7 or less. In our application with electric dipole transitions and strong fields the detuning may be an appreciable fraction of the natural frequency.

At first such a concept may seem strange, as the usual interpretation of the radiation problem is that of quantum jumps between the discrete energy levels of the system. Such a picture, however, rests on the assumption that the perturbation is small and is effective only in causing transitions between these unperturbed levels. When the perturbation is strong the only rigorous method of solution is to go back and solve the problem of a quantum system strongly coupled to the electromagnetic field. Under such a procedure it should not seem surprising that conditions of optimum interaction would differ from small signal theory. For the electric dipole case such a shift might be looked upon as a sort of dynamic Stark effect.

From the point of view of the problem at hand the variation of the effective natural frequency with power level implies that given a fixed frequency of operation, there is only one power level at which optimum interaction will occur. Whether or not this variation of the natural frequency is significant depends on the linewidth of the transition. The effect will be less for broader lines.

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[1] This is precisely the same relation as Eq. (3.53). It may be derived as in the text or by Bloch's original arguments. Another simple method is to take the linearly polarized field and separate it into two circularly polarized components. By diagonalizing the Hamiltonian containing the dc field and the counter-rotating term and averaging the latter, Eq. (3.119) is derived as the difference between the new eigenvalues.

4. An Example: Harmonic Generation in Gaseous NH_3

We shall now consider an example using the inversion transition in NH_3 .

a. The Pressure Dependence of the Spectrum

The inversion spectrum of ammonia is made up of many lines, each corresponding to a different rotational mode of the molecule. At low pressures these lines are resolved, each having its own value of absorption coefficient. As the pressure is increased each of these lines broadens with half-width of 30 Mc/mm Hg, while preserving the magnitude of its absorption coefficient. When these lines begin to overlap, the overall absorption coefficient at a given frequency will be the sum of the individual contributions. At high pressures the many lines will be unresolved and will appear as a single broad line with an absorption coefficient which is nearly the sum of the individual absorption coefficients. Thus Q_s , and hence the level of power out, should increase with pressure up to a point where the linewidth of an individual component becomes of the order of the spacing between the lines. For ammonia, this occurs at a pressure of about 200 mm Hg, corresponding to a half width of 6 kMc.

b. Saturation

For most gases with transitions in the microwave range we have $T_1 = T_2$.[1] Since NT_2 is a constant and $N \propto$ pressure, increasing the pressure will reduce T_1 and T_2 and hence will reduce saturation. The effects of saturation should then be most predominant at low pressures.

By taking an operating pressure of 300 mm Hg where the line has nearly its maximum absorption coefficient,[60] $\gamma = 7 \times 10^{-3}$ cm^{-1} and by using the following data for NH_3 :

$$\mu = 1.47 \times 10^{-18} \text{ esu}$$

$$\Omega = 2\pi \times 24 \text{ kMc}$$

$$\Delta\nu = 1/2\pi\, T_2 = 30 \text{ Mc/mm Hg} \qquad ,$$

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[1] See Townes and Schawlow, Ref. (59), pp. 352, for a discussion of this.

we find

$$\frac{1}{Q_s} = 1.4 \times 10^{-3}$$

and

$$(\Omega\, T_2) = 2.67 \qquad .$$

The relations for output power (3.100) and (3.111) are

$$P_{out}(\text{watts}) = 4.7 \times 10^{-10} \frac{f_2^2}{f_1} E_1^6(\text{esu}) \qquad ,$$

where the third harmonic frequency, 3ω , is near 24 kMc, and

$$P_{out}(\text{watts}) = 3.1 \times 10^{-10} f_2^2 E_1^6(\text{esu}) \qquad ,$$

where $3\omega \approx 72$ kMc and $Q_0 = 5{,}000$. Plots of the theoretical output power per c.c. of cavity volume for the two cases are plotted in Fig. 3.2, where the effects of saturation have been included. In Fig. 3.3 the saturation parameters S , (3.90) and (3.108) are plotted for the two cases of interest. For both plots the quantities are plotted against E_1^2 which is proportional to the power supplied at the fundamental.

A similar calculation using HCN , ($\gamma = 9 \times 10^{-3}$ cm^{-1} , $\mu = 3 \times 10^{-18}$, $\Omega = 2\pi \times 88.6$ kMc) gives

$$P_{out}(\text{watts}) = 0.55 \times 10^{-10} \frac{f_2^2}{f_1^2} E_1^6(\text{esu}) \qquad .$$

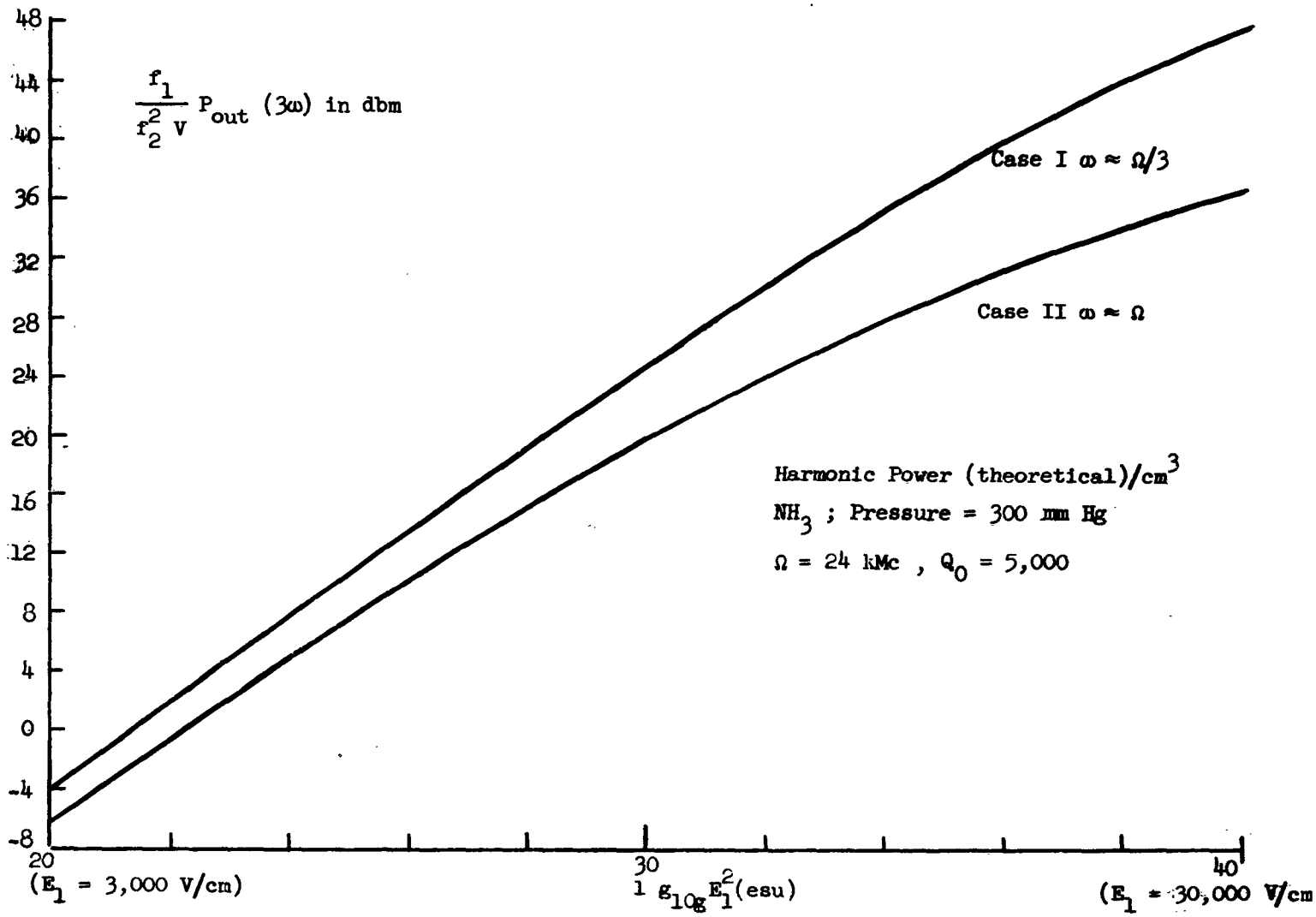

FIG. 3.2--Theoretical third harmonic power for the two cases considered vs fundamental field strength. The inversion transition in NH_3 is taken as the active transition.

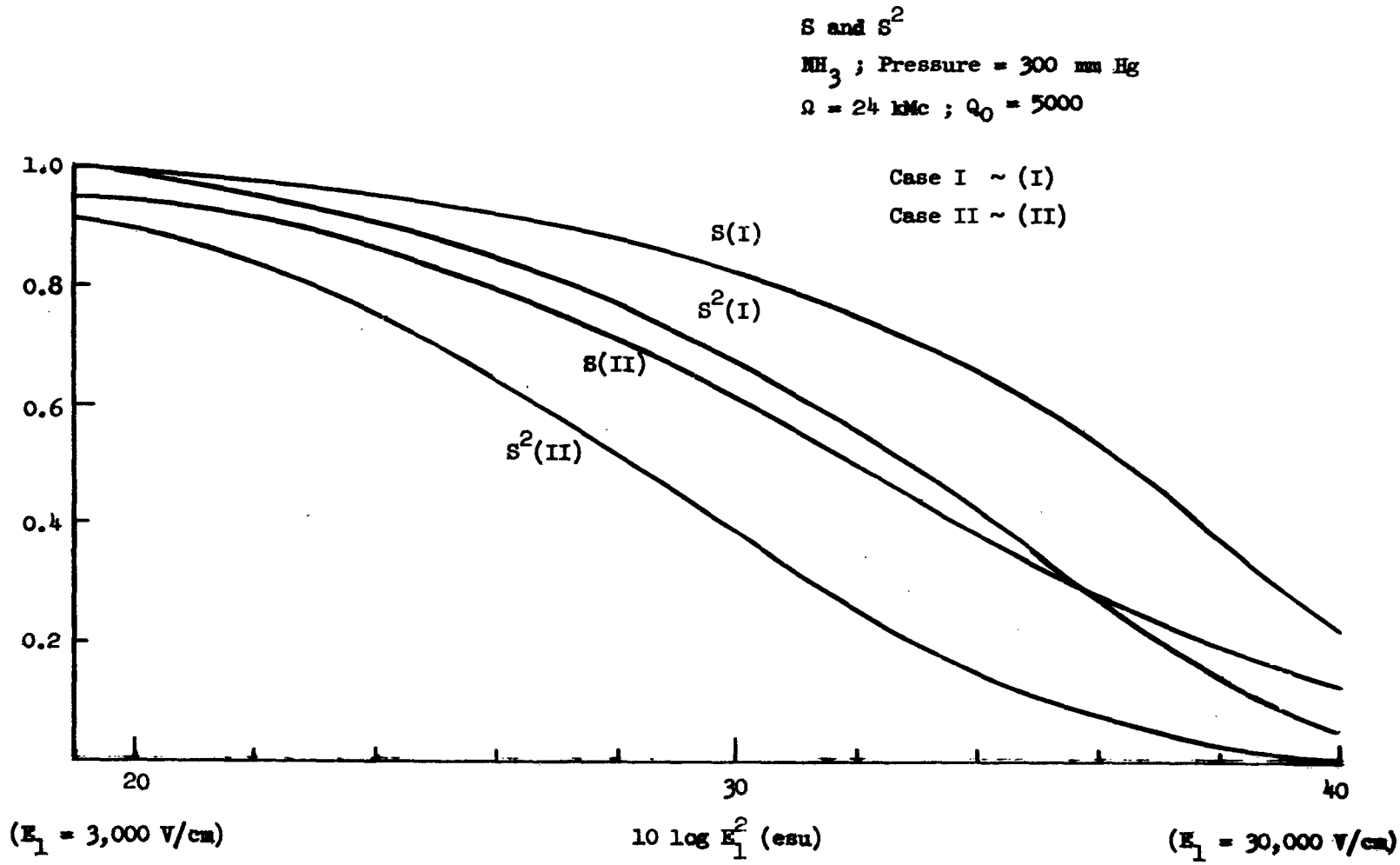

FIG. 3.3--Saturation parameters S and S_2 vs fundamental field strength. The inversion transition in NH_3 is taken as the active transition.

I. CONCLUSIONS

In this chapter a detailed calculation of the process of third harmonic generation in a two-level system has been performed. The value of the nonlinearity has been related to the constants of the quantum system and its surroundings, which here is a cavity. The effects of saturation and the losses in the form of Q's have been derived from the same formalism. The dependence of the nonlinearity on the parameters of the system has been discussed and an example has been given using the well known inversion transition in ammonia.

The particular system studied, (the two-level system) is the simplest of all quantum mechanical systems and is clearly only an approximation to any real situation. It does demonstrate, however, that even such a simple system can show nonlinear properties. Other quantum systems containing three or more levels will display similar nonlinear properties whose magnitude and frequency range will depend on the particular system involved. For example, in Chapter V, a three-level system is considered as a second harmonic generator. Other possibilities exist for a two-level system; second harmonic generation may be performed by the use of a dc bias,[61] and a form of parametric amplification is possible.[(1)] We shall next consider the parametric process.

[(1)] See Chapter IV

CHAPTER IV

PARAMETRIC EFFECTS IN A TWO-LEVEL ELECTRIC DIPOLE SYSTEM

A. INTRODUCTION

In the preceding chapter it was shown that a two-level electric dipole system behaved in a nonlinear manner and its use as a third harmonic generator was calculated. Here another application of nonlinear phenomena, namely parametric amplification or oscillation, is considered using the same two-level system. This process has one very important difference from harmonic generation processes. For the latter there exists an output (however small) for any level of input. To obtain parametric oscillation (sometimes called subfrequency oscillation) the level of the applied "pump" signal must exceed some critical value determined by the nonlinearity and the circuit parameters. This value is known as the threshold. We shall calculate the threshold for such a process, relating it to the circuit Q and to the parameters of the two-level system.

The quantum mechanical system to be considered consists of two levels with energies E_1 and E_2, where the natural frequency is defined as $\Omega = (E_2 - E_1)/\hbar$. The interaction of the system with the radiation fields will be taken to be via an induced electric dipole. In the energy representation the perturbing Hamiltonian will then contain no diagonal components, as a result of which higher order processes connecting the two states must contain an odd number of photons.

There are two interesting types of parametric processes possible using such a system. In the first, four frequencies, ω_1, ω_2, ω_3, ω_4 are present. Energy conservation requires $\omega_1 + \omega_2 + \omega_3 + \omega_4 = 0$, where $\omega > 0$ for absorption and $\omega < 0$ for emission. By setting $\omega_1 = \omega_2 = \omega_p$, $\omega_3 = -\omega_i$, $\omega_4 = -\omega_s$ and providing cavity resonances at ω_i and ω_s, a parametric amplifier is possible where

$$2\omega_p = \omega_s + \omega_i \quad . \tag{4.1}$$

In such a system there will be electromagnetic fields at ω_p , ω_i and ω_s . This is shown schematically in Fig. 4.1.

In the second process the atomic resonance acts as the idler, $\omega_i = \Omega$, and no electromagnetic field need be present at ω_i . Again by setting $\omega_1 = \omega_2 = \omega_p$, the frequency condition is

$$2\omega_p = \omega_s + \Omega \quad . \tag{4.2}$$

This is essentially a Raman type process in which the excitation is by two photons, and is shown in Fig. 4.2. Here a cavity resonance need only be provided at ω_s in order to obtain the parametric process. It is this latter process which will now be described.

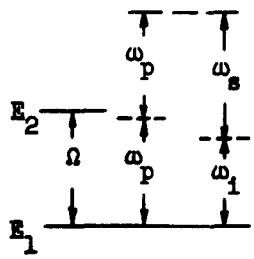

FIG. 4.1--Energy level diagram for the first type of parametric process;

$$2\omega_p = \omega_s + \omega_i \quad .$$

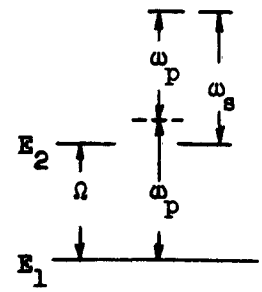

FIG. 4.2--Energy level diagram for the second type of parametric process;

$$2\omega_p = \omega_s + \Omega \quad .$$

B. THE EQUATIONS OF MOTION

The equations of motion for an induced electric dipole may be derived in the following manner:[1]

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[1] These equations are derived in a report by E. T. Jaynes.[62] Their equivalence to the density matrix formulation is demonstrated in Appendix C.

1. Assume only two energy levels are involved, so that the state of the system can be represented as

$$\psi = a_1(t)|u_1\rangle + a_2(t)|u_2\rangle \quad , \tag{4.3}$$

where $|u_1\rangle$ and $|u_2\rangle$ are the eigenfunctions of the unperturbed system.

2. The Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 - \mu_{op} \cdot E \quad ,$$

where $\mathcal{H}_0$ is the unperturbed Hamiltonian, μ_{op} is the dipole operator, and E is the radiation electric field.

3. In matrix notation, these are defined as

$$\mu_{op} = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} ; \quad \mathcal{H} = \begin{pmatrix} E_1 & -\mu_{12} \cdot E \\ -\mu_{12} \cdot E & E_2 \end{pmatrix}, \tag{4.4}$$

where u_{12} is the matrix element of μ_{op} between the two states, and E_1 and E_2 are the eigenvalues of the unperturbed Hamiltonian.

4. The dipole moment is given by the effective value of the dipole operator, $P = \langle \mu_{op} \rangle$.

5. Time derivatives are calculated from the commutator with the Hamiltonian,

$$\dot{P} = -\frac{1}{i\hbar} \left[\mathcal{H}, P\right] \quad . \tag{4.5}$$

6. From Eqs. (4.4) and (4.5) the following equations of motion are obtained:

$$\ddot{P} + \Omega^2 P = -\left(\frac{2\mu_{12}}{\hbar}\right)^2 WE \tag{4.6}$$

and

$$\dot{W} = E\dot{P} \quad , \tag{4.7}$$

where

$$\Omega = \frac{E_2 - E_1}{\hbar}$$

$$W = \frac{1}{2}\hbar\Omega(a_2a_2^* - a_1a_1^*) \quad ,$$

and W is proportional to the energy stored in the dipole system, referred to the equal population condition as the zero point of energy.

Equation (4.6) describes the dipole moment, P, as an harmonic oscillator driven by the electric field through a coupling constant proportional to W. If the populations are equal, the coupling to the electric field is zero, which means that the dipole does not "see" the radiation field. The maximum coupling to the field occurs when the population difference is a maximum.

Equation (4.7) equates power absorbed to the rate of change of stored energy; $\dot{P}$ is equivalent to a current density so the $E\dot{P}$ is the power delivered to the dipolar system by the radiation field; $\dot{W}$, in turn, is the rate of change of energy stored in the dipolar system. To account for loss mechanisms that might exist, Eqs. (4.6) and (4.7) are modified to

$$\ddot{P} + \frac{2}{T_2}\dot{P} + \Omega^2 P = -\left(\frac{2\mu_{12}}{\hbar}\right)^2 WE \tag{4.8}$$

$$\dot{W} + \frac{W - W_e}{T_1} = E\dot{P} \quad , \tag{4.9}$$

where T_2 is the relaxation time associated with the decay of the dipole moment, and T_1 is the relaxation time for the decay of stored energy. The W_e is the steady-state value for the unperturbed energy, which, for a system in thermal equilibrium, is given by the Boltzmann distribution.

Equations (4.8) and (4.9) involve the three variables W, P and E, and so an additional equation is necessary for a unique solution. From Slater's normal mode expansion for the fields in a resonant cavity, Eq. (4.10) can be obtained:

$$E = \frac{4\pi N\omega^2 fPV^{\frac{1}{2}}}{\omega_a^2 - \omega^2 + i\,\dfrac{\omega\,\omega_a}{Q_L}}, \tag{4.10}$$

where ω_a = resonant frequency for the unperturbed cavity,

Q_L = loaded quality factor for the cavity,

f = the filling factor,

V = cavity volume, and

N = number of interacting dipoles per unit volume.

It is assumed, in Eq. (4.10), that one normal mode field predominates, and cgs units are used.

C. PARAMETRIC AMPLIFICATION OR OSCILLATION

A steady-state solution to Eqs. (4.8), (4.9) and (4.10) can be obtained by letting

$$P = \frac{1}{2}\sum_{\alpha}\left(P_{\alpha}e^{j\omega_{\alpha}t} + P_{-\alpha}e^{-j\omega_{\alpha}t}\right)$$

$$E = \frac{1}{2}\sum_{\alpha}\left(E_{\alpha}e^{j\omega_{\alpha}t} + E_{-\alpha}e^{-j\omega_{\alpha}t}\right),$$

where $P_{-\alpha} = P_{\alpha}^{*}$ and $E_{-\alpha} = E_{\alpha}^{*}$, as required to give real values for E and P . Each value of α corresponds to one frequency present.

By combining Eqs. (4.8) and (4.9) with the expansions above and using harmonic balance, we get

$$\left[(\Omega^2 - \omega_\ell^2) + \frac{j2\omega_\ell}{T_2}\right] P_\ell = -\left(\frac{2\mu_{12}}{\hbar}\right)^2 W_0 E_\ell$$

$$- \frac{1}{4}\left(\frac{2\mu_{12}}{\hbar}\right)^2 \sum_{n \neq \ell} \sum_{r} \frac{E_n E_r j(\omega_\ell - \omega_n - \omega_r)}{j(\omega_\ell - \omega_n) + \frac{1}{T_1}} P_{\ell-n-r} \quad , \quad (4.11)$$

where $P_{\ell-n-r}$ = moment at frequency $\omega_\ell - (\omega_n + \omega_r)$, and

$$W_0 = W_e - \frac{jT_1}{4} \sum_{y} \omega_y P_{-y} E_y \quad . \qquad (4.12)$$

The term W_0 is proportional to the average value of the population difference, and is different from W_e because of the saturation caused by the presence of the fields.

Considering now the case of a cavity containing active dipoles and resonant at two frequencies ω_s and ω_p , let us define another frequency, ω_i , by the relationship

$$2\omega_p = \omega_s + \omega_i \quad . \qquad (4.13)$$

The quantities ω_p , ω_s and ω_i , are, respectively, the pump, signal and idler frequencies of the parametric system. Since the cavity does not resonate at ω_i , then E_i is zero, but P has a component at that frequency.

The amplitude of the pump field, E_p , required for parametric oscillation is reduced as the pump frequency approaches Ω . For this

reason, let

$$\omega_p = \Omega(1 + \epsilon)$$
$$\omega_i = \Omega(1 + X)$$
$$\omega_s = \Omega(1 + 2\epsilon - X) \quad , \tag{4.14}$$

where ϵ , $X \ll 1$. The term X is introduced to represent the shift of the natural frequency Ω due to the presence of the strong pump fields. From Eqs. (4.11) and (4.12), we get

$$\left[\Omega^2\left(-4\epsilon + 2X + \frac{\delta^2}{\epsilon - X}\right) + \frac{j2\Omega}{T_2}\right] P_s - \frac{\delta^2\Omega^2}{\epsilon - X} P_{-i}$$
$$\cong -\left(\frac{2\mu_{12}}{\hbar}\right)^2 W_0 \left(1 - \frac{\delta^2}{2\epsilon(\epsilon - X)}\right) E_s \tag{4.15}$$

$$\frac{\delta^2\Omega^2}{\epsilon - X} P_s + \left[-\Omega^2\left(2X + \frac{\delta^2}{\epsilon - X}\right) - \frac{2j\Omega}{T_2}\right] P_{-i}$$
$$\cong \left(\frac{2\mu_{12}}{\hbar}\right)^2 \frac{W_0\delta^2}{2\epsilon(\epsilon - X)} E_s \tag{4.16}$$

$$W_0 \cong \frac{W_e}{1 + \frac{\delta^2}{\epsilon^2}} \quad , \tag{4.17}$$

where

$$\delta^2 = \left(\frac{\mu_{12}E_p}{\hbar\Omega}\right)^2 .$$

In the derivation of Eqs. (4.16), (4.17) and (4.18) the following assumptions have been made:

(a) $\epsilon - \chi \gg 1/\Omega T_1$

(b) $T_1 = T_2$

(c) The pump amplitudes are much more intense than the signal and idler amplitudes so that only first order terms in signal and idler have been included.

Equation (4.18) expresses the saturation effect. For low values of pump field, we have $W_0 = W_e$, and as the amplitude of the pump field increases, W_0 approaches zero, which means that the populations tend to equalize. A normal population distribution corresponds to a negative value for W_e, and similarly a population inversion means that W_e is positive. For a normal population, the range of W_0 is $0 > W_0 > W_e$.

There is a relationship between δ^2, ϵ and χ so as to optimize the parametric effect. This relationship can be obtained by considering the determinant, Δ, formed from the coefficients of the dipole moments P_s and P_{-i}:

$$\Delta = 4\Omega^4 \left[\delta^2 - \chi(\chi - 2\epsilon)\right] + \frac{j4\Omega^4}{\Omega T_2}\left[\frac{(\epsilon - \chi)^2 + \epsilon^2}{\epsilon - \chi}\right] . \qquad (4.18)$$

The magnitude of Δ becomes a minimum near the condition for which

$$\delta^2 = \chi(\chi - 2\epsilon) , \qquad (4.19)$$

which means that Eq. (4.19) expresses the condition for optimizing the dipole moments. Using the value for δ^2 given by Eq. (4.19), P_s is given by

$$P_s = \left(\frac{2\mu_{12}}{\hbar}\right)^2 \frac{W_0 \Omega T_2}{j4\Omega^2} \frac{\epsilon - \chi}{\epsilon\left[(\epsilon - \chi)^2 + \epsilon^2\right]} \left[\chi^2 + \frac{j}{\Omega T_2}\frac{2\epsilon^2 - \chi^2}{\epsilon - \chi}\right] E_s . \qquad (4.20)$$

Equating the imaginary terms that result from substituting the above expression for M_s into Eq. (4.10), the circuit equation, we obtain the oscillation condition in terms of the loaded Q of the resonator:

$$\frac{1}{Q_L} = \frac{1}{H} \frac{(\epsilon - \chi)\chi^2}{\epsilon\left[(\epsilon - \chi)^2 + \epsilon^2\right]\left[1 + \frac{\chi(\chi - 2\epsilon)}{\epsilon^2}\right]} , \tag{4.21}$$

where

$$\frac{1}{H} = -\left(\frac{2\mu_{12}}{\hbar}\right)^2 \frac{E_a^{\,2}}{2W_a} \frac{W_e N_J T_2}{4\Omega} \tag{4.22}$$

N_J = population of the lower state

W_a = energy stored in the cavity $= \frac{1}{8\pi}\int E_a^2 dV$.

The derivation of Eq. (4.21) assumes that P_s and E_a are uniform over the interaction region. A negative sign is used in Eq. (4.22) to make H positive, as $W_e < 0$ for the normal population distribution.

The real terms that appear from the substitution of Eq. (4.20) into Eq. (4.10) are cancelled by choosing the appropriate value for ω_a , the resonant frequency of the cavity.

By letting $x = \chi/\epsilon$, Eq. (4.21) becomes

$$\frac{1}{Q_L} = \frac{1}{H} \frac{x^2}{\left[(1 - x)^2 + 1\right]\left[1 - x\right]} . \tag{4.23}$$

From Eq. (4.19) it is seen that $\delta^2/\epsilon^2 = x(x - 2)$, so that the permissible range for x is $x > 2$ or $x < 0$. Since the right hand side of Eq. (4.23) must be positive, the region of interest for x is $x < 0$, which means that ω_p and ω_s are both either larger or smaller than Ω .

Equation (4.23) may be written in terms of the on-resonance unsaturated absorption coefficient given in Appendix D:

$$\gamma = -\frac{2\pi N_J T_2 W_e}{c}\left(\frac{2\mu_{12}}{\hbar}\right)^2 , \tag{4.24}$$

where c is the velocity of light. Assuming a filling factor of unity for the resonant cavity, we then find that

$$\frac{1}{H} = \frac{\gamma\lambda}{4\pi} , \tag{4.25}$$

where λ is the wavelength. Combining Eqs. (4.23) and (4.25) results in

$$\frac{4\pi}{\gamma\lambda Q_L} = \frac{x^2}{\left[(1-x)^2+1\right]\left[1-x\right]} \equiv f(x) . \tag{4.26}$$

The function $f(x)$ has a maximum value approximately equal to 0.15, which means that we must have $4\pi/\gamma\lambda Q_L < 0.15$ for oscillations to occur. For a rotational mode of oscillation in a gas at room temperature at $\lambda = 1$ mm, a strong absorption line might have $\gamma = 10^{-1}$ cm^{-1}, which means that $Q_L > (4\pi/1.5) \times 10^3$. If Q_L is specified, then x is given by Eq. (4.26). As an example, with $Q_L = 1.2 \times 10^4$, we find that $x \simeq -1$. In terms of ϵ, this means

$$\omega_p = \Omega(1+\epsilon)$$

$$\omega_i = \Omega(1-\epsilon)$$

$$\omega_s = \Omega(1+3\epsilon)$$

$$E_p = \frac{h\Omega}{\mu_{12}}\sqrt{x(x-2)}\,|\epsilon| = \frac{h\Omega}{\mu_{12}}\sqrt{3}\,|\epsilon| .$$

For $\mu_{12} = 10^{-18}$, we have $E_p \cong 10^3 \epsilon$ kv/cm . With $\epsilon = 0.01$, then we find $E_p = 10$ kv/cm and $f_s - f_p = 6$ kMc/s is the difference between the signal and pump frequencies.

D. CONCLUSIONS

The preceding discussion has indicated a manner in which a two-level system can function as a parametric amplifier. It differs from usual parametric amplifiers in that the quantum system provides the idler[1] and the pump frequency equals half of the sum of the signal and idler frequencies.[2]

By providing a dc bias, operation can occur where $\omega_p = \omega_s + \omega_i$. Other schemes using more than two levels offer the possibility of parametric processes which may prove more efficient than the one here presented.

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[1] In this respect it is similar to Suhl's ferrimagnetic amplifier, which can use a mode of the sample for the idler.

[2] Subharmonic pumping of a parametric amplifier has been considered by Mortenson.[63]

CHAPTER V

THE THEORY OF SECOND HARMONIC GENERATION IN A THREE-LEVEL SYSTEM

In this chapter we shall be concerned with the interaction of radiation with a quantum mechanical system consisting of three levels. The system may have only three levels in the frequency region of interest, as in the case of an $S = 1$ spin system, or if there are more than three levels we may consider those most strongly coupled to the fields. Such a three-level system can act as a three-frequency mixer, a special case being second harmonic generation.

Using the density matrix approach, the source of the nonlinear effect is pointed out and the problem of harmonic generation is considered in detail. The dependence of the nonlinearity on the parameters of the system is considered.

A. EQUATIONS OF MOTION

Let the system under consideration consist of three energy levels E_1, E_2, and E_3, in order of increasing energy and define the natural frequencies as in Fig. 5.1.

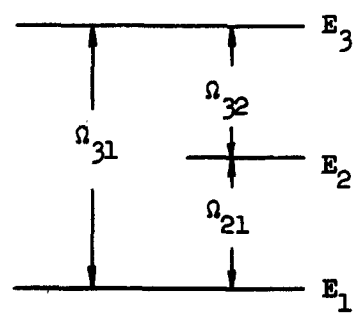

FIG. 5.1--Energy level diagram for a three-level system.

The Hamiltonian may be taken as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad , \tag{5.2}$$

where $\mathcal{H}'$ is the perturbation resulting from the application of external fields and $\mathcal{H}'_{ij}$ is the matrix element of the perturbation taken between levels i and j. The energy representation is used and it is assumed that there exist nonzero matrix elements connecting all of the levels.

We may write the equations of motion of the system using the density matrix formulation in the standard manner.[1] We shall assume that the longitudinal relaxation times are equal while the transverse times may be arbitrary. The assumption of equal longitudinal times simplifies the equations for the diagonal components and the resulting expressions for the saturation effects. Such an assumption is physically justified, as it is usually the case that such times are equal.[64] Further, we are not here interested in effects which depend in any way on such discrepancies in relaxation times; their effect would be merely to alter the details of the operation and would in no way affect the principles involved.

The equations for the three-level system are:

$$\dot{\rho}_{11} + \frac{(\rho_{11} - \rho_{11}^{e})}{T_1} = \frac{1}{i\hbar}\left[\mathcal{H}'_{12}\,\rho_{21} + \mathcal{H}'_{13}\,\rho_{31} - \rho_{12}\,\mathcal{H}'_{21} - \rho_{13}\,\mathcal{H}'_{31}\right] \tag{5.2a}$$

$$\dot{\rho}_{22} + \frac{(\rho_{22} - \rho_{22}^{e})}{T_1} = \frac{1}{i\hbar}\left[\mathcal{H}'_{21}\,\rho_{12} + \mathcal{H}'_{23}\,\rho_{32} - \rho_{21}\,\mathcal{H}'_{12} - \rho_{23}\,\mathcal{H}'_{32}\right] \tag{5.2b}$$

$$\dot{\rho}_{33} + \frac{(\rho_{33} - \rho_{33}^{e})}{T_1} = \frac{1}{i\hbar}\left[\mathcal{H}'_{31}\,\rho_{13} + \mathcal{H}'_{32}\,\rho_{23} - \rho_{31}\,\mathcal{H}'_{13} - \rho_{32}\,\mathcal{H}'_{23}\right] \tag{5.2c}$$

---

[1] See Appendix A.

and

$$\dot{\rho}_{12} + \frac{1}{\tau_{12}} \rho_{12} - i\, \Omega_{21}\rho_{12} = \frac{1}{i\hbar} \left[(\rho_{22} - \rho_{11})\mathcal{H}'_{12} + \rho_{32}\, \mathcal{H}'_{13} - \rho_{13}\, \mathcal{H}'_{32} \right] \quad (5.2d)$$

$$\dot{\rho}_{23} + \frac{1}{\tau_{23}} \rho_{23} - i\, \Omega_{32}\rho_{23} = \frac{1}{i\hbar} \left[(\rho_{33} - \rho_{22})\mathcal{H}'_{23} + \rho_{13}\, \mathcal{H}'_{21} - \rho_{21}\, \mathcal{H}'_{13} \right] \quad (5.2e)$$

$$\dot{\rho}_{13} + \frac{1}{\tau_{13}} \rho_{13} - i\, \Omega_{31}\rho_{13} = \frac{1}{i\hbar} \left[(\rho_{33} - \rho_{11})\mathcal{H}'_{13} + \rho_{23}\, \mathcal{H}'_{12} - \rho_{12}\, \mathcal{H}'_{23} \right] . \quad (5.2f)$$

Let us examine these equations. The first three describe the behavior of the diagonal components which are essentially the probability of occupancy of the three levels. In the absence of an external perturbation, $\mathcal{H}' = 0$, these quantities take on their equilibrium values. If $\mathcal{H}' \neq 0$, then they are modified, giving rise to saturation effects. The off-diagonal equations describe the coupling of the states, and it is these which describe the absorption and emission of radiation. Let us specifically consider the equation for the coupling of the 2-3 transition. The first term on the right hand side of the expression for ρ_{23} gives the direct coupling due to the perturbation $\mathcal{H}'_{23}$ which, to be effective, must be almost resonant with the frequency Ω_{32} . In addition to the direct coupling there are two additional terms which give rise to indirect coupling. The first, $\rho_{13}\, \mathcal{H}'_{21}$, shows that if there is coupling of the 1-3 transition, $\rho_{13} \neq 0$, then the perturbation $\mathcal{H}'_{21}$ will mix with this to give a resultant coupling of the 2-3 transition. The last term is of the same nature. Since ρ_{13} will be seen to be proportional to $\mathcal{H}'_{13}$, this coupling term is proportional to $\mathcal{H}'_{21}\, \mathcal{H}'_{13}$ and is seen to be of second order. Such a process involves two photons and is nonlinear in character. The other two equations are of the same nature, displaying both linear and second order coupling.

We may now qualitatively understand the behavior of this system as a frequency mixer. Let us suppose that we apply two radiation fields at frequencies ω_1 and ω_2 . Let us further postulate that they are approximately resonant with the 1-3 and 1-2 transitions, respectively.[1]

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[1] In general, any two frequencies can be mixed, but unless they are approximately resonant with the natural frequencies the effect will be small.

These perturbations will then, in a linear fashion, drive the system and give nonzero values to the components ρ_{13} and ρ_{21}. These will then mix with the perturbations $\mathcal{H}_{21}$ and $\mathcal{H}_{13}$ and give a driving term for ρ_{23} at a frequency $\omega_3 = \omega_1 - \omega_2$. As shown in Chapter II, we may calculate the component of the dipole moment at the frequency ω_3, and since it is proportional to ρ_{23} we see that the fields at frequencies ω_1 and ω_2 will mix to generate a component of the dipole moment at the difference frequency.(1) If we now provide a cavity resonance at this frequency, we can extract power and the system acts as a mixer.(2)

A similar type of parametric process has been considered by Anderson.[33] There he applies a pump field resonant with Ω_{31} and allows for cavity resonances at $\omega_1 \cong \Omega_{21}$ and $\omega_2 \cong \Omega_{32}$ where $\omega_1 + \omega_2 = \Omega_{31}$. Above a given threshold pump power level determined by the Q's of the cavities one can achieve a form of parametric amplification or oscillation at the frequencies ω_1 and ω_2. It is similar in operation to Suhl's ferromagnetic amplifier.[34,35]

We shall now consider the specific case of second harmonic generation using the same three-level system.

B. RESONANT HARMONIC GENERATION

We shall start by assuming that we have a three-level system in which the intermediate level with energy E_2 lies approximately midway between the outer levels which have energies E_1 and E_3. We shall assume that there exist matrix elements connecting all the levels and that the longitudinal relaxation times are equal. We shall assume magnetic dipole interactions and let there be a strong field applied at the fundamental frequency

$$H(\omega) = H_1 \cos(\omega t - \phi) \quad ,$$

(1) It should be noted that there will also be generated a component of dipole moment at the sum frequency but because of the resonant nature of the quantum system this will be very small, as it does not correspond to any of the natural transition frequencies of the system.

(2) The magnitude of the power out will be proportional to the product of the power at frequencies ω_1 and ω_2 and will be nonzero for any finite value of this product.

and a weaker second harmonic field which is generated by the nonlinear process, given by

$$H(2\omega) = H_2 \cos(2\omega t) \quad .$$

We need only consider perturbations which are almost resonant with the various transitions, as the effect of nonresonant perturbations is very small.[1] We may then write our perturbing Hamiltonian as

$$\left.\begin{aligned}
\mathcal{H}'_{12} &= -\mu_{12} H_1 \cos(\omega t - \phi) = \frac{-\mu_{12} H_1}{2}\left[e^{i(\omega t - \phi)} + e^{-i(\omega t - \phi)}\right] \\
\mathcal{H}'_{23} &= -\mu_{23} H_1 \cos(\omega t - \phi) = \frac{-\mu_{23} H_1}{2}\left[e^{i(\omega t - \phi)} + e^{-i(\omega t - \phi)}\right] \\
\mathcal{H}'_{13} &= -\mu_{13} H_2 \cos 2\omega t = -\frac{\mu_{13} H_2}{2}\left[e^{i2\omega t} + e^{-i2\omega t}\right]
\end{aligned}\right\} . \qquad (5.3)$$

Let us now define the quantities β_{ij} which measure the strength of the perturbations in dimensions of frequency

$$\left.\begin{aligned}
\beta_{12} &= \frac{\mu_{12} H_1}{2\hbar} e^{-i\phi} \\
\beta_{23} &= \frac{\mu_{23} H_1}{2\hbar} e^{-i\phi} \\
\beta_{13} &= \frac{\mu_{13} H_2}{2\hbar} \\
\text{and the conjugate quantities} & \\
\beta_{21} &= \beta^*_{12} \\
\beta_{32} &= \beta^*_{23} \\
\beta_{31} &= \beta^*_{13}
\end{aligned}\right\} . \qquad (5.4)$$

[1] The magnitude of nonresonant perturbations is found to be of the order of $\mathcal{H}'/\omega$, while resonant perturbations are of the order of $\mathcal{H}'/\Delta\Omega$, where $\Delta\Omega$ is the linewidth. Since in any reasonable situation $\omega \gg \Delta\Omega$, we may neglect the nonresonant terms.

From a careful examination of Eqs. (5.2), we see that the "natural" frequencies of the various components of the density matrix are

$$\rho_{11} \ , \ \rho_{22} \ , \ \rho_{33} \ , \text{ all "dc"}$$

$$\rho_{12} \sim \Omega_{21} \qquad \rho_{21} \sim -\Omega_{21}$$

$$\rho_{23} \sim \Omega_{32} \qquad \rho_{32} \sim -\Omega_{32}$$

$$\rho_{13} \sim \Omega_{31} \qquad \rho_{31} \sim -\Omega_{31} \quad .$$

Since only those perturbations which are almost resonant will have any effect, we assume a solution of the form

$$\begin{aligned} \rho_{11} &= \lambda_{11} \ , \quad \rho_{12} = \lambda_{12}\, e^{i\omega t} \\ \rho_{22} &= \lambda_{22} \ , \quad \rho_{23} = \lambda_{23}\, e^{i\omega t} \ , \\ \rho_{33} &= \lambda_{33} \ , \quad \rho_{13} = \lambda_{13}\, e^{i2\omega t} \end{aligned} \tag{5.5}$$

where the λ are constants, which are in general complex. By using harmonic balance, our equations become

$$(\lambda_{11} - \lambda_{11}^{e}) = i\, T_1\, (\beta_{12}\, \lambda_{21} + \beta_{13}\, \lambda_{31} - \beta_{21}\, \lambda_{12} - \beta_{31}\, \lambda_{13}) \tag{6a}$$

$$(\lambda_{22} - \lambda_{22}^{e}) = i\, T_1\, (\beta_{21}\, \lambda_{12} + \beta_{23}\, \lambda_{32} - \beta_{12}\, \lambda_{21} - \beta_{32}\, \lambda_{23}) \tag{6b}$$

$$(\lambda_{33} - \lambda_{33}^{e}) = i\, T_1\, (\beta_{31}\, \lambda_{13} + \beta_{32}\, \lambda_{23} - \beta_{13}\, \lambda_{31} - \beta_{23}\, \lambda_{32}) \tag{6c}$$

$$\left[(\Omega_{21} - \omega) + \frac{i}{\tau_{12}}\right] \lambda_{12} = \left[(\lambda_{11} - \lambda_{22})\, \beta_{12} + \beta_{32}\, \lambda_{13} - \beta_{13}\, \lambda_{32}\right] \tag{6d}$$

$$\left[(\Omega_{32} - \omega) + \frac{i}{\tau_{23}}\right] \lambda_{23} = \left[(\lambda_{22} - \lambda_{33})\, \beta_{23} + \beta_{13}\, \lambda_{21} - \beta_{21}\, \lambda_{13}\right] \tag{6e}$$

$$\left[(\Omega_{31} - 2\omega) + \frac{i}{\tau_{13}}\right] \lambda_{13} = \left[(\lambda_{11} - \lambda_{33})\, \beta_{13} + \beta_{23}\, \lambda_{12} - \beta_{12}\, \lambda_{23}\right] \ . \tag{6f}$$

We may now proceed to solve these equations using the following assumptions. First, assume that the frequency ω is such that $2\omega = \Omega_{31}$, and take the fundamental fields to be much larger than the harmonic fields. Then we have for the two components λ_{12} and λ_{23} their values as determined by first order interactions:

$$\lambda_{12} = \frac{(\lambda_{11} - \lambda_{22})\,\beta_{12}}{(\Omega_{21} - \omega) + \frac{i}{\tau_{12}}} \tag{5.7}$$

$$\lambda_{23} = \frac{(\lambda_{22} - \lambda_{33})\,\beta_{23}}{(\Omega_{32} - \omega) + \frac{i}{\tau_{23}}} \quad . \tag{5.8}$$

By substituting these in Eq. (5.6f) and using the fact that $2\omega = \Omega_{31}$, we have the relation for λ_{13} :

$$\lambda_{13} = i\,\tau_{13}\,\beta_{13}\,(\lambda_{33} - \lambda_{11}) + \frac{\tau_{13}\,\beta_{12}\,\beta_{23}}{\left(\delta + \frac{i}{\tau_{12}}\right)\left(\delta - \frac{i}{\tau_{23}}\right)}$$

$$\times \left[i\,\delta(\lambda_{33} - \lambda_{11}) + \frac{1}{\tau_{12}}(\lambda_{22} - \lambda_{33}) - \frac{1}{\tau_{23}}(\lambda_{11} - \lambda_{22}) \right] , \tag{5.9}$$

where $\delta = \Omega_{21} - \omega = -(\Omega_{32} - \omega)$. We now substitute these in the equations for the diagonal components, giving

$$\left.\begin{aligned}
\lambda_{11} - \lambda_{11}^{e} &= i\,T_1 \left[\frac{\beta_{12}\,\beta_{21}\,(\lambda_{11} - \lambda_{22})}{\delta - \frac{i}{\tau_{12}}} - \text{c.c.} \right] \\
\lambda_{33} - \lambda_{33}^{e} &= i\,T_1 \left[\frac{\beta_{32}\,\beta_{23}\,(\lambda_{22} - \lambda_{33})}{-\delta + \frac{i}{\tau_{23}}} - \text{c.c.} \right] \\
(\lambda_{22} - \lambda_{22}^{e}) &= -(\lambda_{11} - \lambda_{11}^{e}) - (\lambda_{33} - \lambda_{33}^{e})
\end{aligned}\right\} , \tag{5.10}$$

where we have included only the largest terms, and where c.c. is the complex conjugate quantity. By performing some algebra, we find the following:

$$\lambda_{11} = \frac{(A + \lambda_{11}^{e})(1 + 2B) - (B + \lambda_{33}^{e})A}{(1 + 2A)(1 + 2B) - AB} \tag{5.11}$$

$$\lambda_{22} = \frac{(1 + A)(1 + B) - (1 + A)\lambda_{33}^{e} - (1 + B)\lambda_{11}^{e}}{(1 + 2A)(1 + 2B) - AB} \tag{5.12}$$

$$\lambda_{33} = \frac{(1 + 2A)(B + \lambda_{33}^{e}) - B(A + \lambda_{11}^{e})}{(1 + 2A)(1 + 2B) - AB} \tag{5.13}$$

$$\lambda_{11} - \lambda_{33} = \frac{\lambda_{11}^{e}\ (1 + 3B) - \lambda_{33}^{e}\ (1 + 3A) + (A - B)}{(1 + 2A)(1 + 2B) - AB}\ , \tag{5.14}$$

where

$$A = \frac{2\ T_1\ \beta_{12}\ \beta_{21}}{\tau_{12}\left[\delta^2 + \frac{1}{\tau_{12}^2}\right]} \tag{5.15}$$

$$B = \frac{2\ T_1\ \beta_{23}\ \beta_{32}}{\tau_{12}\left[\delta^2 + \frac{1}{\tau_{23}^2}\right]}\ . \tag{5.16}$$

C. MACROSCOPIC MAGNETIZATION AND CAVITY REACTION

1. Magnetization

Given the density matrix, we can proceed to calculate the values of all the observables of the system. In particular, we are interested in the components of the magnetic dipole moment. The prescription for finding

the value of an observable, Q, is

$$\langle Q \rangle = \mathrm{Tr}\,(\rho Q) \quad . \tag{5.17}$$

We find for the dipole moment per unit volume or for the magnetization at the harmonic

$$M_2 = N\,(\rho_{31}\,\mu_{13} + \rho_{13}\,\mu_{31}) \quad , \tag{5.18}$$

and at the fundamental,

$$M_1 = N\,(\rho_{21}\,\mu_{12} + \rho_{12}\,\mu_{21} + \rho_{23}\,\mu_{32} + \rho_{32}\,\mu_{23}) \quad , \tag{5.19}$$

where N is the number of systems per unit volume. The second harmonic component of M will determine the amount of output power generated, while the component at the frequency ω determines the amount of resistive loading at the fundamental.

2. Cavity Reaction

We may determine the fields generated in the cavity by the magnetization from the relation

$$H = \frac{1}{\chi_c} M \quad , \tag{5.20}$$

where the cavity susceptibility, χ_c, is given by

$$\frac{1}{\chi_c} = \frac{4\pi\omega^2 f V^{\frac{1}{2}}}{\omega_n^2 - \omega^2 + i\,\dfrac{\omega\omega_n}{Q_n}} \quad . \tag{5.21}$$

Here, H and M vary as $e^{i\omega t}$ and we have the definition

$$M f V^{\frac{1}{2}} = \int_{\text{cavity}} \underline{M}(\underline{r}) \cdot \underline{U}_n(\underline{r})\, dV \quad , \tag{5.22}$$

where $\mathbf{U}_n(\mathbf{r})$ is the normal mode function for the cavity. It is assumed that there is only one mode near the frequency ω, and Q_n is the loaded Q of the cavity mode. As described in Chapter III, we must allow for different filling factors for the two components of M_2. By substituting (5.9) into (5.18) and using this in conjunction with (5.20) and (5.21), we have

$$\frac{H_2}{2}\left[\frac{1}{Q_2} + \frac{4\pi f_1 N \mu_{13} \mu_{31} \tau_{13} (\lambda_{11} - \lambda_{33})}{\hbar}\right] = \frac{4\pi f_2 V^{\frac{1}{2}} N \mu_{31} \tau_{13} \beta_{12} \beta_{23}}{\left(\delta + \frac{1}{\tau_{12}}\right)\left(\delta - \frac{1}{\tau_{23}}\right)}$$

$$\times \left[\delta(\lambda_{33} - \lambda_{11}) + \frac{1}{\tau_{23}} (\lambda_{11} - \lambda_{22}) - \frac{1}{\tau_{12}} (\lambda_{22} - \lambda_{33})\right] , \qquad (5.23)$$

where now we have assumed that the cavity is on resonance, f_1 is defined as the filling factor for the component of M_2 proportional to H_2, f_2 is the filling factor for the component of M_2 proportional to H_1^2, and Q_2 is the loaded Q of the cavity. By defining the magnetic Q of the sample at 2ω, Q_{m2}, as

$$\frac{1}{Q_{m2}} = \frac{4\pi N \tau_{13} \mu_{13} \mu_{31} \left(\lambda_{11}^e - \lambda_{33}^e\right)}{\hbar} , \qquad (5.24)$$

Eq. (5.23) becomes

$$H_2\left[\frac{1}{Q_2} + \frac{f_1 S_{13}}{Q_{m2}}\right] = \frac{2 f_2 V^{\frac{1}{2}} \hbar}{\mu_{13}(\lambda_{11}^e - \lambda_{33}^e) Q_{m2}} \frac{\beta_{12} \beta_{23}}{\left(\delta + \frac{1}{\tau_{12}}\right)\left(\delta - \frac{1}{\tau_{23}}\right)}$$

$$\times \left[\delta(\lambda_{33} - \lambda_{11}) + \frac{1}{\tau_{23}} (\lambda_{11} - \lambda_{22}) - \frac{1}{\tau_{12}} (\lambda_{22} - \lambda_{33})\right] , \qquad (5.25)$$

where S_{13} is a saturation parameter defined as

$$S_{13} = \frac{\lambda_{11} - \lambda_{33}}{\lambda_{11}^{e} - \lambda_{33}^{e}} \quad . \tag{5.26}$$

D. CHOICE OF δ

Let us now suppose that we are in a position to vary the value of the energy E_2 relative to a fixed value of $E_3 - E_1$. In a paramagnetic solid this can be done by varying the angle and magnitude of the magnetic field relative to the crystal axes. We shall look for the value or values of δ which will maximize the nonlinearity of the system. This maximization will occur, when for a fixed H_1 we maximize H_2 , [Eq. (5.25)]. Let us first assume that the levels are equally spaced, $\delta = 0$. In this case the term in brackets reduces to

$$\frac{1}{\tau_{23}} (\lambda_{11} - \lambda_{22}) - \frac{1}{\tau_{12}} (\lambda_{22} - \lambda_{33}) \quad . \tag{5.27}$$

If we now assume further that the linewidths of the two transitions are equal, $\tau_{23} = \tau_{12}$, substitute for λ_{11} , λ_{22} , and λ_{33} from (5.11), (5.12), and (5.13), and expand the Boltzmann term for the equilibrium values, keeping only the linear term, we get for (5.27)

$$\frac{1}{\tau_{12}} \frac{\hbar \Omega_{31}}{2\ kT} (B - A) \quad . \tag{5.28}$$

We see that, under these assumptions, the nonlinear term is nonzero only if $B \neq A$, which implies $|\mu_{12}| \neq |\mu_{23}|$. Even if $B \neq A$, we see that the term for $\delta = 0$ depends on the difference between quantities and hence will not contribute significantly to the effect. We thus set (5.27) equal to zero and the expression for H_2 becomes

$$H_2 \left[\frac{1}{Q_2} + \frac{f_1 S_{13}}{Q_{m2}} \right] = - \frac{2 f_2 V^{\frac{1}{2}} \hbar \beta_{12} \beta_{23} S_{13}}{\mu_{13} Q_{m2}} \frac{\delta}{\delta^2 + \left(\frac{1}{\tau_{12}}\right)^2} \quad , \tag{5.29}$$

which is maximized for $\delta = 1/\tau_{12}$. Hence we find that the maximum value for H_2 occurs when E_2 lies one linewidth from the value $(E_1 + E_3)/2$, or alternatively, when the fundamental signal at ω sees both the transitions at Ω_{21} and Ω_{32} at their half-power points. Upon setting $\delta = 1/\tau_{12}$, we have for H_2

$$H_2 = \frac{-f_2 V^{\frac{1}{2}} S_{13} \hbar \beta_{12} \beta_{23} \tau_{12}}{\mu_{13} Q_{m2} \left[\frac{1}{Q_2} + \frac{f_1 S_{13}}{Q_{m2}} \right]} . \tag{5.30}$$

E. HARMONIC POWER

The power coupled out of the cavity may be found from the relation

$$P(2\omega) = \frac{2\omega}{Q_e} \frac{1}{4\pi} \int \overline{H_2^2 \, dV}$$

$$= \frac{2\omega}{Q_e} \frac{\overline{H_2^2}}{8\pi} , \tag{5.31}$$

where the bar signifies time average. By substituting from (5.30) into (5.31), we obtain

$$P(2\omega) = \frac{2\omega f_2^2 V S_{13}^2 (\beta_{12} \beta_{23} \tau_{12} \hbar)^2}{8\pi Q_{m2}^2 \mu_{13}^2} \cdot \frac{1}{Q_e \left[\frac{1}{Q_0} + \frac{1}{Q_e} + \frac{f_1 S_{13}}{Q_{m2}} \right]^2} , \tag{5.32}$$

where we have used $1/Q_2 = 1/Q_0 + 1/Q_e$. From (5.32) we see that the apparent source Q is a parallel combination of the cavity Q and a modified magnetic Q , the modification involving the filling factor

and including the effects of saturation. The source Q is then

$$\frac{1}{Q_{source}} = \frac{1}{Q_0} + \frac{f_1 S_{13}}{Q_{m2}} \quad . \tag{5.33}$$

The question of population inversion is the same as in the case of the two-level system: if the population of levels 1 and 3 is in a normal state, then the quantum system presents loss, reducing the source Q ; if levels 1 and 3 are inverted then Q_{m2} becomes negative, the source Q (5.33) is increased, and the possibility for oscillations exists.

Assuming that the external coupling is chosen to be optimum, $Q_e = Q_{source}$, our expression for the power becomes

$$P(2\omega) = \frac{\omega f_2^2 V S_{13}^2 (\mu_{12} \mu_{23} \tau_{12})^2 H_1^4 Q_{source}}{256\pi \hbar^2 \mu_{13}^2 Q_{m2}^2} \quad . \tag{5.34}$$

We may consider the above under two special situations. If we are at low power levels where there is no saturation, $S_{13} = 1$, and the effective magnetic Q , Q_{m2}/f_1 , determines the source Q , as would be the case for efficient operation, we have for the power

$$P(2\omega) = \frac{\omega f_2^2 V (\mu_{12} \mu_{23} \tau_{12})^2 H_1^4}{256\pi \hbar^2 \mu_{13}^2 Q_{m2} f_1} \quad ,$$

while at high power levels the saturation reduces the loading of the sample and we have Eq. (5.34) with $Q_{source} = Q_0$.

F. SATURATION

The phenomenon of saturation occurs when the populations of levels 1 and 3 tend to equalize and is described by the saturation parameter S_{13} defined in Eq. (5.26). The exact value of S_{13} must be found from (5.14) and will, in general, be complicated. If, however, we make the

simplifying assumption that $A = B$, i.e., $|\mu_{12}| = |\mu_{23}|$, then we have

$$S_{13} = \frac{1}{1 + \frac{\tau_{12} T_1 \mu_{12}^2 H_1^2}{4 \hbar^2}} \quad . \tag{5.36}$$

When the fundamental field strength is such that

$$H_1^2 \geq \frac{4 \hbar^2}{\tau_{12} T_1 \mu_{12}^2} \quad , \tag{5.37}$$

then saturation will start to occur. If we examine the expression for the output power (5.35) and Q_{m2}, (5.24), we see that the power is proportional to $\tau_{12}^2 \tau_{13}^2$ and that we desire large τ_{12} and τ_{13} or narrow resonance lines. From (5.37) we see that to reduce saturation we desire as small a value of $\tau_{12} T_1$ as possible. These two requirements point out the important fact that we desire as small a value of T_1 as is possible, consistent with a narrow linewidth. This requirement is in sharp contrast to maser theory, where saturation and a large value of T_1 are desired.

Assuming that we reach saturation, by dropping the 1 in the denominator of (5.36), we find for the saturated output power

$$P_{sat}(2\omega) = \frac{\omega f_2^2 V Q_0 \hbar^2}{16\pi \mu_{13}^2 Q_{m2}^2 T_1^2} \quad , \tag{5.38}$$

or by substituting for Q_{m2}, Eq. (5.24),

$$P_{sat}(2\omega) = \frac{\pi \omega f_2^2 V Q_0 \mu_{13}^2 \tau_{13}^2 N^2 (\lambda_{11}^e - \lambda_{33}^e)^2}{T_1^2} \quad . \tag{5.39}$$

G. DEPENDENCE ON PARAMETERS OF THE SYSTEM

From this relation for the saturated power and the equivalent expression for the low-level, nonsaturated case (5.35), we can examine the dependence on the parameters of the atom and the cavity.

1. Filling Factor

First of all we see that the output power is proportional to the volume of the cavity, V, and to the square of the filling factor, f_2, defined in Eq. (5.22). The dependence on the square of the filling factor emphasizes the importance of good circuit design.

2. Dipole Moments

The low-level expression (5.35) shows that the output is proportional to the square of the dipole moments of the 1-2 and 2-3 transitions and is independent of the moment of the 1-3 transition – the μ_{13}^2 in the denominator is cancelled by the same term in Q_{m2}. The value of the moment μ_{13} must be large enough to make $1/Q_{m2} \gg 1/Q_0$, however. We see that we desire large dipole moments, especially at the 1-2 and 2-3 transitions. In the saturated case the output is proportional to μ_{13}^2 and is independent of μ_{12} and μ_{23}. We thus see that for high power operation, a large μ_{13} is extremely desirable. For this case μ_{12} and μ_{23} do determine the applied power level necessary to cause saturation from (5.37). The dependence on dipole moments is seen to be critical in both cases. If paramagnetic substances were to be used, this strong dependence on μ would point to the use of materials with large effective spins.

3. Relaxation Times and Concentration

In (5.35) for the unsaturated case T_1, the longitudinal relaxation time does not appear. The transverse relaxation time appears in the form $\tau_{12}^2 \tau_{13}$ – the latter factor is obtained from Q_{m2}. The concentration, N, comes in linearly through Q_{m2}, and so at low power levels a maximization of $N\tau^3$ will result in the maximum nonlinearity. At saturation power levels, the ratio τ^2/T_1^2 points out the desirability of making T_1 and τ as nearly equal as possible (we have the restriction, $T_1 \geq \tau$, from the definition of these quantities). This less strict condition on T_1 should make possible the use of a wider class of materials than maser applications.

Under saturation conditions we find that the power is proportional to the square of the quantity $N\tau$. For high power operation $N\tau$ should be maximized; for low power levels, $N\tau^3$. Since τ generally decreases with concentration, a large change in N usually results in a less significant change in the product $N\tau$, although perhaps it results in a more important change in $N\tau^3$. We here neglect entirely the effects of cross-relaxation.

4. Temperature Dependence

The last major dependence is that of temperature. In the formulation it arises both in the temperature dependence of the relaxation times and in the Boltzmann factor. In the latter case we have

$$\lambda_{11}^{e} - \lambda_{33}^{e} \cong \frac{\hbar\,\Omega_{31}}{3\,kT} \quad ,$$

assuming three levels only. The Boltzmann factor comes in through the magnetic Q , yielding a lower value of Q_{m2} and hence a stronger non-linear effect for lower temperatures. By again assuming low power levels, where (5.35) applies, we see that $P(2\omega)$ varies inversely as the first power of T . For saturated conditions (5.39), the Boltzmann factor introduces a factor of T^{-2} but the temperature dependence of T_1 will in most instances more than cancel the T^{-2} . Hence, low temperature operation has the effect of increasing the magnitude of the nonlinearity for low power levels while increasing the effects of saturation for high power operation. For high power operation no advantage is gained by operating below room temperature unless a material is used in which either T_1 is independent of temperature or where τ also increases with decreasing temperature.

Low temperature operation may, however, be useful in another application, namely mixing. If it were desired, for example, to down-convert from a frequency ω_1 to a lower frequency ω_2 at low signal levels, then a three-level system with suitably placed energy levels could be used. Low temperature operation would increase the magnitude of the nonlinearity as well as reduce circuit noise. The details of this process will not be presented here.

5. Nonresonant Behavior

Throughout this chapter we have assumed that $2\omega = \Omega_{31}$. Such a condition is not required for harmonic generation but does serve to increase the magnitude of the nonlinear effect by reducing the resonance denominator. By operating on resonance, the nonlinearity possesses a resistive character, while off resonance it would be mainly reactive.

Another aspect of off resonance behavior is concerned with the choice of δ . Previously it was shown that $\delta = 1/\tau_{12}$ gave the maximum nonlinearity when saturation was ignored. If saturation is included, we must compare the variation in the nonlinearity given by (5.29),

$$H_2 \propto \frac{\delta\, S_{13}}{\delta^2 + \left(\frac{1}{\tau_{12}}\right)^2} \quad , \tag{5.40}$$

with the more exact saturation expression for S_{13} ,

$$S_{13} = \frac{1}{1 + \dfrac{T_1\, \mu_{12}^2\, H_1^2}{2\, \hbar^2\, \tau_{12} \left[\delta^2 + \left(\frac{1}{\tau_{12}}\right)^2\right]}} \quad . \tag{5.41}$$

In the limits of saturation we have

$$H_2 \propto \delta\, \frac{\tau_{12}}{T_1} \tag{5.42}$$

which shows that the saturation power should increase with increasing δ because the fundamental absorption responsible for saturation is reduced.

In the preceding discussion it has been assumed that the fundamental field, H_1 , is given and is continuously variable. In actual practice, from an applications point of view, it will usually be the case that the level of the fundamental power will be fixed. It is then desirable to maximize the output power for a given input power by varying δ .

To do such a maximization mathematically would be an extremely involved task due to the complicated dependence of the efficiency on δ . Specifically dependent on δ are the Q at the fundamental (5.45), the saturation (5.36) which affects the source Q (5.33), the fundamental Q (5.45) and the output power, (5.39) and finally the dependence not specifically included in the analysis, (5.40). Such a maximization would be most easily accomplished in practice by experimentally varying δ , for example, by altering the direction and magnitude of an applied magnetic field.

H. FUNDAMENTAL ABSORPTION AND CAVITY LOADING

From Eqs. (5.19), (5.7), and (5.8), we have the magnetization at the fundamental:

$$M_1^{(+)} = \frac{N \mu_{12}^2 H_1}{2 \hbar \left[\delta^2 + \left(\frac{1}{\tau_{12}}\right)^2\right]} \left[\delta(\lambda_{11} + \lambda_{33} - 2\lambda_{22}) + \frac{1}{\tau_{12}} (\lambda_{33} - \lambda_{11})\right] , \tag{5.43}$$

where $M_1^{(+)}$ is the component of M_1 varying as $e^{i\omega t}$, and we have again assumed $\mu_{12} = \mu_{23}$ and $\tau_{12} = \tau_{23}$. The first term will, as before, be small, leaving

$$M_1^{(+)} = \frac{i N \mu_{12}^2 H_1 \tau_{12} (\lambda_{33} - \lambda_{11})}{2 \hbar (1 + \delta^2 \tau_{12}^2)} . \tag{5.44}$$

By using the cavity susceptibility, we find that the fundamental loading of the cavity by the sample is given by a Q

$$\frac{1}{Q_1} = \frac{f S_{13}}{Q_{m1} (1 + \delta^2 \tau_{12}^2)} , \tag{5.45}$$

where

$$\frac{1}{Q_{m1}} = \frac{2\pi N \mu_{12} \mu_{21} \tau_{12} (\lambda_{11}^{e} - \lambda_{33}^{e})}{\hbar} , \qquad (5.46)$$

and f is the filling factor. From this we see that the loading is reduced if the filling factor is small or if saturation has occurred, or if the system is detuned, i.e., large δ .

I. RATIO OF FIRST AND SECOND ORDER MAGNETIZATIONS

Upon taking the ratio of the magnitudes of the first and second order magnetizations under the same assumptions leading to the derivation of the power expressions, we find

$$\frac{M_2}{M_1} \approx \frac{\mu_{13} \tau_{13} H_1^2}{4\hbar H_1} . \qquad (5.47)$$

For a magnetic dipole we have $\mu \sim 10^{-20}$, so

$$\frac{M_2}{M_1} \approx 2 \times 10^6 \tau_{13} \frac{H_1^2}{H_1} .$$

If a material had a linewidth corresponding to $\tau_{13} = 0.5 \times 10^{-6}$, or around one megacycle, then for $H_1 = 1$ oe the second order magnetization is comparable to the first. For an electric dipole system with its much larger dipole moments $\mu \sim 10^{-18}$, we would have for the ratio of the polarizations

$$\frac{P_2}{P_1} \approx 10^8 \tau_{13} \frac{E_1^2}{E_1} .$$

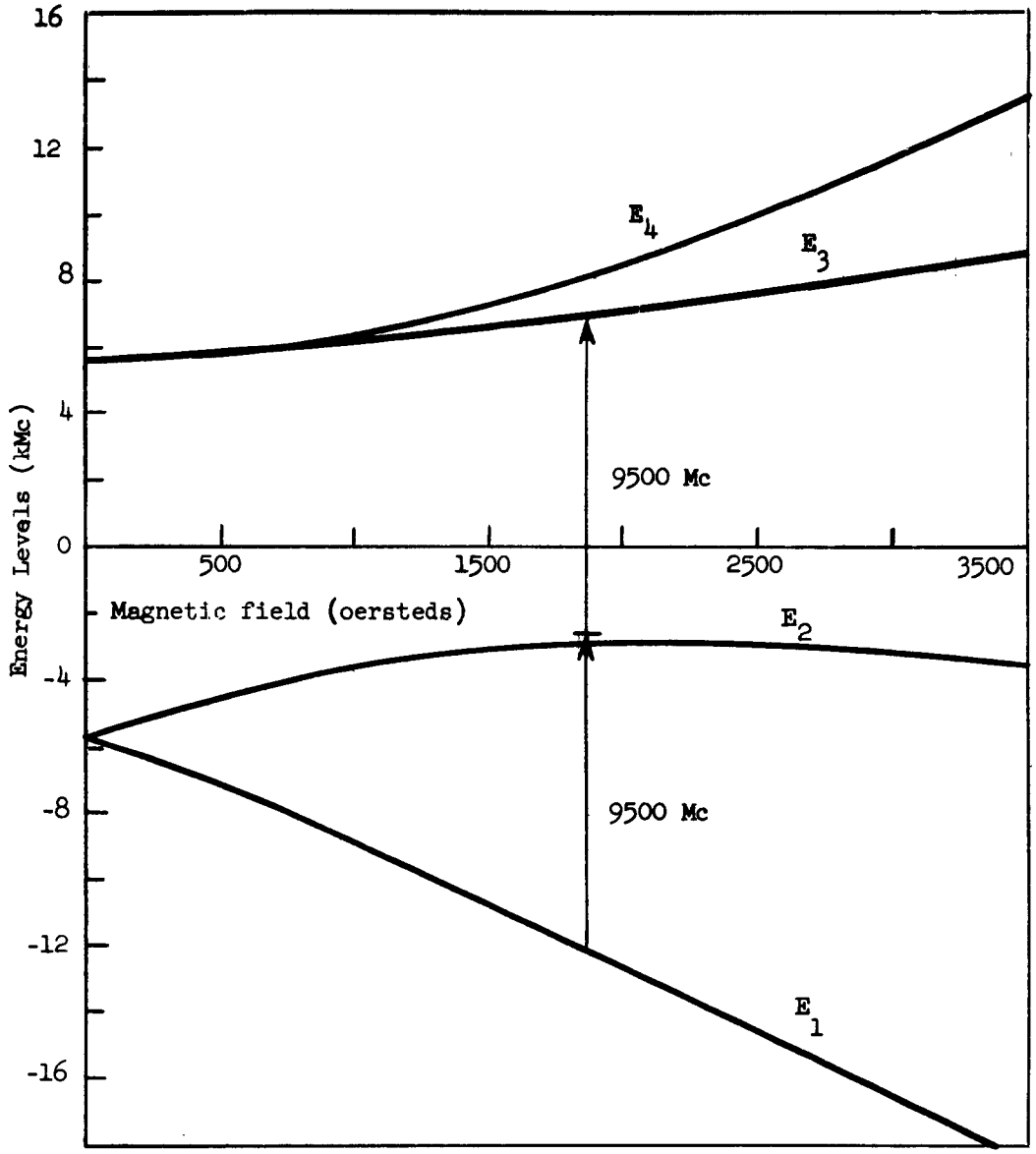


FIG. 5.2--Energy levels for 90° ruby.

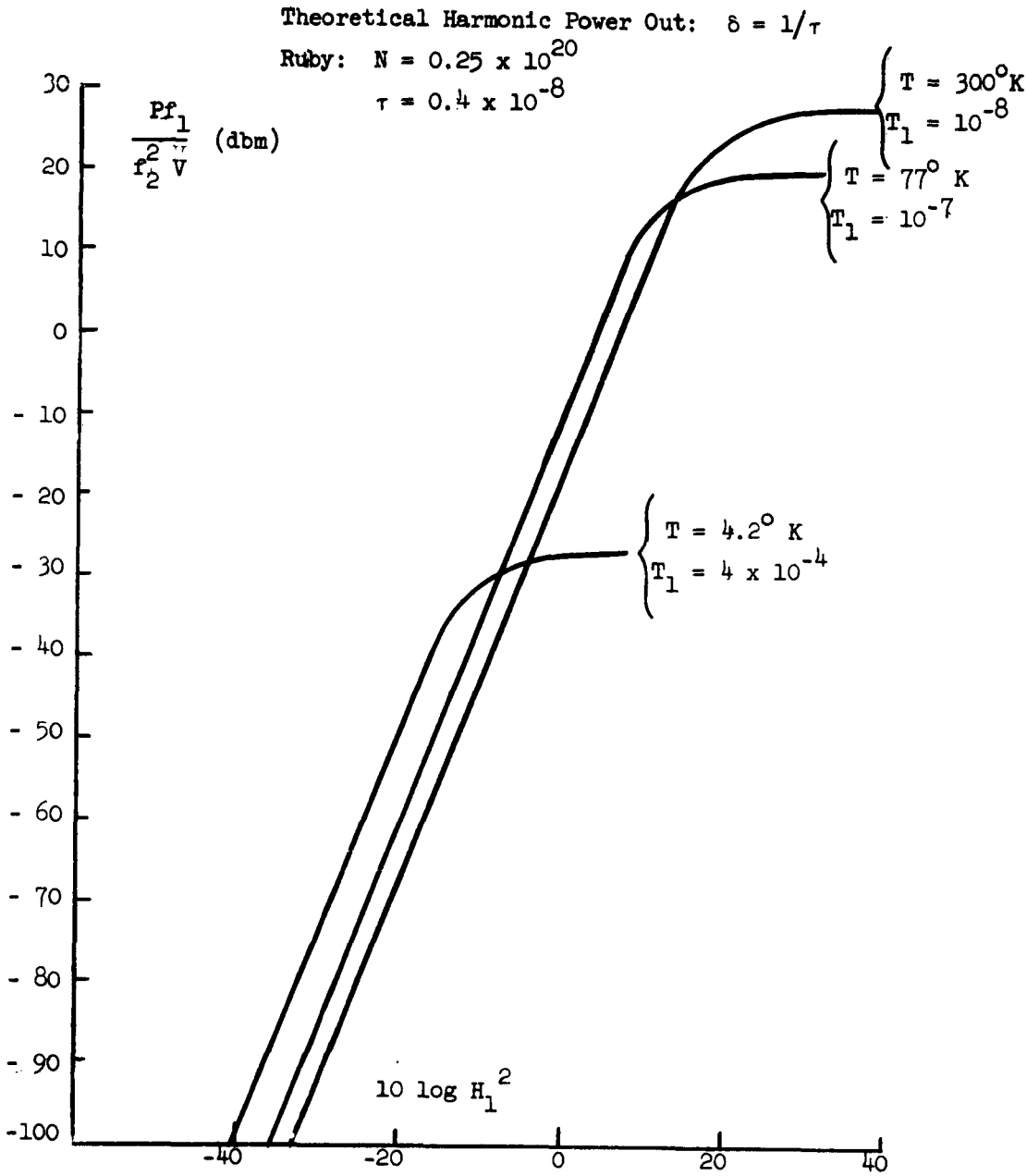


FIG. 5.3--Theoretical harmonic power,

If τ_{13} were 10^{-7} sec, then for $E_1 = 0.1$ esu or 30 volts/cm, we have $P_2 \approx P_1$. An electric dipole system with the desired selection rules and energy levels would thus display an enormous nonlinear effect.

J. EXAMPLE

As a brief example let us consider the use of ruby as the active substance. A plot of the ground state $S = 3/2$ energy levels for H_{dc} at 90° to the c-axis is shown in Fig. 5.2, where the curve is taken from the analytical work of Chang and Siegman.[65] The matrix elements are calculated to be

$$\mu_{12} = \mu_{23} = 2.1\ \mu_B$$

$$\mu_{13} = 1.15\ \mu_B \quad ,$$

where μ_B is the Bohr magneton. We shall take $N = 0.25 \times 10^{20}$ spins/cm^3; then, from Strandberg, the linewidth corresponds to $\tau = 0.4 \times 10^{-8}$ sec. The operating frequency is taken to be 9.5 kMc for the fundamental and 19.0 kMc for the harmonic. With the assumed spin-lattice relaxation times of 10^{-8} sec at 300°K, 10^{-7} sec at 77°K and 4×10^{-4} at 4.2°K and an unloaded cavity Q of 5000, the output power as a function of fundamental field strength is plotted for the three temperature ranges in Fig. 5.3. The increase in low-level power at low temperatures and the effects of saturation are clearly seen in this plot.

K. CONCLUSIONS

We have seen that the three-level system can act as a frequency converter and in particular as a harmonic generator. The dependence on the parameters of the system has been considered and in particular the desire for a short spin-lattice relaxation time has been pointed out. For microwave frequencies the system does not seem as well suited for high power applications as does, for example, a ferrite, but at higher frequencies, using materials with large spin and large crystal field splittings or electric dipole transitions, this system may find use. Perhaps the most useful application of this system would be as a low-level mixer which was mentioned previously.

CHAPTER VI

EXPERIMENTAL EVIDENCE OF THIRD HARMONIC GENERATION IN A TWO-LEVEL SYSTEM

The experiment described in this chapter was undertaken to complement the theoretical work of Chapter III. The primary objective of the experiment was to observe the harmonic generation effect, predicted by the theory and previously unobserved, and, if observable, to obtain as much quantitative and qualitative information as possible. The experiment was successful inasmuch as the effect was indeed observed, giving harmonic powers in excess of 10 milliwatts. The qualitative results generally agreed with predictions, but the quantitative results, in particular the output power, were only in fair agreement with theory.

A. THE OPERATING SUBSTANCE, NH_3

The material used in the verification of the possibility of harmonic generation in a two-level system was ammonia gas. Specifically, use was made of the inversion transition occurring near 24 kMc. The use of ammonia had several advantages: first, it is readily available and fairly easily handled; second, there is extensive knowledge of its spectrum due to previous spectroscopic studies; third, its spectrum displays a very strong absorption line in the neighborhood of 24 kMc which is a convenient frequency range with the equipment available.

It was further decided to perform the experiment for case I[1] where the pump was applied near one-third of the natural frequency of 24 kMc, putting the fundamental in the range of X-band and the third harmonic at K-band.

B. THE CAVITY

In spite of the very strong absorption line in ammonia, the magnitude of the predicted nonlinearity is such as to require a resonant system at

[1] See Chapter III.

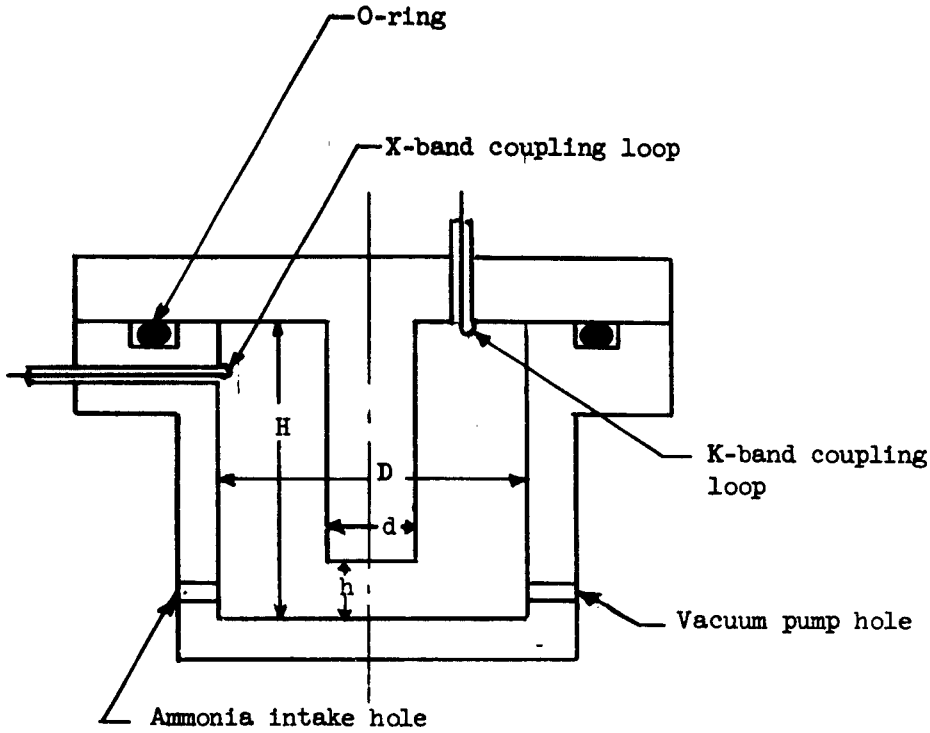
both the fundamental and the harmonic; the former is required in order to get the required fundamental field strengths for reasonable power levels, and the latter is required since the harmonic power output is proportional to the cavity Q at the harmonic. The cavity must then be resonant at ω and 3ω, preferably with high Q's at both frequencies, and must have a region in which the electric fields at the two frequencies are strong and essentially parallel.

The design decided upon was a re-entrant cavity similar to a foreshortened quarter-wave line with the interaction region near the gap. A test cavity was built in which both the height of the cavity and the length of the post were variable. Cold test measurements were made at various frequencies and plots of cavity height vs post height were made for a fixed resonant frequency. This was done both for frequencies near the fundamental and near the third harmonic.

Finally, cavity dimensions giving simultaneous resonances at ω and 3ω were found by comparing the two sets of iso-frequency curves. An intersection satisfying the desired conditions was found as the intersection of the foreshortened $3\lambda/4$ and foreshortened $9\lambda/4$ at the fundamental and harmonic, respectively. A cross section of the cavity is shown in Fig. 6.1 along with the pertinent dimensions.

The coupling to the cavity at both the fundamental and harmonic was achieved by the use of magnetic loops. These in turn were fed from a small coaxial line with an OD of 0.094 in. It was necessary to construct a coaxial-to-waveguide transition for the harmonic in order to be able to work at K-band in the waveguide. The coupling loss at X-band was 1.5 db and at K-band was 5 db, giving a net loss of greater than 6 db.

In order to permit the evacuation of the cavity, "O" rings were inserted in the joint between the base and the top, as shown in Fig. 6.1. The major source of vacuum problems in the cavity resulted from leakage along the center conductor of the coaxial coupling loops. The vacuum conditions were satisfactory for short term operation, but over long periods of time enough air would leak in to cause breakdown. This breakdown will be discussed later.



H = .965"
h = .130"
D = .800"
d = .250"

FIG. 6.1--Cross section of the cavity.

C. EXPERIMENTAL SETUP AND OPERATION

A schematic of the experimental setup is shown in Fig. 6.2. The power source was a 2J51 magnetron operated with a 2 μsec pulse at 50 pps, giving a duty cycle of 10^{-4}. After passing through a directional coupler to lower the power level the signal was put through a low-pass filter in order to remove magnetron harmonics. It was then passed through an attenuator which was used to vary the level of the applied power. The maximum available power was about 1 kw peak. Both the indicent and reflected power were monitored by crystal detectors and an E-H tuner was used to match into the cavity.

On the output side (K-band) the coaxial to waveguide transition was followed by a slide-screw tuner, a frequency meter, a precision attenuator and a crystal detector.

In all the experiments performed, the gas in the cavity was at a constant pressure and was not circulated. In order to determine if the source of the effect was some general property of the gas, dry nitrogen, argon and air were also used in the experiment.

D. EXPERIMENTAL RESULTS

The experiment was performed using four gases; ammonia, air, dry nitrogen, and argon. Only the ammonia gave any harmonic generation under the desired operating conditions. The cavity was matched to the waveguide at the fundamental so that the reflected power was down 10 to 20 db from the incident. Under these circumstances output powers on the order of 10 mw were observed at the third harmonic.

1. Breakdown

Operation at high power levels was frequently limited by breakdown of the gas in the cavity. The input power level at which the cavity broke down was a function of the gas, the operating pressure and the condition of the cavity, especially the input loop. Once breakdown had occurred, the cavity had to be disassembled and cleaned before it could be used again. In some runs maximum power (1 kw) could be applied to the ammonia without breakdown, while in others slight air leaks caused breakdown at low power levels. That the breakdown was due to the air could be

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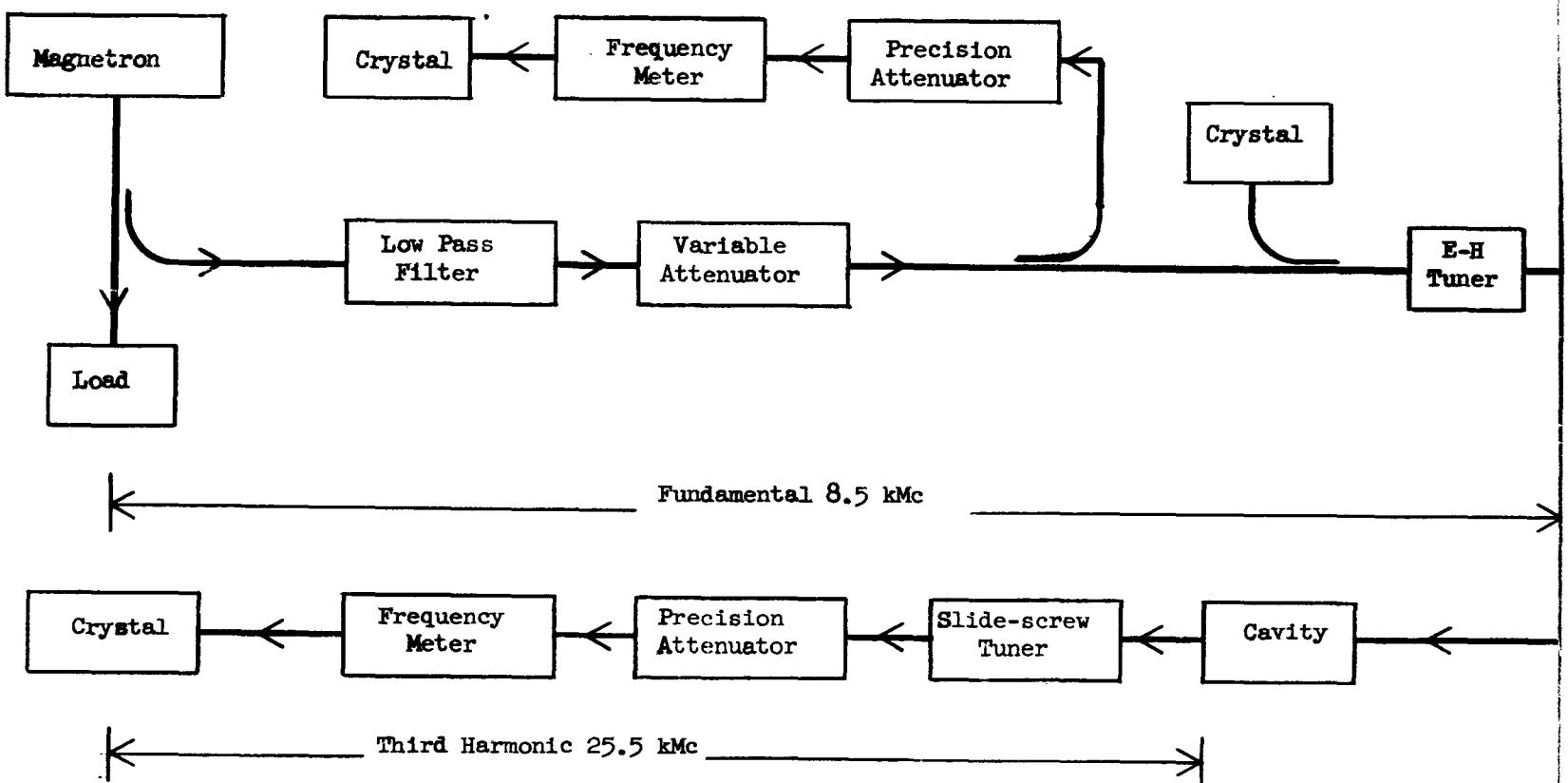

FIG. 6.2--Schematic of experimental setup.

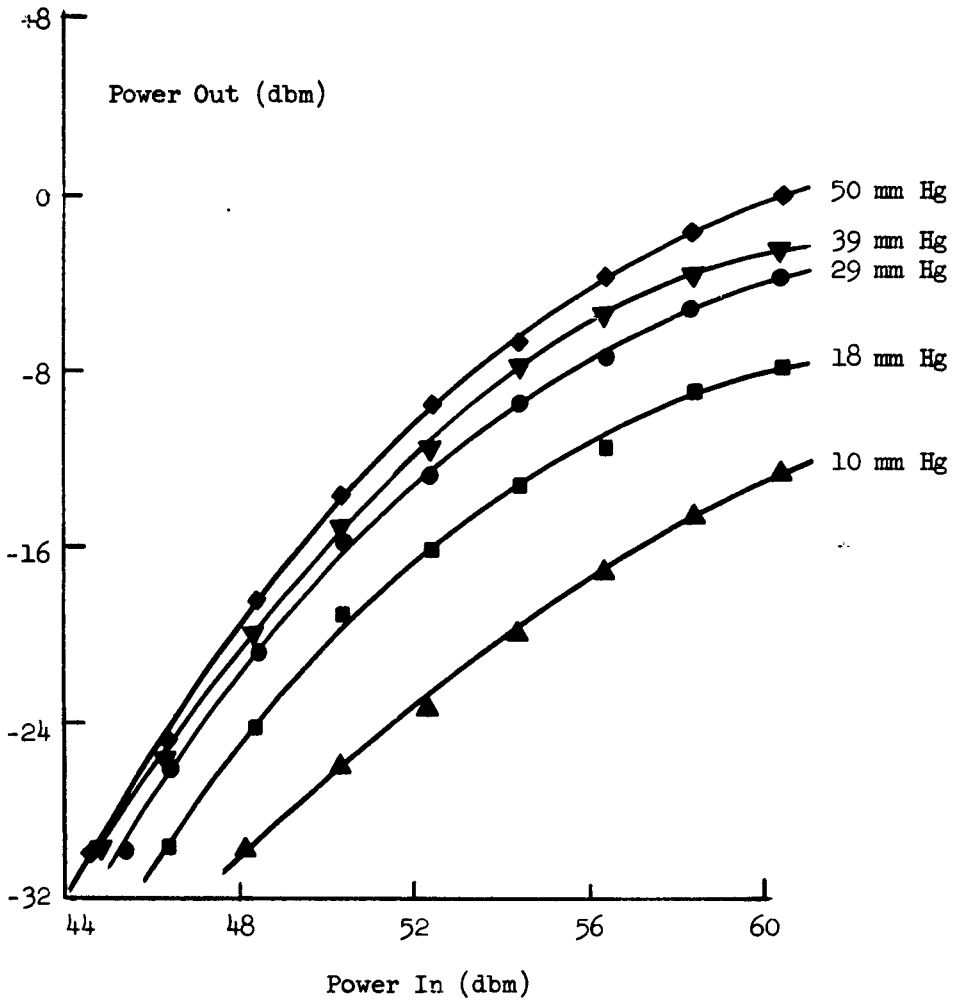

FIG. 6.3--Experimental results for low pressure range.

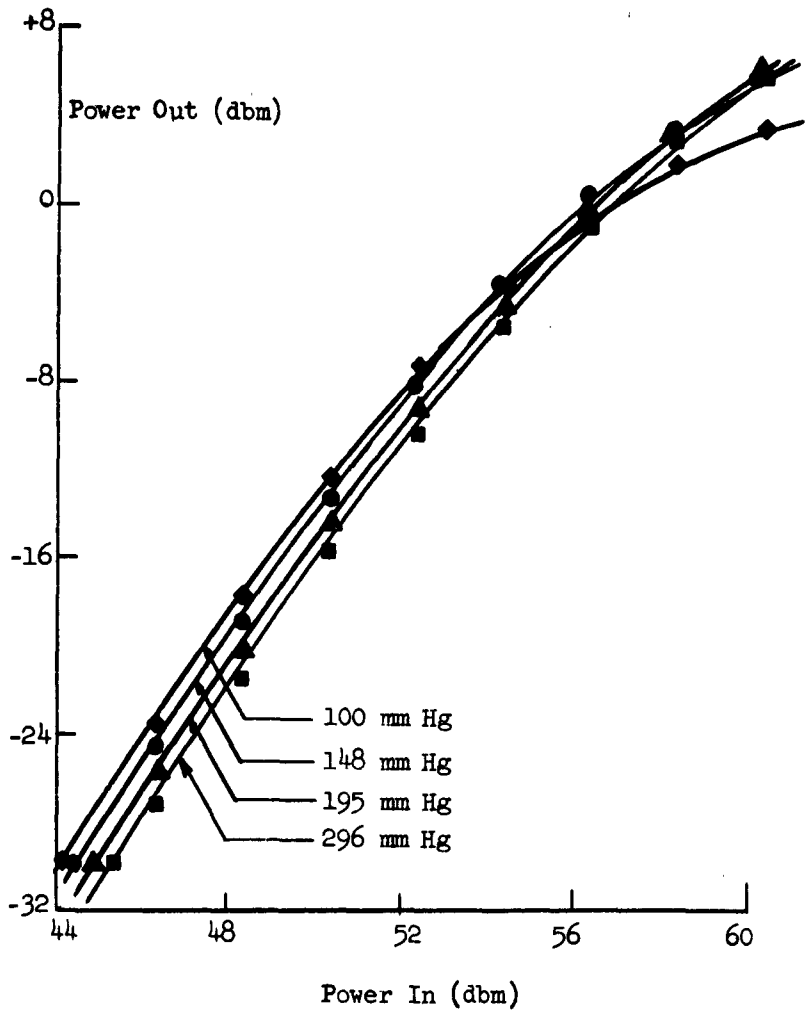

FIG. 6.4--Experimental results for high pressure range.

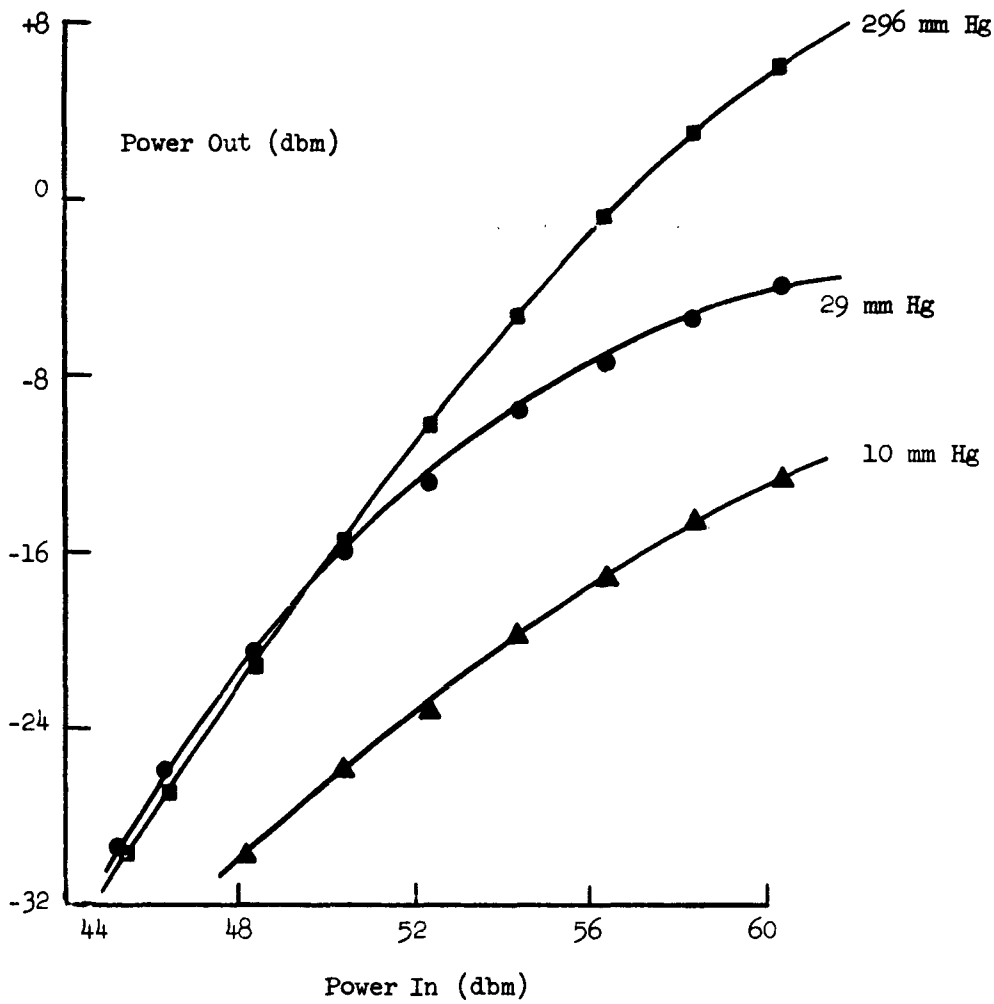

FIG. 6.5--Comparison of results for low and high pressure ranges.

E. DISCUSSION

1. Qualitative

In general, most all of the experimental results qualitatively agree with the theoretical predictions. First of all, for a fixed low input power level the output power increases with pressure up to around 100 mm Hg, after which it is relatively independent of pressure. This is in agreement with the fact that the overall intensity of the ammonia line increases with pressure due to the overlap of the broadened individual components as explained in Chapter III, section H.4. This increase should continue until the width of an individual component approximately equals the overall frequency spread of these components. At the pressure of 100 mm Hg, the full linewidth is 6 kMc, which includes most of the strong components of the line, thus giving a good agreement.

Since the operation corresponds to $3\omega \approx \Omega$, saturation should be caused by the quantum system absorbing the generated harmonic power. In this case the saturation denominator is of the form $(1 + \text{const}\ T_1 T_2 E_1^6)$ where $T_2 = T_1$ and is inversely proportional to pressure and E_1 is the fundamental field strength. The saturation should then be minimized (saturation denominator minimum) for higher pressures. A comparison of the experimental curves shows this to be true, the effects of saturation being minimum at the highest pressure examined, 300 mm Hg.

2. Quantitative

A quantative comparison of the experimental results with theory, in particular the magnitude of the harmonic power, is quite difficult because of the large number of unknown factors in the experimental setup. The most critical unknown is the filling factor, f_2, which depends upon the magnitude and orientation of the fundamental and harmonic fields within the cavity. Because of the use of higher order modes and the irregular geometry of the cavity, the filling factor is not known even approximately. This is further complicated by the fact that the assumption that the interaction occurs only in the gap region appears unjustified. Since the output power depends on f_2^2, this uncertainty is magnified. We shall then only be able to speak in order-of-magnitude terms.

Calculating the field strength in the gap region from a knowledge of R/Q , Q , and the dimensions of the gap gives a value equal to 200 esu at an input power level of 1000 watts. Assuming the interaction to occur in the gap, as originally anticipated, the saturation should be much larger than observed. Further, the power expected from fields of 200 esu is much larger than observed. Evaluating the fields in the other parts of the cavity from a uniform field approximation yields numbers much more in line with the observed output power levels and saturation. This then points to the distinct possibility that the power is generated throughout the cavity and not just in the interaction region. From the results obtained by use of this cavity it is impossible to decide exactly where the interaction takes place.

By assuming some order of magnitude values for the quantities involved, we may make a comparison with theory. Assuming $E_1 = 50$ esu for $P_{in} = 1000$ watts, $V = 6\ cm^3$, $f_2 = 0.1$, $f_1 = 1$, the power expected from the cavity is (from Fig. 3.2, Chapter III) $P(3\omega) = 250$ mw , compared to an observed value of 10 mw. Including the coupling losses of over 6 db, the disagreement is near 6 db, which is well within the limits of the above assumptions.

F. CONCLUSIONS

From this work we can conclude that all evidence points to the existence of the nonlinear effect predicted. The results do not, however, allow a detailed comparison with theory because of the many experimental uncertainties involved. In order to more fully understand the effect and to compare experiment with theory, a much more detailed experiment should be performed. For such an experiment the cavity should be of a regular geometrical shape so that the field configurations are known analytically. In this way both the filling factors and the magnitude of the fields may be found. One possible cavity which might be used is one in which both modes are TEM, such as the shorted coaxial line. For this case the filling factor may approach 0.25. In a practical application, the Fabry-Perot resonator would appear as the best cavity, yielding a high Q and large volume.

CHAPTER VII

EXPERIMENTAL EVIDENCE OF SECOND HARMONIC GENERATION IN A THREE-LEVEL PARAMAGNETIC SYSTEM

In Chapter V, a theory was derived which suggested that it should be possible to obtain a second-order nonlinearity in a three-level system. Such a nonlinearity would allow the mixing of two frequencies ω_1 and ω_2 to obtain their sum and difference frequencies, a special case of which is second harmonic generation. The detailed aspects of this process were considered in Chapter V. Briefly, when the three levels are approximately equally spaced and the selection rules allow transitions between all three levels, then second harmonic generation may occur when the output frequency, 2ω, is equal to the frequency spacing of the extreme levels, $(E_3 - E_1)/\hbar$. By using a paramagnetic ion as the active substance and by varying the magnitude of the applied dc magnetic field as well as its direction relative to the crystal axes, the above requirements can be satisfied. Since this effect had not previously been experimentally observed, a preliminary experiment designed as an attempt to observe the effect was performed. This experiment and the results will now be described.

A. MATERIAL: RUBY

The material used in the experiment was ruby. This was chosen because of its availability and the fact that its spectrum is well known. Chang and Siegman[65] have calculated, from the known spin Hamiltonian, the energy levels and matrix elements, and the latter have been experimentally checked by Ammann.[66] These calculations of Chang and Siegman were used to choose the approximate operating point and no preliminary spectroscopy was done to check their calculations. The ruby sample used was borrowed from R. Morris, and was a cylinder of pink ruby 10 mm in diameter and 2.5 mm high. The c-axis of the crystal was subsequently found by X-ray diffraction techniques to lie 2.5° from the normal to the crystal face.

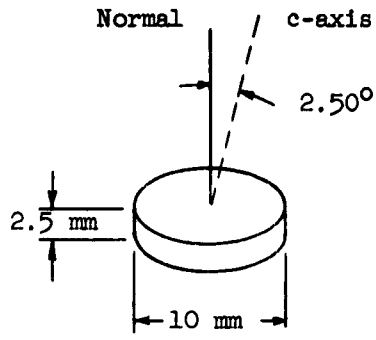

FIG. 7.1--Ruby sample used.

B. OPERATING POINT

Because of the limited availability of rf power sources the operating frequency was chosen to be 9.5 kMc fundamental, and 19.0 kMc harmonic. From Chang and Siegman, an operating point in ruby satisfying the conditions mentioned above and corresponding to the frequency 9.5 kMc should occur with the direction of the dc magnetic field at 90° to the optical or c-axis with magnetic fields of the order of 2000 oersteds. Denoting the ruby c-axis as $\hat{z}$ and the plane of H_0 as the x-z plane, then H_0 is along the x-axis. The strongest matrix elements for the fundamental interaction, corresponding to the 1-2 and 2-3 transitions, are found to be along the y-axis, while those for the harmonic or 1-3 transition are along the dc field or x-axis, the same relative orientation as in the case of second harmonic generation in a ferrite.

C. THE CAVITY

Because of the anticipated low level of the observed harmonic, it was decided to perform the experiment in a microwave cavity resonant at both fundamental and harmonic in order to enhance the magnitude of the effect. It was further decided to place the sample against the wall of the cavity where the rf magnetic fields parallel to the wall would be large. Because of the spatial orthogonality of the fundamental field H_1 and the resultant harmonic magnetic dipole moment $M_2(2\omega)$, it was

necessary to choose cavity modes which would have orthogonal H fields, both of which were parallel to the wall where the sample was to be placed. A piece of rectangular, X-band waveguide shorted at one end and aperture coupled at both the fundamental and second harmonic was used as the cavity (see Fig. 7.2). At the fundamental, the cavity was resonant in the TE_{011} mode, while at the harmonic several closely-spaced modes were available for use. Looking from the X-band aperture, the TM_{120} and TM_{121} were among the suitable modes. In cold test without the ruby sample, the frequencies of these modes were found to lie where they were expected. With the ruby sample in the cavity, however, the modes near the second harmonic were perturbed considerably and the precise determination of the mode configurations was not possible. Since the sample did not affect the X-band resonant frequency significantly (lying in the weak electric field region) it was easy to arrange the dimensions for fundamental resonance. In order to obtain the K-band resonance a movable short was attached to the cavity and the sample was placed on the wall near the short. Due to the large dielectric constant of the ruby ($\epsilon \approx 10$) the K-band fields were drawn into this region and the tuner was made more effective. (Since this waveguide was cut off to the fundamental, it did not affect the X-band resonance.) By this means, a 2:1 ratio of the resonant frequencies was achieved. The loaded Q's at fundamental and harmonic were both 300.

D. EXPERIMENTAL SETUP

A schematic drawing of the experimental setup is shown below in Fig. 7.3. The power source was a 2J51 magnetron operated in a pulsed mode with a pulse repetition rate of 60 pps and a pulse length of 0.38 μsec. A shorting switch was used to measure both the incident power and the power reflected from the cavity under operating conditions. A low pass filter with a rated 40 db rejection was used to reduce the harmonics generated from within the magnetron. A Varian magnet was used to provide the necessary magnetic fields and a simple biased crystal detector was used for detection of the harmonic output power. Under operating conditions the cavity was matched in at the fundamental so that the reflected power was 12 db below the incident.

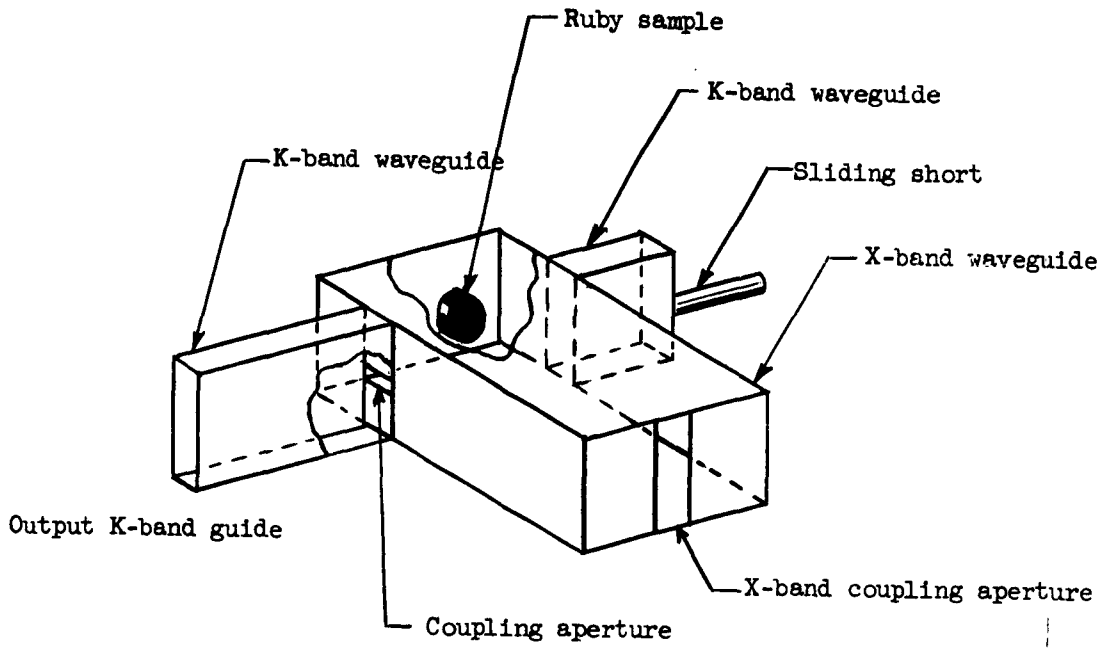

FIG. 7.2--Cutaway drawing of the cavity.

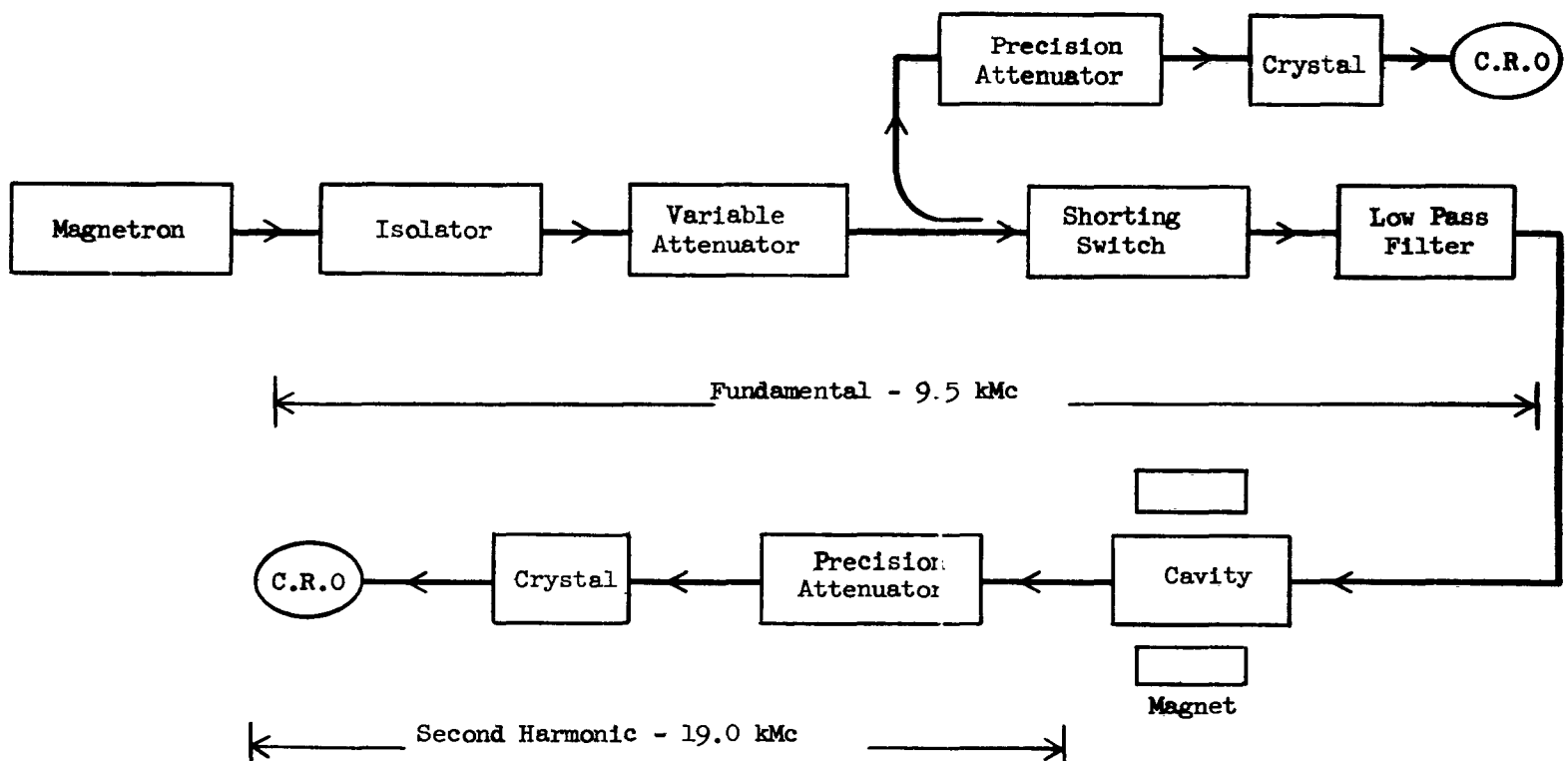

FIG. 7.3--Schematic of experimental setup.

E. RESULTS

The following are the qualitative results of the experiment:

(a) Under the application of several kilowatts of X-band power at 9.503 kMc, harmonic powers on the order of tens of microwatts were observed at 19.006 kMc.

(b) For a fixed level of input power the magnitude of the output power was critically dependent on the magnitude of the applied magnetic field and its angle relative to the crystal axis. No power was observed, to within the level of the detection scheme, when the magnet was off resonance. The width of these resonances was typically 20-30 oe.

(c) As the angle θ of the magnet relative to the crystal axis was varied, the magnetic field at which optimum interaction occurred changed in qualitative agreement with a curve of

$E_3(\theta, H_0) - E_1(\theta, H_0) = \text{const.}$

(d) For a fixed angle θ there appeared three values of magnetic field at which harmonic power occurred, two near 1900 oe and one near 1700 oe. The latter response was small compared to the other two.

F. INTERPRETATION

First of all, from the fact that the harmonic power observed was critically dependent on the magnitude of the magnetic field and its orientation, it is concluded that a nonlinear process within the material itself is responsible for the harmonic generation. From the relatively good agreement between the experimental operating conditions (particularly the value of H_0) and those predicted, it is felt that the nonlinear process described in Chapter V is responsible.

The reasons for the relatively low efficiency are felt to be the following: First and foremost is the fact that the filling factor, f, of the ruby is most probably very small. This arises from the fact that the ruby sample was placed in the cavity so as to allow for enough tuning at K-band to satisfy the 2:1 resonant frequency requirements, and not placed so as to attempt to maximize the filling factor. Since the output power depends on the square of the filling factor, a small value of that quantity would severely reduce the power out. From the sample dimensions and the cavity size the filling factor is at most 0.03 and probably near 0.01.

The second reason for lower efficiency has to do with saturation. Although the sample may not be oriented correctly relative to the fundamental and harmonic fields for optimum harmonic generation (small f), it will still absorb the fundamental power and will tend to saturate. It is felt that saturation had started to occur prior to achieving detectable harmonic power levels at input power levels $\approx$ 200 watts. In a more detailed experiment it would be necessary to know the cavity fields, in the presence of the ruby sample, quite precisely in order to optimize the filling factor.

It should be noted that the requirements on the orientation of the cavity fields are more strict here than in the case of the maser. This is a result of the fact that in a maser the pump signal saturates its transition followed by the amplifying effect at the signal transition. As such, both frequencies need only independently see strong transitions in the crystal, typically in the x-y plane. In the case of harmonic generation, the re-radiation of 2ω photons occurs simultaneously with the absorption of two photons at ω, and hence the relative orientations in space of the fundamental and harmonic cavity fields is critical.

Since the nonlinearity and hence the magnitude of the harmonic generated depends strongly on the location of the middle level relative to the midpoint between the outer levels, and this in turn, for a fixed ω, is dependent on the operating point (θ, H_0), the power out will be a critical function of the operating point. Unfortunately the location of the c-axis was not known to within 3° so no precise knowledge of the operating point was available.

Taking into account the above factors, it is felt that a careful optimization would result in several orders of magnitude improvement in the efficiency.

We may explain the appearance of three operating points where harmonic generation occurred from the following argument: If the expression for the harmonic power were written in general terms where we do not assume that $2\omega = (E_3 - E_1)/\hbar$, then the expressions for output power would contain a general denominator of the form $(2\omega - \Omega_{31})(\omega - \Omega_{21})(\omega - \Omega_{32})$. This presents the possibility of three points of resonant behavior, namely when $2\omega = \Omega_{31}$, $\omega = \Omega_{21}$, $\omega = \Omega_{32}$, for fixed ω. The dependence on angle and magnetic field

of these three operating points is only approximately known and would have to be investigated in detail experimentally. Qualitatively, however, for $\omega/2\pi = 9.5$ kMc and $\theta \approx 90^{\circ}$, the resonance conditions $2\omega = \Omega_{31}$ and $\omega = \Omega_{21}$ should be satisfied for magnetic fields differing only slightly in value, while $\omega = \Omega_{32}$ will be satisfied for a much lower value of H_0. These predictions are a consequence of an analysis of the known data on ruby. The experimental data are again qualitatively in agreement with these predictions. Here, as in the determination of the magnitude of the power output, a precise knowledge of $E_1(\theta, H)$ is needed for any measure of the quantitative agreement.

G. CONCLUSIONS

From the results of this experiment we can conclude that the predicted nonlinear effect does, in fact, exist, but that its magnitude appears to be smaller than anticipated. An exact quantitative comparison was not possible due to the large uncertainty in some of the parameters involved. Such a quantitative experiment should be performed both to better check the theory and to determine the feasibility of possible applications. In such an experiment such things as temperature and concentration dependence as well as the effect of the location of the center level should be examined. In particular, the prediction that optimum harmonic generation occurs when the levels are not equally spaced should prove an interesting check of the theory.

Other experimental work along this line could involve the use of different materials with larger zero-field splittings for use at higher frequencies as well as the examination of materials with faster spin-lattice relaxation times to reduce the effects of saturation. Consideration of processes other than harmonic generation, such as mixing, should also prove interesting.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this research has been to study the phenomena of nonlinear or multiple quantum effects and to discuss possible applications. We have found that a quantum mechanical system with discrete energy levels can behave in a nonlinear as well as in a linear manner. The nonlinear effects occur as a result of interactions which involve more than a single quantum of electromagnetic radiation, whereas the linear effect, used in masers, is a single quantum effect. These multiple quantum phenomena then make it possible to use a suitable quantum system for nonlinear applications.

A general discussion of multiple quantum phenomena and the mechanism of indirect coupling responsible for the effect was presented in Chapter II. Following this discussion, three specific applications were considered: harmonic generation in a two-level system; parametric effects in a two-level system; harmonic generation in a three-level system. Although these are admittedly simple quantum systems, being at best an approximation to the real case, their solutions do yield insight into more complicated systems. Further, in many cases only a few levels will really be of importance in an interaction and the problem can be simplified to a two-, three- or perhaps a four-level problem soluble by the methods presented here.

The general character of these phenomena differ from single quantum, maser-like phenomena. In particular it is found that population inversion is not required for many of the phenomena and that the saturation effects are generally to be avoided. These requirements, along with the strong dependence on the magnitude of the dipole moments involved, make the criteria for the choice of materials different than for maser applications. This may make possible the use of new materials and will require considerable materials research.

The ultimate application of these principles will probably be in the millimeter wave to optical region of the spectrum, where at present suitable nonlinear materials are not known. Using the nonlinear effects discussed here, mixing, modulation, demodulation and other applications should be possible at these frequencies.

Because of the fact that the study of this field is relatively new, little has been done. There then exists much work to do in the future. In particular, more experimentation is needed in order to verify the quantitative aspects of the theory. Should these experimental results appear as promising as the theory indicates, then many and various applications can be considered. When this state is reached an intensive study of materials will have to be made to find suitable ones for the various desired applications.

In summary, this new field appears quite interesting scientifically, both from the point of view of providing a better understanding of radiation processes and from the application standpoint. Much research is needed, however, before the ultimate feasibility of application is known.

APPENDIX A

THE DENSITY MATRIX

It is the purpose of this appendix to familiarize the reader with some aspects of the density matrix, in particular its description of the interaction of radiation with matter. No attempt will be made to prove the relations stated; for those interested in proofs and further details, references 67-71 may be consulted.

Let us suppose we have a series of possible states of the atom ψ_i which we may expand in terms of a complete set of kets $|n\rangle$

$$\psi_i = \sum_n a_{in} |n\rangle \quad . \qquad (A.1)$$

The expectation value of an operator Q in the state ψ_i is defined as

$$\langle Q\rangle_i = \langle \psi_i | Q | \psi_i \rangle \quad . \qquad (A.2)$$

In terms of the kets $|n\rangle$ this may be written

$$\langle Q\rangle_i = \sum_{n,m} a^*_{in} a_{im} \langle n|Q|m\rangle$$

$$= \sum_{n,m} a^*_{in} a_{im} Q_{nm} \quad , \qquad (A.3)$$

where

$$Q_{nm} = \langle n|Q|m\rangle \quad . \qquad (A.4)$$

If the atom may be in one of a group of states ψ_i with a probability ω_i , where we have the obvious restriction

$$\sum_i \omega_i = 1 \qquad , \qquad (A.5)$$

then the expectation value of the operator Q in the arbitrary state ψ is

$$\langle\psi|Q|\psi\rangle = \sum_i \omega_i \langle Q\rangle_i \qquad , \qquad (A.6)$$

where we have taken into account the statistical behavior of matter as well as the intrinsic statistical nature of quantum mechanics, Eq. (A.3). By substituting Eq. (A.3) in Eq. (A.6), we obtain

$$\langle Q\rangle = \sum_i \sum_{n,m} \omega_i a^*_{in} a_{im} Q_{nm} \qquad . \qquad (A.7)$$

Define the density matrix ρ as

$$\rho_{mn} = \sum_i \omega_i a^*_{in} a_{im} \qquad , \qquad (A.8)$$

and then

$$\langle Q\rangle = \sum_{n,m} \rho_{mn} Q_{nm} \qquad . \qquad (A.9)$$

By performing the sum over n , we have

$$\langle Q\rangle = \sum_m (\rho Q)_{mm} \qquad (A.10)$$

$$= \mathrm{Tr}\,(\rho Q) \qquad , \qquad (A.11)$$

which gives the prescription for finding the expectation value of an observable.

We shall state, without proof, two additional properties of the density matrix which we shall use:

(a) $\mathrm{Tr}\,\rho = 1$,

or

$$\sum_n \rho_{nn} = 1 \quad ; \tag{A.12}$$

(b) $\rho_{nm} = \rho^*_{mn}$. (A.13)

The first relation states that the sum of the diagonal elements is unity. If we should use the energy representation where our kets are the eigenkets of $\mathcal{H}_0$, the unperturbed Hamiltonian, then the numbers ρ_{nn} may be interpreted as occupation numbers of the various states, n , normalized to a single molecule. In this representation it is easily seen that each diagonal element is non-negative; this is true in general, however, for any representation.

The second relation merely states that the density matrix is Hermitian. This simplifies solving for the density matrix as it reduces by half the number of off-diagonal elements to be found.

We should like to now find the time development of the density matrix. Let us divide the Hamiltonian into three parts:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + V \quad . \tag{A.14}$$

The first term is the Hamiltonian of the atom, including the possibility of static magnetic fields, and is time-independent. The second term, $\mathcal{H}'$, shall represent the perturbation due to electromagnetic radiation. The third term, V , represents the interaction between the atoms and the lattice and between the atoms themselves and will give rise to spin-lattice and spin-spin relaxation.

By explicitly writing down the components of the density matrix, taking their time derivatives, and using Schrödinger's equation, the equation of motion for ρ can be shown to be

$$i\hbar\dot{\rho} = [\mathcal{H},\rho] \quad , \qquad (A.15)$$

where $[\mathcal{H},\rho]$ is the commutator of these quantities. We shall now assume we are in the energy representation,

$$(\mathcal{H}_0)_{nm} = E_m \, \delta_{nm} \quad , \qquad (A.16)$$

and shall for the time being neglect the interaction V in the Hamiltonian. The equations then become

$n = m$:

$$i\hbar\dot{\rho}_{nn} = \sum_k (\mathcal{H}'_{nk} \, \rho_{kn} - \rho_{nk} \, \mathcal{H}'_{kn}) \quad , \qquad (A.17)$$

and

$n \neq m$:

$$i\hbar\dot{\rho}_{nm} = (E_n - E_m)\rho_{nm} + \sum_k (\mathcal{H}'_{nk} \, \rho_{km} - \rho_{nk} \, \mathcal{H}'_{km}) \quad . \qquad (A.18)$$

These equations suffer from the fact that they do not give the correct equilibrium value for ρ in the limit $\mathcal{H}' \to 0$. It is shown in texts on the subject that in thermal equilibrium the density operator is given by

$$\rho = \frac{\exp\,(-\mathcal{H}_0/kT)}{\mathrm{Tr}\,\exp(-\mathcal{H}_0/kT)} \quad . \qquad (A.19)$$

From this expression we see that the off-diagonal elements are zero

while the diagonal elements are given by

$$\rho_{nn} = \frac{\exp\,(-\,E_n/kT)}{\sum_m \exp\,(-\,E_m/kT)} \quad . \qquad (A.20)$$

From Eqs. (A.17) and (A.18) it is seen that if the system is perturbed from equilibrium and the perturbation is removed, then ρ_{nn} will remain constant while ρ_{nm} will oscillate sinusoidally with a frequency $\omega = (E_n - E_m)/\hbar$ which is not in agreement with (A.19). The reason for this is that the relaxation mechanisms which give rise to thermal equilibrium have been neglected. As the exact nature of the perturbation V is not known, its effects are usually phenomenologically added via longitudinal and transverse relaxation times, T_{ij} and τ_{ij}, respectively.

With the transverse relaxation times added, the off-diagonal equations become

$n \neq m$:

$$i\hbar\dot{\rho}_{nm} + (E_m - E_n)\rho_{nm} + \frac{i\hbar}{\tau_{nm}}\rho_{nm} = \sum_k (\mathcal{H}'_{nk}\,\rho_{km} - \rho_{nk}\,\mathcal{H}'_{km}) \;, \qquad (A.21)$$

where to satisfy hermiticity we require $\tau_{nm} = \tau_{mn}$. By the insertion of this relaxation term, ρ_{nm} is seen to decay to zero when $\mathcal{H}' = 0$, as required by (A.19).

For the diagonal equations we introduce the transition probability, W_{ij}, defined as the probability per unit time that the system will make a transition from state i to state j due to relaxation processes. The diagonal equations then become

$m = n$:

$$i\hbar\dot{\rho}_{nn} = i\,\hbar \sum_k (\rho_{kk}\,W_{kn} - \rho_{nn}\,W_{nk}) + \sum_k (\mathcal{H}'_{nk}\,\rho_{kn} - \rho_{nk}\,\mathcal{H}'_{kn}) \quad . \qquad (A.22)$$

In the absence of radiation fields, $\mathcal{H}' \to 0$, we demand ρ_{nn} tend to its equilibrium value ρ^e_{nn} given by Eq. (A.19). At equilibrium we have $\dot{\rho}_{nn} = 0$ for all n , putting a condition on the relaxation terms

$$\sum_k (\rho^e_{kk} W_{kn} - \rho^e_{nn} W_{nk}) = 0 \quad , \text{all } n \qquad . \qquad (A.23)$$

It is then assumed that the sum vanishes term by term, (the principle of detailed balance) giving

$$\rho^e_{kk} W_{kn} - \rho^e_{nn} W_{nk} = 0 \quad , \text{all } n , k \qquad . \qquad (A.24)$$

We then define a relaxation time $T_{nk} = T_{kn}$ by

$$\frac{\rho^e_{kk}}{W_{nk}} = \frac{\rho^e_{nn}}{W_{kn}} = T_{nk} \qquad . \qquad (A.25)$$

In words, these two forms of relaxation times have the following interpretation:

(a) The transverse relaxation time τ_{ij} gives the decay time of the term ρ_{ij} which is a measure of the correlation between states i and j and is the usual T_2 of paramagnetic resonance terminology. It is proportional to the inverse of the linewidth of the transition $i \to j$.

(b) The longitudinal relaxation time T_{ij} is a measure of the time required for the transition $i \to j$ to thermalize with the lattice and is the T_1 of paramagnetic resonance.

We may make a simplification of Eq. (A.22) if we assume all longitudinal relaxation times equal to T_1 . In this case we have

$$i\hbar\dot{\rho} + \frac{i\hbar}{T_1}(\rho_{nn} - \rho^e_{nn}) = \sum_k (\mathcal{H}'_{nk} \rho_{kn} - \rho_{nk} \mathcal{H}'_{kn}) \qquad . \qquad (A.26)$$

Equations (A.21) and (A.22) constitute the density matrix formulation of the interaction of radiation with matter. In principle, when solved, they will give us all the information we need to analyze the problems herein considered.

APPENDIX B

RELATION BETWEEN THE DENSITY MATRIX EQUATIONS OF MOTION AND THE RATE EQUATIONS

Consider an M-level quantum mechanical system. The equations of motion for this system in terms of the density matrix are

$n = m$:

$$i\hbar\dot{\rho}_{nn} = i\hbar \sum_{k=1}^{M} (\rho_{kk} W_{kn} - \rho_{nn} W_{nk}) + \sum_{k=1}^{M} (\mathcal{H}_{nk} \rho_{kn} - \rho_{nk} \mathcal{H}_{kn}) \quad , \tag{B.1}$$

$n \neq m$:

$$i\hbar\dot{\rho}_{nm} + (E_m - E_n) \rho_{nm} + \frac{i\hbar}{\tau_{nm}} \rho_{nm} = \sum_{k=1}^{M} (\mathcal{H}_{nk}\rho_{km} - \rho_{nk} \mathcal{H}_{km}) \quad , \tag{B.2}$$

where the matrices are taken with respect to the eigenkets of the unperturbed Hamiltonian, $\mathcal{H}_0$, (energy representation). The quantity W_{kn} is the probability per unit time that the system will go from state k to n due to relaxation mechanisms. The quantities $\tau_{nm} = \tau_{mn}$ are the transverse relaxation times which are related to the linewidth of a Lorentzian line by $\tau_{nm} = 1/\pi \Delta \nu_{nm}$, where $\Delta \nu_{nm}$ is the full linewidth at half intensity.

Let us assume that the applied perturbations vary sinusoidally in time and that no more than one of these frequencies is near any allowed transition. We may then write the perturbation in the form

$$\mathcal{H}_{nk} = \mathcal{H}'_{nk} \left(e^{i\omega_{nk}t} + e^{-i\omega_{nk}t} \right) \quad , \tag{B.3}$$

where $\omega_{nk} \approx \Omega_{nk}$ and[1]

$$\Omega_{nk} = \frac{E_n - E_k}{\hbar} \quad . \tag{B.4}$$

Under these assumptions the solutions to (B.2) to first order in the perturbation are

$$\rho_{nm} = \frac{\mathcal{H}'_{nm}}{\hbar} \frac{(\rho_{mm} - \rho_{nn})\, e^{i\omega_{mn} t}}{(\Omega_{mn} - \omega_{mn}) + \frac{1}{\tau_{mn}}} \quad . \tag{B.5}$$

Substituting (B.5) into (B.1) gives

$$\dot{\rho}_{nn} + \sum_{k=1}^{M} (\rho_{nn} W_{nk} - \rho_{kk} W_{kn}) = \sum_{k=1}^{M} \frac{\mathcal{H}'_{nk} \mathcal{H}'_{kn}}{\hbar^2} (\rho_{kk} - \rho_{nn}) \frac{2\tau_{nk}}{1 + \tau_{nk}^2 (\Omega_{nk} - \omega_{nk})^2} \quad . \tag{B.6}$$

By defining the quantities

$$\Gamma_{nk} = \frac{\mathcal{H}'_{nk} \mathcal{H}'_{kn}}{\hbar^2} \cdot \frac{2\tau_{nk}}{1 + \tau_{nk}^2 (\Omega_{nk} - \omega_{nk})^2} \quad , \tag{B.7}$$

the equations for the diagonal components become

$$\dot{\rho}_{nn} + \sum_{k=1}^{M} (\rho_{nn} W_{nk} - \rho_{kk} W_{kn}) + \sum_{k=1}^{M} \Gamma_{nk} (\rho_{nn} - \rho_{kk}) = 0 \quad , \tag{B.8}$$

where the quantities Γ_{nk} represent the transition probabilities due to the applied radiation fields.

---

[1] By convention we have $\Omega_{nk} = -\Omega_{kn}$ and $\omega_{nk} = -\omega_{kn}$.

If we consider a system containing N identical independent systems, then the population density or the number of systems in the level i is given by

$$n_i = N\rho_{ii} \quad . \tag{B.9}$$

Multiplying (B.8) by N and using (B.9) gives

$$\dot{n}_i + \sum_{k=1}^{M} (n_i W_{ik} - n_k W_{ki}) + \sum_{k=1}^{M} \Gamma_{ik} (n_i - n_k) = 0 \quad , \tag{B.10}$$

which is recognized as the familiar rate equation.[2]

Thus the rate equations are equivalent to the diagonal equations of the density matrix.

APPENDIX C

DERIVATION OF JAYNES' NEOCLASSICAL EQUATIONS FROM THE DENSITY MATRIX

In showing the equivalence between Jaynes' semiclassical equations[62] and formulation in terms of the density matrix we shall begin with the equations of motion for a two-level quantum system neglecting the effects of relaxation terms. Let the energy levels be as shown in Fig. C.1,

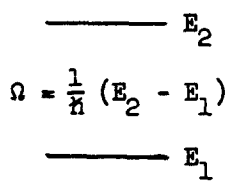

FIG. C.1--Energy level diagram for a two-level system.

and take the form of the Hamiltonian to be

$$\mathcal{H}'_{12} = \mathcal{H}'_{21} = -\mu E \quad ,$$

$$\mathcal{H}'_{11} = \mathcal{H}'_{22} = 0 \quad . \qquad \text{(C.1)}$$

In the energy representation the equations of motion become

$$\dot{\rho}_{11} = -\frac{\mu E}{i\hbar}(\rho_{21} - \rho_{12}) \qquad \text{(C.2a)}$$

$$\dot{\rho}_{22} = -\frac{\mu E}{i\hbar}(\rho_{12} - \rho_{21}) \qquad \text{(C.2b)}$$

and

$$\dot{\rho}_{12} - i\,\Omega\,\rho_{12} = -\frac{\mu E}{i\hbar}(\rho_{22} - \rho_{11}) \tag{C.2c}$$

$$\dot{\rho}_{21} + i\,\Omega\,\rho_{21} = -\frac{\mu E}{i\hbar}(\rho_{11} - \rho_{22}) \quad . \tag{C.2d}$$

The expectation value of the dipole moment M is given by

$$M = \langle \mu_{op} \rangle = \mu\,(\rho_{12} + \rho_{21}) \quad , \tag{C.3}$$

where $\mu = \text{const} = \mu_{12} = \mu_{21}$. The energy of the unperturbed Hamiltonian relative to a zero of energy lying midway between the levels is denoted by W and is given by

$$W = \langle \mathcal{H}_0 \rangle = \frac{1}{2}\hbar\,\Omega\,(\rho_{22} - \rho_{11}) \quad . \tag{C.4}$$

The first derivatives of these quantities are found to be

$$\begin{aligned} \dot{M} &= \mu\,(\dot{\rho}_{12} + \dot{\rho}_{21}) \\ &= i\,\Omega\,\mu\,(\rho_{12} - \rho_{21}) \quad , \end{aligned} \tag{C.5}$$

and

$$\begin{aligned} \dot{W} &= \frac{1}{2}\hbar\,\Omega\,(\dot{\rho}_{22} - \dot{\rho}_{11}) \\ &= i\,E\,\Omega\,\mu\,(\rho_{12} - \rho_{21}) \quad , \end{aligned} \tag{C.6}$$

where we have used the equations of motion (C.2) to eliminate the time derivatives. From (C.5) and (C.6) we may derive the first of Jaynes' equations:

$$\dot{W} = E\,\dot{M} \quad . \tag{C.7}$$

Taking the time derivative of (C.5), we have

$$\ddot{M} = i\,\Omega\,\mu\,(\dot{\rho}_{12} - \dot{\rho}_{21})$$

$$= -\,\Omega^2\,\mu\,(\rho_{12} + \rho_{21}) + \left(\frac{2\mu}{\hbar}\right)^2 \frac{\hbar\Omega E}{2}\,(\rho_{11} - \rho_{22}) \quad ,$$

and by substituting from (C.3) and (C.4) we obtain

$$\ddot{M} + \Omega^2\,M = -\left(\frac{2\mu}{\hbar}\right)^2 W\,E \qquad . \qquad (C.8)$$

These two equations, (C.7) and (C.8), constitute two of Jaynes' neoclassical equations. The first, (C.7), states that the rate of increase in the energy of the quantum system, $\dot{W}$, is equal to the product of a field, E , and a current $\dot{M}$. The second, (C.8), describes the time development of the dipole moment, M , which is seen to be the equation of an undamped harmonic oscillator driven by the field E through a coupling constant proportional to W . These form a set of coupled nonlinear differential equations and have been proposed by Jaynes as a method of studying the interaction of radiation with matter.

The third equation is simply a description of how the resultant dipole moment M generates the fields E and may be written in many forms. The one used in this paper is simply to define a complex cavity susceptibility $(\chi_c' = \chi_c' - i\chi_c'')$ and then to relate the dipole moment M to the field E by

$$E = \frac{1}{\chi_c}\,M \qquad . \qquad (C.9)$$

We may phenomenologically add relaxation terms to (C.7) and (C.8) in the following way. First consider (C.7) which describes the energy of the system, and let the characteristic time in which it can exchange energy with the "lattice," or thermalize, be T_1 . Then in the absence of a perturbation, $E = 0$, the system will return to thermal equilibrium

if we add a term $(W - W^e)/T_1$, giving

$$\dot{W} + \frac{W - W^e}{T_1} = E\,\dot{M} \qquad . \qquad (C.10)$$

The equation for M , (C.8), may be altered to account for relaxation mechanisms if we add a term $2\dot{M}/T_2$ in the form of a damping term. This predicts a decay time of T_2 for the dipole moment. The modified equation is

$$\ddot{M} + \frac{2}{T_2}\dot{M} + \Omega^2 M = -\left(\frac{2\mu}{\hbar}\right)^2 E\,W \qquad . \qquad (C.11)$$

If we add the same terms to the density matrix we get the modified equations including relaxation

$$\dot{\rho}_{11} + \frac{(\rho_{11} - \rho_{11}^e)}{T_1} = -\frac{\mu E}{i\hbar}(\rho_{21} - \rho_{12}) \qquad (C.12a)$$

$$\dot{\rho}_{12} - i\,\Omega\,\rho_{12} + \frac{1}{T_2}\rho_{12} = -\frac{\mu E}{i\hbar}(\rho_{22} - \rho_{11}) \quad , \qquad (C.12b)$$

where we have included only one diagonal and one off-diagonal equation. From these equations we find the following derived equations

$$\dot{W} + \frac{W - W^e}{T_1} = E(\dot{M} + \frac{1}{T_2}M) \qquad (C.13)$$

$$\ddot{M} + \frac{2}{T_2}\dot{M} + \left(\Omega^2 + \frac{1}{T_2^2}\right)M = -\left(\frac{2\mu}{\hbar}\right)^2 E\,W \qquad . \qquad (C.14)$$

Upon comparing these with (C.10) and (C.11), we see that they differ slightly in that they have additional terms proportional to $1/T_2$ and $(1/T_2)^2$. This is not unexpected since the terms were added phenomenologically

and cannot be expected to be valid when their effect is large. If T_2 is not too small, we see that the additional terms are negligible since the natural frequencies $\Omega \sim 10^{11}$ and T_2 is typically 10^{-9}. By neglecting small quantities we see that (C.13) and (C.14) are the same as (C.10) and (C.11).

In studying the interaction of radiation with a two-level system we can either use the density matrix equations (C.12) or Jaynes' equations with relaxation added (C.10) and (C.11).

It should also be mentioned in passing that Feynman, et al.,[72] have shown that for the two-level system one can write the equations of motion in general as:

$$\dot{\underset{\sim}{r}} = \underset{\sim}{\omega} \times \underset{\sim}{r} \quad , \qquad (C.15)$$

where

$$\underset{\sim}{r} = (r_1 , r_2 , r_3) \quad , \qquad (C.16)$$

$$\omega = (\omega_1 , \omega_2 , \omega_3) \quad , \qquad (C.17)$$

and

$$\begin{aligned} r_1 &\equiv \rho_{12} + \rho_{21} \\ r_2 &\equiv i(\rho_{21} - \rho_{12}) \\ r_3 &\equiv \rho_{22} - \rho_{11} \quad , \end{aligned} \qquad (C.18)$$

and

$$\begin{aligned} \omega_1 &= (V_{12} + V_{21})/\hbar \\ \omega_2 &= i(V_{21} - V_{12})/\hbar \\ \omega_3 &= \Omega \quad . \end{aligned} \qquad (C.19)$$

No use will be specifically made of these equations in the form (C.15); they are merely mentioned for completeness.

APPENDIX D

DERIVATION OF THE ABSORPTION COEFFICIENT

If we have an electromagnetic field propagating with the velocity c, the energy flow is given by the Poynting vector

$$\underset{\sim}{S} = \frac{c}{4\pi} \underset{\sim}{E} \times \underset{\sim}{H} \quad , \qquad (D.1)$$

which for $\underset{\sim}{E}$ perpendicular to $\underset{\sim}{H}$ is

$$|S| = \frac{c}{4\pi} E^2 \quad . \qquad (D.2)$$

Performing a time average results in

$$|\bar{S}| = \frac{c}{8\pi} E_0^2 \text{ (ergs/cm}^2\text{)} \quad , \qquad (D.3)$$

where we have assumed $E = E_0 \cos \omega t$.

If we have a sample which has a resonance at this frequency, the density of power absorbed in the absence of saturation is

$$P = \frac{\omega N \Delta^e T_2 \mu^2 E_0^2}{2\hbar} \text{ (ergs/cm}^3\text{)} \quad . \qquad (D.4)$$

Considering a volume 1 cm square and dz long, the power absorbed is

$$dP = \frac{\omega N \Delta^e T_2 \mu^2 E_0^2}{2\hbar} dz \text{ (ergs)} \quad . \qquad (D.5)$$

The absorption coefficient is defined as

$$\gamma = \frac{-\frac{dP}{dz}}{P} \quad , \qquad (D.6)$$

where $-dP/dz$ is the power absorbed per unit length. Using (D.3) and (D.5) in (D.6) gives[1]

$$\gamma = \frac{\omega}{c} \frac{4\pi N\Delta^e T_2 \mu^2}{\hbar} \quad , \qquad (D.7)$$

or

$$\gamma = \frac{\omega}{c} \frac{1}{Q_s} \quad , \qquad (D.8)$$

where Q_s is the sample Q defined in Chapter III.

---

[1] See Gordy, et al.,[73] Eqs. (4.10), (4.14), and (4.15a).

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