PHYSICAL REVIEW B VOLUME 8, NUMBER 8 15 OCTOBER 1973

Theory of Second-Harmonic Generation at Microwave Frequencies by Paramagnetic Materials

F. Persico and G. Vetri

Istituto di Fisica dell'Università and Gruppo di Fisica Teorica del Gruppo Nazionale di Struttura della Materia, Consiglio Nazionale delle Ricerche, Palermo, Italy

(Received 5 February 1973)

A quantum-mechanical theory of second-harmonic generation in paramagnetic materials is developed when the incoming radiation is in the microwave range, and it is shown to be in agreement with the experimental results of other authors. The theory is also compared with a density-matrix approach based on phenomenological relaxation times, previously developed by Boscaino *et al.* A qualitative model of the phenomenon of second-harmonic generation is discussed, and as a by-product of this work, approximate analytical solutions are obtained of the eigenvalue problem of a set of two-level systems coupled to a strong monocromatic field.

I. INTRODUCTION

When a field of electromagnetic radiation is present in a region of space occupied by a system of few-level objects which can interact with the radiation itself, absorption and emission processes of quanta of the field by the objects can occur, if suitable conservation rules which stem from the invariance properties of the Hamiltonian of the system happen to be satisfied. At the same time, the internal state of each of the few-level objects may be thought to change in connection with the changes induced in the electromagnetic field. If the degrees of freedom of the radiation field are not too highly excited, the behavior of the system may be described as approximately "linear," in the sense that frequency-mixing processes, with the appearance of radiation of frequency different from that initially present, should be negligible. On the contrary, when the occupation numbers of photons interacting with the few-level objects become high enough, one would expect "nonlinear" aspects of the interaction between electromagnetic radiation and matter to show up in the form, for example, of the frequency-converting processes described above.

A range of frequency particularly suitable for experimental observations of phenomena of this kind is the microwave region, because of the great amount of experience which has been accumulated in the last thirty years in the field of microwave spectroscopy and of the sophisticated experimental and theoretical techniques which have been developed in connection with ESR experiments. Along these lines, the first experimental work was performed by Boscaino *et al.*[1] in 1968, by subjecting a set of paramagnetic atoms, contained as impurities in a host crystal, to a strong electromagnetic field of frequency $\omega = 2$ GHz, and by observing the output of the system at $2\omega = 4$ GHz. As a function of an external static magnetic field, by which essentially the distances ω_0 between the various possible couples of levels could be varied, the power generated at 2ω presented peaks of rather complicated structure. In a subsequent paper[2] complete sets of measurements were presented (also on noncrystalline paramagnetic samples) which essentially confirmed the former results and made it clear that peaks in the second-harmonic output occur whenever either the incoming or the outgoing 2ω radiation fields are in resonance with any two suitable levels of the magnetic atoms ($\omega_0 \sim \omega$ and $\omega_0 \sim 2\omega$, respectively). Moreover the peak at $\omega_0 \sim \omega$ develops a dip at the center at high power levels of the ω radiation, acquiring the aspect of an antiresonance. Boscaino *et al.*[2] were also able to present a theory which was based on a density-matrix approach to the problem with the use of relaxation times. By solving approximately the equations of motion for the density-matrix operators, they obtained components of the total magnetic moment of the system which varied at frequency 2ω, thus providing a source for emission of second harmonics. The theory proved to be extremely successful in relating all the experimental data to each other in a coherent fashion and even in predicting such unusual features as the dip at the center of the $\omega_0 \sim \omega$ peaks. The situation, however, remained rather obscure from the point of view of the physical aspects of the phenomenon, since the role played by the introduction of the phenomenological relaxation times in determining the features of the experimental results was not clearly discernible from the role played by more intrinsic quantum-mechanical properties of the system, and since a modelistic picture of the generation of second harmonics was lacking.

The fully quantum-mechanical treatment of second-harmonic generation by an isolated spin $S = \frac{1}{2}$ yielded results[3] which were in qualitative agreement with the experimental data, but essentially failed to explain important features of the 2ω lines

such as the dip at the center of the $\omega_0 \sim \omega$ lines. A much more satisfactory agreement with experiments was successively obtained by considering the problem of N spins[4] and by taking into account the coherence properties of the spin system. Along these lines most of the experimental features could be explained. The aim of the present paper is to present in a unified and self-consistent fashion the results of the purely quantum-mechanical approach to the problem of second-harmonic generation by paramagnetic materials, to extend the calculations previously published as preliminary results,[3,4] to compare their predictions with those of the density-matrix approach and with the experimental results, and finally, to present a modelistic semiclassical representation of frequency conversion by a paramagnet. In this way it shall be possible to obtain a clear picture of the fundamental aspects of the phenomenon, among which the role played by superradiance shall be particularly stressed.

In Sec. II the Hamiltonian of the system is found and the coupling constants are calculated for the paramagnetic materials on which systematic experiments have been performed. Because of mathematical difficulties these coupling constants are calculated for a geometry of the cavity in which the electromagnetic fields are established similar to but different from that adopted in the actual experimental setup, in such a way that the calculated constants should not differ essentially from the actual ones. The results of this section shall be found very useful to evaluate the order of magnitude of effects connected with the structure of the $\omega_0 \sim \omega$ lines. In Sec. III the technique which permits the calculation of the transition amplitudes which generate second harmonics is discussed from a general point of view, and this technique is applied in Sec. IV to the calculation of second-harmonic generation by a single spin $S=\frac{1}{2}$. In this section a brief comparison with the experimental results shows the inadequacy of the single-spin theory in predicting the structure of the experimental lines. In Sec. V we treat the N-spins problem in the neighborhood of $\omega_0 \sim \omega$, obtaining transition amplitudes which are in agreement with the experiments, and we discuss a physical semiclassical model for the generation of second harmonics by the N spins. As a by-product of this section we also present approximate analytical solutions of the eigenvalue problem of a set of two-level objects coupled by a linear interaction to a monochromatic radiation field, not necessarily in resonance with the objects themselves. In Sec. VI the region around $\omega_0 \sim 2\omega$ is investigated, and the physical model used in Sec. V is shown to behave reasonably also for the lines in this region. Finally, Sec. VII is devoted to the comparison of the single-spin with the N-spin results, to the comparison of our N-spin theory with the density-matrix theories and to a discussion about a possible experiment aimed towards clarify the role of superradiance in the intermediate steps of the process by which power is converted to second harmonics.

II. SPIN-PHOTON HAMILTONIAN

A. Spins

Complete sets of measurements[2] have been performed on Cr^{3+} in Al_2O_3 and on diphenylpicrylhydrazyl (DPPH). As is well known, the spin-orbit interaction and the octahedral field leave a quartet as the ground state of the Cr^{3+} ion, which can be described by a spin $S=\frac{3}{2}$ formalism. The trigonal distortion of the octahedron of oxygen atoms surrounding the ion causes further splitting of the levels, and the Hamiltonian for this system in an external magnetic field can be expressed in terms of the tensors $\overleftrightarrow{g}$ and $\overleftrightarrow{D}$ as[5]

$$\mathcal{H}=\mu_B(\vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S})+\vec{S}\cdot\overleftrightarrow{D}\cdot\vec{S}. \tag{2.1}$$

In order to have the possibility of varying the angle between the static magnetic field and the microwave fields without trouble from anisotropy, the experiments have been performed with the static field along the z axis, and with the c axis of the crystal along the y axis of the reference system. In such a reference frame the Hamiltonian (2.1) can be written as

$$\mathcal{H}=g_\perp\mu_B HS_z-\tfrac{1}{2}D[S_z^2-\tfrac{1}{3}S(S+1)]-\tfrac{1}{4}D(S_+^2+S_-^2), \tag{2.2}$$

where[6]

$$D\simeq 5.746\ \text{GHz},\quad g\simeq 1.9867 \tag{2.3}$$

The eigenstates of (2.2) can be calculated as

$$|n'\rangle=\sum_{m=-3/2}^{3/2}\alpha(n',m)|m\rangle, \tag{2.4}$$

where the α's are numbers which have a complicated dependence on H. In an ESR experiment with a microwave field h of 2.7 GHz in the x-z plane, the only magnetically allowed transitions are $|\frac{1}{2}'\rangle \rightarrow |\frac{3}{2}'\rangle$ (~ 500 G) and $|-\frac{3}{2}'\rangle \rightarrow |-\frac{1}{2}'\rangle$ ($\sim 2\,500$ G). The matrix elements of S_x and S_z between these two couples of states can be calculated as

$$\langle\tfrac{1}{2}'|S_x|\tfrac{3}{2}'\rangle\sim 1,\qquad \langle\tfrac{1}{2}'|S_z|\tfrac{3}{2}'\rangle=0\quad (H\sim 500\ \text{G}),$$

$$\langle-\tfrac{3}{2}'|S_x|-\tfrac{1}{2}'\rangle\sim 0.2,\quad \langle-\tfrac{3}{2}'|S_z|-\tfrac{1}{2}'\rangle=0 \tag{2.5}$$

$$(H\sim 2\,500\ \text{G}).$$

Each of the two couples of levels can then be treated independently of the other, and it is seen from (2.5) that it can be assimilated to a spin $S=\frac{1}{2}$ with an appropriate effective magnetic moment. The interaction Hamiltonian with h shall then be of the form

$$\gamma_{\text{eff}}\,h(S_x\cos\theta+S_z\sin\theta),$$

where θ is the angle between the direction of h and the x axis. The splitting within each of the two pairs of levels due to the interplay of the trigonal distorsion and the external magnetic field can be formally represented in the Hamiltonian by a term $\omega_0 S_z$ ($\hbar = 1$), so that the Hamiltonian for each pair of levels interacting with a microwave field in the x-z plane shall be written

$$\mathcal{H} = \omega_0 S_z + \gamma_{eff}\, h(S_x \cos\theta + S_z \sin\theta), \tag{2.6}$$

where we find approximately

$$\gamma_{eff} \sim \begin{cases} 6\ \text{MHz/G} & (|\tfrac{1}{2}'\rangle \rightarrow |\tfrac{3}{2}'\rangle) \\ 1.2\ \text{MHz/G} & (|-\tfrac{3}{2}'\rangle \rightarrow |-\tfrac{1}{2}'\rangle). \end{cases} \tag{2.7}$$

We shall adopt the values (2.7) in our calculations on Cr^{3+} ions, neglecting the slight variation of γ_{eff} in the range of values of ω_0 we shall be interested in.

DPPH, on the other hand, is a free radical with an unpaired electron. In a concentrated crystal a single ESR line is observed with a $g \simeq 2.0036$, the line being slightly anisotropic. This anisotropy is difficult to observe at 2.7 GHz and we shall neglect it. The line is strongly exchange narrowed, and in a dilute liquid solution the line broadens into five peaks which can be described by a $S = \frac{1}{2}$ Hamiltonian

$$\mathcal{H} = g\mu_B \vec{S}\cdot\vec{H} + A(\vec{I}_1\cdot\vec{S} + \vec{I}_2\cdot\vec{S}), \tag{2.8}$$

where $\vec{I}_1$ and $\vec{I}_2$ are the nuclear spins of the two N atoms where the unpaired electron spends most of his time.[7] The simple form of (2.8) is due to the fact that terms depending on the relative orientation of the molecule and of the external field H are averaged out by the rapid motion of the molecule itself in the liquid. If the solution is not liquid (as in the case of the experiments to which we refer in this paper), the five resonances merge into a single isotropic line about 40 G broad. As in the case of Cr^{3+} discussed, we shall disregard the broadening and we shall describe DPPH by the Hamiltonian (2.6) with the same value of γ_{eff} as for free electrons.

B. Photons

We shall describe the electric and magnetic fields in the cavity as usual in terms of the normal modes $\vec{\varphi}_k^{\pm}(\vec{r})$ of the cavity itself:

$$\vec{E}(\vec{r}) = i\sum_k (\tfrac{1}{2}\omega_k)^{1/2}[a_k\vec{\varphi}_k^{-}(\vec{r}) + a_k^{\dagger}\vec{\varphi}_k^{+}(\vec{r})],$$

$$\vec{H}(\vec{r}) = \sum_k (c^2/2\omega_k)^{1/2}[a_k\nabla\times\vec{\varphi}_k^{-}(\vec{r}) + a_k^{\dagger}\nabla\times\vec{\varphi}_k^{+}(\vec{r})],$$

where $\vec{\varphi}_k^{+}(\vec{r}) = [\vec{\varphi}_k^{-}(\vec{r})]^*$ is the eigenfunction of the operator ∇^2 with the appropriate boundary conditions, corresponding to the eigenvalue ω_k^2/c^2, and the a_k are the Bose operators for the kth mode of the system. The Hamiltonian of the cavity then takes the form

$$\mathcal{H} = \sum_k \omega_k a_k^{\dagger} a_k .$$

In the experiments under consideration, bimodal cavities have been used, that is, cavities where only two modes can be appreciably populated and the others are strongly damped or need in order to be excited frequencies that are too high. We shall call α and β the operators pertaining to the two modes, and we shall assume that the cavity is tuned so that $\omega_\beta = 2\omega_\alpha \equiv 2\omega$. Therefore the effective Hamiltonian of the cavity is

$$\mathcal{H} = \omega\alpha^{\dagger}\alpha + 2\omega\beta^{\dagger}\beta, \tag{2.9}$$

and the fields are

$$\vec{E}(\vec{r}) = i(\omega/2)^{1/2}[\alpha\vec{\varphi}_\alpha^{-}(\vec{r}) + \alpha^{\dagger}\vec{\varphi}_\alpha^{+}(\vec{r}) + \beta\sqrt{2}\,\vec{\varphi}_\beta^{-}(\vec{r}) + \beta^{\dagger}\sqrt{2}\,\vec{\varphi}_\beta^{+}(\vec{r})],$$

$$\vec{H}(\vec{r}) = (c^2/4\omega)^{1/2}[\alpha\sqrt{2}\,\nabla\times\vec{\varphi}_\alpha^{-}(\vec{r}) + \alpha^{\dagger}\sqrt{2}\,\nabla\times\vec{\varphi}_\alpha^{+}(\vec{r}) + \beta\nabla\times\vec{\varphi}_\beta^{-}(\vec{r}) + \beta^{\dagger}\nabla\times\vec{\varphi}_\beta^{+}(\vec{r})]. \tag{2.10}$$

In actual experiments the 2ω mode (5.4 GHz) is the TE_{101} of a rectangular cavity. This is the lowest-frequency mode of the cavity, and the ω mode is created by introducing a thin metallic slab of varying length which makes the cavity a partly reentrant one. The ω field is therefore of irregular form and difficult to calculate. We have therefore in our calculations changed to a coaxial cylindrical cavity, so adjusted that the frequencies of its TE_{111} and TE_{011} modes are 2.7 and 5.4 GHz, respectively. If the length of the cavity is 9 cm and the outer and inner radii 3 cm and 4.5 mm, respectively, then the normalized eigenfunctions for the two modes in cylindrical coordinate are approximately[8]

$$\text{TE}_{111}: \begin{cases} \varphi_\alpha^{r} \sim (1/2.4r)[J_1(0.58r) - 0.007N_1(0.58r)] \times \sin\theta\sin(0.35z), \\ \varphi_\alpha^{\theta} \sim (1/4.1)[J_1'(0.58r) - 0.07N_1'(0.58r)] \times \cos\theta\sin(0.35z), \\ \varphi_\alpha^{z} = 0 \end{cases} \tag{2.11a}$$

and

$$\text{TE}_{011}: \begin{cases} \varphi_\beta^{r} = 0, \\ \varphi_\beta^{\theta} \simeq (1/4.7)[J_1(1.38r) + 0.26N_1(1.38r)] \times \sin(0.35z), \\ \varphi_\beta^{z} = 0, \end{cases} \tag{2.11b}$$

where J_1 and N_1 are the Bessel and Neumann functions of order one. In the experiment we wish to study, the sample is placed at the bottom of the rectangular cavity ($z = 0$ plane) in a region between the slab and the walls where the α and β magnetic

fields are parallel and the electric field is null. Moreover, the sample is small enough so that the $\vec{r}$ dependence of the fields within the sample itself can be disregarded. We obtain a similar configuration in the coaxial cylindrical cavity along the line $z=0$, $\theta=0$ at the bottom of the cavity, as can be seen from (2.11) upon application of the curl operator. Along this line the only component of the magnetic field is radial, and we find

$$(\nabla\times\vec{\varphi}_\alpha)^r \simeq 0.09[J_1'(0.58r) - 0.07N_1'(0.58r)],$$

$$(\nabla\times\vec{\varphi}_\beta)^r \simeq 0.08[J_1(1.38r) + 0.26N_1(1.38r)].$$

When these expressions are used to plot the ratio

$$R(r) = (\nabla\times\vec{\varphi}_\beta)^r/(\nabla\times\vec{\varphi}_\alpha)^r$$

as a function of r, it is easy to see that it does not differ much from the free-space value of 2, except in a small tract near the inner conductor, where it may become very small.

C. Interaction

We now turn to the approximate determination of the constants in the interaction Hamiltonian. Placing the sample at $r\sim 1.5$ cm along the line $z=0$, $\theta=0$, and assuming that the fields are homogeneous over the volume occupied by the spins, we find from the final expressions in Sec. II B

$$|\nabla\times\vec{\varphi}_\alpha|\sim 0.02\ \text{cm}^{-5/2},\quad |\nabla\times\vec{\varphi}_\beta|\sim 0.04\ \text{cm}^{-5/2};$$

substituting in (2.10), we have for the magnetic fields

$$|h_\alpha|\sim 8.2\times10^{-10}(\alpha+\alpha^\dagger)\ \text{G},$$

$$|h_\beta|\sim 1.2\times10^{-9}(\beta+\beta^\dagger)\ \text{G}.$$

From (2.6) and (2.9) we have finally the total Hamiltonian of the system

$$\mathcal{H} = \omega\alpha^\dagger\alpha + 2\omega\beta^\dagger\beta + \omega_0\sum_n S_z^n + [\epsilon(\alpha+\alpha^\dagger) + \lambda(\beta+\beta^\dagger)]\sum_n (S_x^n\cos\theta + S_z^n\sin\theta), \tag{2.12}$$

where the index n runs over the paramagnetic centers, $\omega\sim 2.7$ GHz, and where for each of the paramagnetic centers considered in Sec. II A

$$\epsilon\simeq 4.8\times10^{-3}\ \text{Hz},\quad \lambda\simeq 7.1\times10^{-3}\ \text{Hz}\quad (|\tfrac{1}{2}'\rangle \rightarrow |\tfrac{3}{2}'\rangle \text{ in } Cr^{3+})$$

$$\epsilon\simeq 9.5\times10^{-4}\ \text{Hz},\quad \lambda\simeq 1.4\times10^{-3}\ \text{Hz}\quad (|-\tfrac{3}{2}'\rangle \rightarrow |-\tfrac{1}{2}'\rangle \text{ in } Cr^{3+})$$

$$\epsilon\simeq 2.5\times10^{-3}\ \text{Hz},\quad \lambda\simeq 3.7\times10^{-3}\ \text{Hz}\quad (|-\tfrac{1}{2}'\rangle \rightarrow |\tfrac{1}{2}'\rangle \text{ in DPPH}).$$

We wish to stress that these values for the coupling parameters are only indicative of the order of magnitude, but they should be rather accurate in their relative magnitudes.

The S_i^n $(i=x,\ z)$ in (2.12) are the spin operators $S^n=\frac{1}{2}$ pertaining to the nth spin in the sample. We may now introduce the total spin operators

$$S_i = \sum_n S_i^n \quad (i=x,\ y,\ z) \tag{2.13}$$

which have angular momentum commutation rules. In terms of these operators, whose introduction is useful in our case of magnetic fields homogeneous over the sample,[9] the Hamiltonian (2.12) takes the form

$$\mathcal{H} = \omega\alpha^\dagger\alpha + 2\omega\beta^\dagger\beta + \omega_0 S_z + [\epsilon(\alpha+\alpha^\dagger) + \lambda(\beta+\beta^\dagger)]\times(S_x\cos\theta + S_z\sin\theta). \tag{2.14}$$

In the rest of this paper we shall use Hamiltonian (2.14) as the starting point of our calculations both in the case of an isolated spin $S=\frac{1}{2}$ and in the case of many spins [in which case the S operators are those defined by (2.13)].

We wish to emphasize that we are neglecting in this simple model all sources of homogeneous and inhomogeneous broadening of the spin levels, except of course that due to the interaction with the electromagnetic field. Therefore each spin feels the presence of the others only through the radiation in the cavity. Furthermore, we have neglected also any broadening of the cavity modes which comes from loss at the walls, that is to say from a finite Q value. These assumptions, of course, can be justifyed only *a posteriori*, when it is shown that this model gives a fair picture of the main features of the generation of second harmonics.

III. GENERAL THEORY

Hamiltonian (2.14) describes the coupling of the spin system to the ω and 2ω modes of the cavity, and should contain all the information needed to calculate the generation of second harmonics. We first split off (2.14) the "free" Hamiltonian

$$\mathcal{H}_0 = \omega\alpha^\dagger\alpha + 2\omega\beta^\dagger\beta + \omega_0 S_z, \tag{3.1}$$

and we label its eigenstates by the symbol $|n,\ m,\ x,\ \Gamma\rangle$, where n and m are the numbers of photons in the ω and 2ω modes, respectively, and x is the value of the z component of the magnetic moment such that

$$S_z|n,\ m,\ x,\ \Gamma\rangle = x|n,\ m,\ x,\ \Gamma\rangle.$$

Γ, on the other hand, represents any set of quantum numbers necessary to specify uniquely the state of the system. We shall be interested in transitions induced by the rest of $\mathcal{H}$ between these states, such that in the final state the number n is decreased and m is increased. These transitions are obviously responsible for the generation of second harmonics. Since the eigenvalues of (3.1) corresponding to the eigenstates $|n,\ m,\ x,\ \Gamma\rangle$ are

$$E_{nmx} = n\omega + 2m\omega + x\omega_0 , \tag{3.2}$$

it is obvious that the simplest among the transitions which conserve energy and generate second harmonics are

$$|n,\ m,\ x,\ \Gamma\rangle \rightarrow |n-1,\ m+1,\ x-1,\ \Gamma\rangle ,$$

$$|n,\ m,\ x,\ \Gamma\rangle \rightarrow |n-3,\ m+1,\ x+1,\ \Gamma\rangle$$

in the region $\omega_0 \sim \omega$, and

$$|n,\ m,\ x,\ \Gamma\rangle \rightarrow |n-2,\ m+2,\ x-1,\ \Gamma\rangle$$

in the region $\omega_0 \sim 2\omega$. In addition to these, we have also

$$|n,\ m,\ x,\ \Gamma\rangle \rightarrow |n-2,\ m+1,\ x,\ \Gamma\rangle ,$$

which would appear to be independent of ω_0. This, however, is not so, as we shall see later, due to the resonant character of the part of the interaction responsible for this transition, which causes it to be important only in the regions $\omega_0 \sim \omega$ and $\omega_0 \sim 2\omega$. We are thus led naturally to consider these two regions of ω_0, the static magnetic field H being swept from 0 upward, as those in which conversion of electromagnetic power to double frequency is permitted at the lowest possible order in ϵ and λ. In all the other regions, energy-conserving transitions which generate second harmonics are of higher order and we shall disregard them. We also wish to point out that when $\theta = 0$, that is, at right angle between the static and microwave magnetic fields, the part of $\mathcal{H}$ which induces the mentioned transitions reduces to

$$\mathcal{H}_{\rm int} = [\epsilon(\alpha + \alpha^\dagger) + \lambda(\beta + \beta^\dagger)]S_x ,$$

where

$$\mathcal{H}_{\rm int} = \mathcal{H} - \mathcal{H}_0 .$$

In this case the parity of $n+m+x$ must be conserved and only transitions of higher order than those hitherto considered are possible. These transitions have been studied in some detail by one of the authors.[10] On the other hand, when $\theta = \frac{1}{2}\pi$ (microwave field parallel to static field), $\mathcal{H}_{\rm int}$ becomes

$$\mathcal{H}_{\rm int} = [\epsilon(\alpha + \alpha^\dagger) + \lambda(\beta + \beta^\dagger)]S_z ,$$

and x being a good quantum number, $\mathcal{H}$ obviously splits into two commuting parts for α and β operators, which can be diagonalized simultaneously, leading to no power conversion.

We are now ready to examine in more detail $\mathcal{H}_{\rm int}$, which we write in the form

$$\mathcal{H}_{\rm int} = \tfrac{1}{2}\epsilon_\perp(S_+\alpha + S_-\alpha^\dagger + S_+\alpha^\dagger + S_-\alpha) + \epsilon_\parallel(S_z\alpha + S_z\alpha^\dagger)$$
$$+ \tfrac{1}{2}\lambda_\perp(S_+\beta + S_-\beta^\dagger + S_+\beta^\dagger + S_-\beta) + \lambda_\parallel(S_z\beta + S_z\beta^\dagger), \tag{3.3}$$

where

$$\epsilon_\perp = \epsilon\cos\theta, \quad \epsilon_\parallel = \epsilon\sin\theta, \quad \lambda_\perp = \lambda\cos\theta, \quad \lambda_\parallel = \lambda\sin\theta$$

and where we have introduced the raising and lowering spin operators

$$S_\pm = S_x \pm iS_y .$$

From the form (3.3) of $\mathcal{H}_{\rm int}$ it is transparent that we cannot use straightforward perturbation theory in order to calculate the transition amplitudes we are interested in, since the operator

$$\tfrac{1}{2}\epsilon_\perp(S_+\alpha + S_-\alpha^\dagger)$$

might give rise to dangerous energy denominators in the region $\omega_0 \sim \omega$, and the same is true for

$$\tfrac{1}{2}\lambda_\perp(S_+\beta + S_-\beta^\dagger)$$

in the region $\omega_0 \sim 2\omega$. Either of these terms, depending on the region of ω_0 we are studying, calls for a nonperturbative treatment. We shall therefore call it V, and consider it together with $\mathcal{H}_0$ with the aim of diagonalizing exactly $\mathcal{H}_0 + V$. We also call $\mathcal{H}'$ the remaining part of $\mathcal{H}_{\rm int}$, and we have

$$\mathcal{H} = \mathcal{H}_0 + V + \mathcal{H}' . \tag{3.4}$$

we may now introduce the resolvent operator

$$G(z) = 1/(z - \mathcal{H}) \tag{3.5}$$

and calculate the transition amplitudes as

$$\frac{1}{2\pi i}\oint \langle n,\ m,\ x,\ \Gamma|\,G(z)\,|n',\ m',\ x',\ \Gamma\rangle\, e^{-izt}\,dz, \tag{3.6}$$

where the contour of integration encircles in a counterclockwise sense all the poles of the integrand on the real axis of the complex z plane. The problem is, of course, to calculate the matrix element in (3.6), and for this we introduce the complete set of eigenstate of $\mathcal{H}_0 + V$ which we shall label $|d_\mu\rangle$ or $|e_\mu\rangle$. In fact, we obviously have

$$\langle n,\ m,\ x,\ \Gamma|\,G(z)\,|n',\ m',\ x',\ \Gamma\rangle$$
$$= \sum_{\mu,\mu'} \langle n,\ m,\ x,\ \Gamma|\,d_\mu\rangle\langle d_\mu|\,G(z)\,|e_{\mu'}\rangle$$
$$\times\langle e_{\mu'}|\,n',\ m',\ x',\ \Gamma\rangle, \tag{3.7}$$

and because of (3.7) the problem is reduced to evaluating the matrix elements of the resolvent between eigenstates of $\mathcal{H}_0 + V$:

$$\langle d_\mu|\,G(z)\,|e_{\mu'}\rangle \equiv \langle d_\mu\,|\frac{1}{z - (\mathcal{H}_0 + V) - \mathcal{H}'}\,|e_{\mu'}\rangle. \tag{3.8}$$

The problem of evaluating (3.8) can be simplified if (3.8) itself is cast in a more convenient form due to Cohen-Tannoudji.[11] A particular subspace which $|d_\mu\rangle$ and $|e_{\mu'}\rangle$ belong to is chosen, and the projection operators P and Q are introduced, which project, respectively, into and out of this subspace. The general criterion according to which this subspace is chosen is that it should be as few-dimensional as possible; but in many instances, as

we shall see below, it is not convenient to reduce it to $|d_\mu\rangle$ and $|e_{\mu'}\rangle$ only. For any operator O, the symbol $O_P \equiv POP$ is defined. It can then be shown that in terms of P and Q

$$G(z)_P = \frac{1}{z-(\mathcal{H}_0+V)_P - R(z)_P}, \tag{3.9}$$

where

$$R(z) = \mathcal{H}' + \mathcal{H}' \frac{Q}{z-(\mathcal{H}_0+V)-Q\mathcal{H}'Q}\mathcal{H}'. \tag{3.10}$$

Operator equation (3.9) is exact, and its improvement on (3.5) lies in the fact that inverting the matrix of $P[z-(\mathcal{H}_0+V)+R]P$ is, in general, easier than inverting the infinite matrix of $z-(\mathcal{H}_0+V)-\mathcal{H}'$. A price is paid of course in increased complexity of the structure of $R(z)_P$ in comparison with that of $\mathcal{H}'$, but this is a price worth being paid since it is generally possible to find approximations for the matrix elements of $R(z)_P$ which very much simplify the computation.

The choice of the dimensionality of the subspace into which P projects any state is, in principle, entirely free, since (3.9) is an exact result, as we have already pointed out. We are going to approximate expression (3.10) however, and therefore the choice of P and Q depends on this approximation in order to have reliable results. Let us assume for example that we wish to calculate a diagonal matrix element $\langle a|G(z)_P|a\rangle$, where $|a\rangle$ is an eigenstate of $\mathcal{H}_0+V$ corresponding to the eigenvalue E_a, and that it is reasonable to expect that the shifts of the eigenvalues of $\mathcal{H}_0+V$ due to $\mathcal{H}'$ are small with respect to the distance between any two unperturbed eigenvalues of $\mathcal{H}_0+V$ itself. We may therefore expect that whatever subspace we choose, the operator $R(z)$ can be formally expanded in powers of $\mathcal{H}'$ as

$$R(z) = \mathcal{H}' + \mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}' + \mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}' + \cdots \tag{3.11}$$

and the expansion truncated to some appropriate term. We then choose the simplest possible subspace consisting of the single vector $|a\rangle$ (and P and Q accordingly) and to fix the ideas decide to truncate expression (3.11) as

$$R(z) \simeq \mathcal{H}' + \mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'. \tag{3.12}$$

Therefore from (3.10) and (3.12)

$$\langle a|G(z)_P^{-1}|a\rangle \simeq z - E_a - \langle a|\mathcal{H}'|a\rangle - \langle a|\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'|a\rangle. \tag{3.13}$$

Introducing the unit operators $\sum |b\rangle\langle b|$ in (3.13), where $|b\rangle$ is an eigenstate of $\mathcal{H}_0+V$, the last term of this expression becomes

$$\langle a|\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'|a\rangle = \sum_b{}' \langle a|\mathcal{H}'|b\rangle\frac{1}{z-E_b}\langle b|\mathcal{H}'|a\rangle, \tag{3.14}$$

where the prime over the $\sum_b$ is a reminder that the effect of the Q operator is such that $|b\rangle \neq |a\rangle$ in (3.14). Introducing (3.14) in (3.13) and inverting, we find

$$\langle a|G(z)_P|a\rangle \simeq \frac{1}{z-E_a-A-\sum_b{}'|B_b^a|^2/(z-E_b)}, \tag{3.15}$$

where we have put

$$\langle a|\mathcal{H}'|a\rangle = A, \quad \langle a|\mathcal{H}'|b\rangle = B_b^a.$$

Equation (3.15) has a queer aspect, because one would expect $\langle a|G(z)_P|a\rangle$ to have poles at all the eigenvalues of $\mathcal{H}$, while (3.15) can only have poles near the eigenvalues E_b of states $|b\rangle$ of $\mathcal{H}_0+V$ which are connected to $|a\rangle$ by $\mathcal{H}'$ at first order. Moreover an ever increasing number of the missing poles near $\{E_c\}$, $\{E_d\}$, ... keep appearing in $\langle a|G(z)_P|a\rangle$, brought in by terms like

$$\sum_{b,c}{}'\frac{B_b^aB_c^bB_a^c}{(z-E_b)(z-E_c)}, \quad \sum_{b,c,d}{}'\frac{B_b^aB_c^bB_d^cB_a^d}{(z-E_b)(z-E_c)(z-E_d)}, \cdots \tag{3.16}$$

in the denominator of (3.15) if, instead of truncating $R(z)$ as in (3.12), one keeps terms like

$$\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'$$

$$\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}', \ \ldots$$

in which the chains of $\mathcal{H}'$ operators connect the state $|a\rangle$ with itself through the eigenstates $\{|c\rangle\}$, $\{|d\rangle\}$, ... of $\mathcal{H}_0+V$ at second, third, ... order.

In fact Eq. (3.15) is wrong as it stands, but for small A and B's the residues of $\langle a|G(z)|a\rangle$ at the poles of $\mathcal{H}$ near $\{E_b\}$, $\{E_c\}$, ... are smaller, the higher the order is at which the states $\{|b\rangle\}$, $\{|c\rangle\}$, ... are connected to $|a\rangle$ by $\mathcal{H}'$, so that the contributions coming from these poles to the integral (3.6) can be neglected and the series for $R(z)$ conveniently truncated. This can be easily seen by first adding the terms (3.16) to the denominator of (3.15), which can then be written as

$$\langle a|G(z)_P|a\rangle \simeq \frac{\prod_{b,c,\ldots}(z-E_b)(z-E_c)\cdots}{(z-E_a-\zeta_a)\prod_{b,c,\ldots}(z-E_b-\zeta_b)(z-E_c-\zeta_c)\cdots}, \tag{3.17}$$

where ζ_i, the shift of the energy E_i caused by $\mathcal{H}'$, is a small quantity which depends on A and B, and then calculating the residues of (3.17) at $E_a+\zeta_a$,

$\{E_b+\zeta_b\}$, $\{E_c+\zeta_c\}$, ... under the assumption that

$$E_b-E_a<E_c-E_a<E_d-E_a<\cdots .$$

It is vital to this way of proceeding, however, that none of the energies E_i $(i\neq a)$ be as near to E_a as $O(\zeta)$. What we have said can easily be generalized to a matrix element $\langle a|G(z)_P|b\rangle$, and it can be concluded that if one wants to develop $R(z)$ as in (3.11) and truncate the development, then the subspace into which P projects should contain all the eigenstates of $\mathcal{H}_0+V$ whose energies are in the neighborhood of E_a and E_b, and through which $|a\rangle$ and $|b\rangle$ are connected by $\mathcal{H}'$ at any order.

On the other hand, the shift of the eigenvalues of $\mathcal{H}_0+V$ due to $\mathcal{H}'$ may not be small. In this situation we cannot expect that the truncation of the series (3.11) for $R(z)$ is legitimate, and we are compelled to find other approximations. It is then desirable to find a criterion to select some partial summations of that series whose contribution to a given matrix element is dominant. If this is possible, then the dimensionality of the P subspace can be reduced without danger of losing important contributions from the residues of the neglected poles.

We may therefore summarize our techniques as follows. We first select the appropriate V out of $\mathcal{H}_{\rm int}$, depending on the range of ω_0 we are interested in, and diagonalize $\mathcal{H}_0+V$. We make appropriate approximations in $R(z)$, and accordingly choose the P and Q operators. We then calculate the matrix elements of (3.9) between the eigenstates of $\mathcal{H}_0+V$ in terms of which we have expressed the initial and final states of our transition. Introducing expression (3.7) in (3.6) and performing the contour integration finally yields the sought-for complex amplitude.

IV. ISOLATED SPIN $S=\frac{1}{2}$

In this section we investigate the generation of the second harmonic by an isolated spin $S=\frac{1}{2}$. We follow the program outlined in Sec. III, and consider separately the two regions $\omega_0\sim\omega$ and $\omega_0\sim 2\omega$.

A. Region $\omega_0\sim\omega$

Since the state of the single spin is uniquely determined by the value of S_z, we do not need Γ to label our states, and the transitions of interest with initial states on the same energy shell are of the sort

$$\begin{aligned}
&|n,\ m,\ -\tfrac{1}{2}\rangle\rightarrow|n-2,\ m+1,\ \tfrac{1}{2}\rangle,\\
&|n-1,\ m,\ \tfrac{1}{2}\rangle\rightarrow|n-2,\ m+1,\ -\tfrac{1}{2}\rangle,\\
&|n,\ m,\ -\tfrac{1}{2}\rangle\rightarrow|n-3,\ m+1,\ \tfrac{1}{2}\rangle,\\
&|n-1,\ m,\ \tfrac{1}{2}\rangle\rightarrow|n-2,\ m+1,\ -\tfrac{1}{2}\rangle
\end{aligned}\qquad (4.1)$$

The part of $\mathcal{H}_{\rm int}$ which contains dangerous terms is obviously

$$V=\tfrac{1}{2}\epsilon_\perp(S_+\alpha+S_-\alpha^\dagger). \qquad (4.2)$$

Since n and m are very large in all the realistic models, from now on we shall approximate $(n\pm1)^{1/2}\sim\sqrt{n}$, $(m\pm1)^{1/2}\sim\sqrt{m}$ unless explicitly stated otherwise. We then easily find the eigenvectors of $\mathcal{H}_0+V$ as[3]

$$\begin{aligned}
|d_+\rangle&=(A^2+1)^{-1/2}(A|n,\ m,\ -\tfrac{1}{2}\rangle+|n-1,\ m,\ \tfrac{1}{2}\rangle),\\
|d_-\rangle&=(A^2+1)^{-1/2}(|n,\ m,\ -\tfrac{1}{2}\rangle-A|n-1,\ m,\ \tfrac{1}{2}\rangle),
\end{aligned}\qquad (4.3)$$

corresponding to the eigenvalues

$$E_\pm=(n+2m)\omega-\tfrac{1}{2}(\omega\mp\gamma), \qquad (4.4)$$

where

$$A=\epsilon_\perp\sqrt{n}/(\gamma-\alpha),\quad \alpha=\omega-\omega_0,\quad \gamma=(\alpha^2+\epsilon_\perp^2 n)^{1/2} \qquad (4.5)$$

We note that eigenstates of $\mathcal{H}_0+V$ coming from $|n-2,\ m+i,\ -\frac{1}{2}\rangle$ and $|n-2i-1,\ m+i,\ \frac{1}{2}\rangle$ with $|i|\ll n$ are of approximately the same energy as $|d\pm\rangle$.

As shown in a previous paper,[3] in order to have the amplitudes of transitions (4.1) we need the matrix elements

$$\langle d_\pm|G(z)_P|e_\pm\rangle=\langle d_\pm|\frac{1}{z-(\mathcal{H}_0+V)_P-R(z)_P}|e_\pm\rangle \qquad (4.6)$$

since the initial and final states in (4.1) can be developed in terms of $|d_\pm\rangle$ and $|e_\pm\rangle$, where $|e_\pm\rangle$ are the eigenstates of $\mathcal{H}_0+V$ formed by the states $|n-2,\ m+1,\ -\frac{1}{2}\rangle$ and $|n-3,\ m+1,\ \frac{1}{2}\rangle$. Since we expect shifts from $\mathcal{H}'$ smaller than those caused by V to the eigenstates of $\mathcal{H}_0$, we develop $R(z)$ as in (3.11) and truncate the series to the lowest nonzero term; for each of the four possible matrix elements (4.6), we have to choose the projection operators P and Q coherently with the theory outlined in Sec. III. We consider first the matrix element $\langle d_+|G(z)_P|e_+\rangle$. All the other states $|f_+\rangle$, $|g_+\rangle$, ... coming from $|n-2i,\ m+i,\ -\frac{1}{2}\rangle$ and $|n-2i-1,\ m+i,\ \frac{1}{2}\rangle$ $(i\ll n)$ have almost the same energy as $|d_+\rangle$ and $|e_+\rangle$, and shall connect these two states in some term of the series (3.11). We have therefore to define P as the projector on a $\mathfrak{N}$-dimensional subspace made up of all the states $|d_+\rangle$, $|e_+\rangle$, $|f_+\rangle$... in an energy shell centered at E_+ and of width comparable to the magnitude of the shifts induced by $\mathcal{H}'$. In view of this approximation, it is not possible to define $\mathfrak{N}$ exactly, and we shall keep it as a parameter in our future calculations. The matrix of $G(z)_P^{-1}$ in this subspace is of the form

$$\begin{vmatrix} \cdots & \cdot & \cdot & \cdot & \\ \cdots & \cdot & \cdot & \cdot & \\ \cdots & \cdot & \cdot & \cdot & \\ & z-E_+^{(d)}-\langle d_+|R(z)_P|d_+\rangle & \langle d_+|R(z)_P|e_+\rangle & \langle d_+|R(z)_P|f_+\rangle & \\ & \langle e_+|R(z)_P|d_+\rangle & z-E_+^{(e)}-\langle e_+|R(z)_P|e_+\rangle & \langle e_+|R(z)_P|f_+\rangle & \\ & \langle f_+|R(z)_P\rangle d_+\rangle & \langle e_+|R(z)_P|f_+\rangle & z-E_+^{(f)}-\langle f_+|R(z)_P|f_+\rangle & \\ & \cdot & \cdot & \cdot & \cdots \\ & \cdot & \cdot & \cdot & \cdots \\ & \cdot & \cdot & \cdot & \cdots \end{vmatrix}_{\mathfrak{N}} . \tag{4.7}$$

This matrix is too complicated to invert exactly, but it can be simplified since the matrix elements of $R(z)_P$ between "noncontiguous" states like $|d_+\rangle$ and $|f_+\rangle$ are orders of magnitude smaller than those between "contiguous" ones like $|d_+\rangle$ and $|e_+\rangle$, so that they can be discarded. Furthermore, it is easy to convince oneself that matrix elements like $\langle d_+|R(z)_P|e_+\rangle$ and $\langle f_+|R(z)_P|g_+\rangle$ have the same value in the approximation $(n\pm i)^{1/2}\sim\sqrt{n}$. We shall call this value $K_{++}(z)$. The same is true for the diagonal matrix elements like $\langle d_+|R(z)_P|d_+\rangle$, which we shall label $R_{++}(z)$. Matrix (4.7) then assumes the form

$$\begin{vmatrix} \cdots & & & & \\ \cdots & & & & \\ \cdots & & & & \\ & z-E_+-R_{++}(z) & K_{++}(z) & 0 & 0 & \\ & K_{++}(z) & z-E_+-R_{++}(z) & K_{++}(z) & 0 & \\ & 0 & K_{++}(z) & z-E_+-R_{++}(z) & K_{++}(z) & \\ & 0 & 0 & K_{++}(z) & z-E_+-R_{++}(z) & \\ & & & & & \cdots \\ & & & & & \cdots \\ & & & & & \cdots \end{vmatrix}_{\mathfrak{N}} , \tag{4.8}$$

which can be easily inverted. In fact the determinant of (4.8) is a persymmetric continuant and can be expressed as[12]

$$\det[G(z)_P^{-1}]\simeq\prod_{x=1}^{\mathfrak{N}}[z-E_+-R_{++}(z)-2K_{++}(z)\cos(x\pi/(\mathfrak{N}+1))] \tag{4.9}$$

while the off-diagonal minors between contiguous states are approximately given by the expression

$$K_{++}(z)[z-E_+-R_{++}(z)]^{\mathfrak{N}-2} \tag{4.10}$$

neglecting terms of higher order in $K_{++}(z)$. Moreover since we expect small shifts of the poles from E_+, we can substitute for $R_{++}(z)$ and $K_{++}(z)$ in (4.9) and (4.10) the values R_{++} and K_{++} that these functions assume at $z=E\equiv(E_++E_-)/2$. With these approximations, we find, using (4.9) and (4.10),

$$\langle d_+|G(z)_P|e_+\rangle=\frac{(z-E_+-R_{++})^{\mathfrak{N}-2}K_{++}}{\prod_{x=1}^{\mathfrak{N}}[z-E_+-R_{++}-2K_{++}\cos(x\pi/(\mathfrak{N}+1))]} . \tag{4.11}$$

Proceeding exactly in the same way we find also

$$\langle d_-|G(z)_P|e_-\rangle=\frac{(z-E_--R_{--})^{\mathfrak{N}-2}K_{--}}{\prod_{x=1}^{\mathfrak{N}}[z-E_--R_{--}-2K_{--}\cos(x\pi/(\mathfrak{N}+1))]} , \tag{4.12}$$

where R_{--} and K_{--} are the values of $R_{--}(z)$ and $K_{--}(z)$ at $z=E$. On the other hand, the matrix elements $\langle d_+|G(z)_P|e_-\rangle$ and $\langle d_-|G(z)_P|e_+\rangle$ have to be found by inverting the $2\mathfrak{N}\times2\mathfrak{N}$ matrix

$$\begin{vmatrix} \cdots & & & & \\ \cdots & & & & \\ \cdots & & & & \\ z-E_+-R_{++} & 0 & K_{++} & K_{+-} & \\ 0 & z-E_--R_{--} & K_{-+} & K_{--} & \\ K_{++} & K_{-+} & z-E_+-R_{++} & 0 & \\ K_{+-} & K_{--} & 0 & z-E_--R_{--} & \\ & & & & \cdots \\ & & & & \cdots \\ & & & & \cdots \end{vmatrix}_{2\mathfrak{N}} \tag{4.13}$$

built on all the $|+\rangle$ and $|-\rangle$ states of suitable energy, where K_{ij} $(i, j = +, -)$ has been calculated at $z = E$. The determinant of (4.13) can be approximately calculated by observing that the dominant feature of this determinant is that its zeros tend to cluster around the points $z = E_+$ and $z = E_-$, which differ by γ. Since γ is large with respect to K_{+-} or K_{-+}, we may use perturbation theory to calculate the shifts of the zeros of the unperturbed determinant obtained from (4.13) by deleting K_{+-} and K_{-+}. The unperturbed determinant assumes the form of the product of two continuants and can then be written as in (4.9)

$$\det[G(z)_P^{-1}] = \prod_{x=1}^{\mathfrak{N}} [z - E_+ - R_{++} - 2K_{++}\cos(x\pi/(\mathfrak{N}+1))] \prod_{y=1}^{\mathfrak{N}} [z - E_- - R_{--} - 2K_{--}\cos(y\pi/(\mathfrak{N}+1))] \tag{4.14}$$

and the shifts of its zeros are readily calculated to be of $O(K^2/\gamma)$. These are very small quantities, and we shall neglect them, assuming the form (4.14) for our determinant (4.13). With the same approximations as in (4.10), we calculate that the expressions for the relevant minors are

$$(z - E_+ - R_{++})^{\mathfrak{N}-1}(z - E_- - R_{--})^{\mathfrak{N}-1} K_{\pm\mp} \tag{4.15}$$

and consequently that

$$\langle d_\pm | G(z)_P | e_\mp \rangle = \frac{(z - E_+ - R_{++})^{\mathfrak{N}-1}(z - E_- - R_{--})^{\mathfrak{N}-1} K_{\pm\mp}}{\prod_{x=1}^{\mathfrak{N}} [z - E_+ - R_{++} - 2K_{++}\cos(x\pi/(\mathfrak{N}+1))] \prod_{y=1}^{\mathfrak{N}} [z - E_- - R_{--} - 2K_{--}\cos(y\pi/(\mathfrak{N}+1))]} . \tag{4.16}$$

Functions (4.11), (4.12), and (4.16) have only simple poles along the real axis, and we now turn to the evaluation of their residues. The residue of (4.11) at pole $z = E_+ + R_{++} + 2K_{++}\cos(x\pi/(\mathfrak{N}+1))$ is obviously given by

$$\mathrm{Res}(x) = \lim_{\theta \to x\pi/(\mathfrak{N}+1)} \frac{1}{2}\left[\cos\theta - \cos\left(\frac{x\pi}{\mathfrak{N}+1}\right)\right] \frac{[\cos(x\pi/(\mathfrak{N}+1))]^{\mathfrak{N}-2}}{\prod_{x'=1}^{\mathfrak{N}} [\cos\theta - \cos(x'\pi/(\mathfrak{N}+1))]} .$$

Using the formula

$$\sin n\theta = 2^{n-1}\sin\theta \prod_{k=1}^{n-1} (\cos\theta - \cos k\pi/n)$$

and L'Hospital's rule, we find

$$\mathrm{Res}(x) = \frac{2^{\mathfrak{N}-1}}{\mathfrak{N}+1}(-1)^{x+1}\left[\cos\left(\frac{x\pi}{\mathfrak{N}+1}\right)\right]^{\mathfrak{N}-2} \sin^2\left(\frac{x\pi}{\mathfrak{N}+1}\right). \tag{4.17}$$

The residues of (4.12) are obviously given by the same formula, while from (4.16) we easily find, neglecting terms of higher order in K/γ,

$$\mathrm{Res}(x) = \frac{K_{\pm\mp}}{\gamma}\frac{2^{\mathfrak{N}-1}}{\mathfrak{N}+1}(-1)^{x+1}\left[\cos\left(\frac{x\pi}{\mathfrak{N}+1}\right)\right]^{\mathfrak{N}-1} \sin^2\left(\frac{x\pi}{\mathfrak{N}+1}\right) . \tag{4.18}$$

with the same formula for $\mathrm{Res}(y)$ substituting y to x in (4.18) and changing the sign.

As discussed in Sec. III, we actually need to calculate the integrals

$$\frac{1}{2\pi i}\oint e^{-iEt}\langle d_\pm | G(z)_P | e_\pm \rangle dz$$

whose linear combinations give the amplitudes for transitions (4.1). Using (4.17) we get

$$\frac{1}{2\pi i}\oint e^{-iEt}\langle d_+ | G(z)_P | e_+ \rangle dz = \sum_{x=1}^{\mathfrak{N}} \left\{ \frac{2^{\mathfrak{N}-1}}{\mathfrak{N}+1}(-1)^{x+1}\left[\cos\left(\frac{x\pi}{\mathfrak{N}+1}\right)\right]^{\mathfrak{N}-2} \sin^2\left(\frac{x\pi}{\mathfrak{N}+1}\right) \times \exp\{-i[E_+ + R_{++} + 2K_{++}\cos(x\pi/(\mathfrak{N}+1))]t\}\right\} . \tag{4.19}$$

To perform the summation in (4.19) we observe that if we associate adjacent terms and approximate

$$F(ax) - F[a(x+1)] \simeq -aF'(ax),$$

then

$$\sum_x (-1)^{x+1} F(ax) \simeq \sum_{\text{odd } x} aF'(ax)$$

$$\simeq \frac{1}{2}\int_0^{\alpha} F'(ax)\,d(ax) = \tfrac{1}{2}[F(\alpha) - F(0)]\,. \qquad (4.20)$$

Formula (4.20) is valid for reasonably well-behaved $F(y)$ in $[0, \alpha]$. Furthermore in (4.19) for large $\mathfrak{N}$ we can discard terms such that

$$\frac{\pi}{3} < \frac{x\pi}{\mathfrak{N}+1} < \frac{2\pi}{3}$$

since they should give a negligible contribution to the summation. With these approximations we can split the sum in (4.19) into two parts, and using (4.20) we get

$$\frac{1}{2\pi i}\oint e^{-izt}\langle d_+|G(z)_P|e_+\rangle\,dz$$

$$\simeq \frac{3/4}{\mathfrak{N}+1}\left(e^{-i(E_+ + R_{++} + K_{++})t} - e^{-i(E_+ + R_{++} - K_{++})t}\right)$$

$$= -\frac{3i/2}{\mathfrak{N}+1}\, e^{-iEt}\, e^{-i(\gamma/2 + R_{++})t}\sin K_{++}\,t\,. \qquad (4.21)$$

In the same way we find

$$\frac{1}{2\pi i}\oint e^{-izt}\langle d_-|G(z)_P|e_-\rangle\,dz$$

$$\simeq -\frac{3i/2}{\mathfrak{N}+1}\, e^{-iEt}\, e^{i(\gamma/2 - R_{--})t}\sin K_{--}\,t \qquad (4.22)$$

and

$$\frac{1}{2\pi i}\oint e^{-izt}\langle d_\pm|G(z)_P|e_\mp\rangle\,dz$$

$$\simeq \frac{K_{\pm\mp}}{\gamma}\,\frac{2^{\mathfrak{N}-1}}{\mathfrak{N}+1}\left\{\sum_{x=1}^{\mathfrak{N}}(-1)^{x+1}\left[\cos\left(\frac{x\pi}{\mathfrak{N}+1}\right)\right]^{\mathfrak{N}-1}\sin^2\left(\frac{x\pi}{\mathfrak{N}+1}\right)\exp\{-i[E_+ + R_{++} + 2K_{++}\cos(\pi x/(\mathfrak{N}+1))]\,t\}\right.$$

$$\left. -\sum_{y=1}^{\mathfrak{N}}(-1)^{y+1}\left[\cos\left(\frac{y\pi}{\mathfrak{N}+1}\right)\right]^{\mathfrak{N}-1}\sin^2\left(\frac{y\pi}{\mathfrak{N}+1}\right)\exp\{-i[E_- + R_{--} + 2K_{--}\cos(y\pi/(\mathfrak{N}+1))]\,t\}\right\}$$

$$\simeq \frac{K_{\pm\mp}}{\gamma}\,\frac{3/8}{\mathfrak{N}+1}\left(e^{-i(E_+ + R_{++} + K_{++})t} + e^{-i(E_+ + R_{++} - K_{++})t} - e^{-i(E_- + R_{--} + K_{--})t} - e^{-i(E_- + R_{--} - K_{--})t}\right)$$

$$= \frac{K_{\pm\mp}}{\gamma}\,\frac{3/4}{\mathfrak{N}+1}\, e^{-iEt}\left(e^{-i(\gamma/2 + R_{++})t}\cos K_{++}\,t - e^{i(\gamma/2 - R_{--})t}\cos K_{--}\,t\right). \qquad (4.23)$$

We have now to evaluate the various R's and K's which appear in our calculations. As we have anticipated, these come from the diagonal and off-diagonal matrix elements of expansion (3.11) for $R(z)$. For large n and to the lowest possible order in ϵ and λ, we find

$$R_{++}(z) = \langle d_+|\mathcal{H}'\frac{Q}{z - \mathcal{H}_0 - V}\mathcal{H}'|d_+\rangle = \langle e_+|\mathcal{H}'\frac{Q}{z - \mathcal{H}_0 - V}\mathcal{H}'|e_+\rangle$$

$$= \langle d_+|\left\{S_+\alpha^\dagger\frac{\epsilon_\perp^2/4}{z - \mathcal{H}_0 - V}S_-\alpha + S_-\alpha\frac{\epsilon_\perp^2/4}{z - \mathcal{H}_0 - V}S_+\alpha^\dagger + S_z\alpha^\dagger\frac{\epsilon_\parallel^2}{z - \mathcal{H}_0 - V}S_z\alpha + S_z\alpha\frac{\epsilon_\parallel^2}{z - \mathcal{H}_0 - V}S_z\alpha^\dagger\right\}|d_+\rangle\,. \qquad (4.24)$$

The last two terms in (4.24) give a contribution of higher order in $\epsilon\sqrt{n}/\omega$ than the first two, and we neglect them. The value of $R_{++}(z)$ at $z = E$ can thus be calculated as

$$R_{++} = \frac{\epsilon_\perp^2 n}{8\omega}\,\frac{1 - A^2}{1 + A^2}\,. \qquad (4.25)$$

When the same procedure is applied to R_{--}, we find

$$R_{--} = \frac{\epsilon_\perp^2 n}{8\omega}\,\frac{A^2 - 1}{A^2 + 1} = -R_{++}\,. \qquad (4.26)$$

Within the same approximations we get

$$K_{++}(z) = \langle d_+|\mathcal{H}'\frac{Q}{z - \mathcal{H}_0 - V}\mathcal{H}'|e_+\rangle$$

$$= \langle d_+|\left(S_z\alpha^\dagger\frac{\epsilon_\parallel\lambda_\perp/2}{z - \mathcal{H}_0 - V}S_+\beta + S_+\beta\frac{\epsilon_\parallel\lambda_\perp/2}{z - \mathcal{H}_0 - V}S_z\alpha^\dagger + S_z\beta\frac{\epsilon_\perp\lambda_\parallel/2}{z - \mathcal{H}_0 - V}S_+\alpha^\dagger + S_+\alpha^\dagger\frac{\epsilon_\perp\lambda_\parallel/2}{z - \mathcal{H}_0 - V}S_z\beta\right)|e_+\rangle.$$

When this expression is evaluated at $z = E$, the result is

$$K_{++} = \frac{(2\epsilon_\perp\lambda_\parallel - \epsilon_\perp\lambda_\parallel)(mn)^{1/2}}{4\omega}\,\frac{A}{A^2 + 1}\,, \qquad (4.27)$$

and the other K's can be expressed in terms of this as

$$K_{--} = -K_{++}\,,\quad K_{+-} = K_{++}/A\,,\quad K_{-+} = -AK_{++}\,. \qquad (4.28)$$

Inserting relationships (4.26) and (4.28) into (4.21), (4.22), and (4.23) and neglecting $R_{++} \ll \frac{1}{2}\gamma$, we obtain

$$\begin{aligned}
&\frac{1}{2\pi i}\oint e^{-i\varepsilon t}\langle d_+|G(z)_P|e_+\rangle \simeq Me^{-i(E+\gamma/2)t}\sin Kt,\\
&\frac{1}{2\pi i}\oint e^{-i\varepsilon t}\langle d_-|G(z)_P|e_-\rangle \simeq Me^{-i(E-\gamma/2)t}\sin Kt,\\
&\frac{1}{2\pi i}\oint e^{-i\varepsilon t}\langle d_+|G(z)_P|e_-\rangle \simeq \frac{K}{A\gamma}Me^{-iEt}\sin\tfrac{1}{2}\gamma t\cos Kt,\\
&\frac{1}{2\pi i}\oint e^{-i\varepsilon t}\langle d_-|G(z)_P|e_+\rangle \simeq -\frac{AK}{\gamma}Me^{-iEt}\sin\tfrac{1}{2}\gamma t\cos Kt,
\end{aligned} \tag{4.29}$$

where $K \equiv k_{++}$ and $M = 3i/2(\mathfrak{N}+1)$. If the appropriate linear combinations of (4.29) are taken in order to give the desired initial and final states, the following expressions are obtained for the amplitudes of transition (4.1):

$$\begin{aligned}
\mathfrak{A}^{n,m,-1/2}_{n-2,m+1,-1/2} &\simeq \frac{M}{A^2+1}\left[\left(e^{i\gamma t/2}-A^2e^{-i\gamma t/2}\right)\sin Kt\right.\\
&\quad\left.+(1-A^2)(K/\gamma)\sin\tfrac{1}{2}\gamma t\cos Kt\right],\\
\mathfrak{A}^{n-1,m,1/2}_{n-3,m+1,1/2} &\simeq \frac{-M}{A^2+1}\left[\left(e^{-i\gamma t/2}-A^2e^{i\gamma t/2}\right)\sin Kt\right.\\
&\quad\left.+(1-A^2)(K/\gamma)\sin\tfrac{1}{2}\gamma t\cos Kt\right]\\
\mathfrak{A}^{n,m,-1/2}_{n-3,m+1,1/2} &\simeq \frac{-MA}{A^2+1}\left[\left(e^{i\gamma t/2}+e^{-i\gamma t/2}\right)\sin Kt\right.\\
&\quad\left.+2(K/\gamma)\sin\tfrac{1}{2}\gamma t\cos Kt\right],\\
\mathfrak{A}^{n-1,m,1/2}_{n-2,m+1,-1/2} &\simeq \frac{-MA}{A^2+1}\left(\left(e^{i\gamma t/2}+e^{-i\gamma t/2}\right)\sin Kt\right.\\
&\quad\left.-\frac{A^4+1}{A^2}\frac{K}{\gamma}\sin\tfrac{1}{2}\gamma t\cos Kt\right),
\end{aligned} \tag{4.30}$$

The transition probabilities for generation of second harmonics can be calculated from (4.30) and the results are substantially the same as those given in a previous paper,[3] apart from the factor involving $\mathfrak{N}$ which was absent in that paper, where a 4×4 subspace for P and Q was chosen. Therefore the conclusions of that paper are valid; the power generated is peaked at $\omega_0 \sim \omega$ as a function of ω_0, but the sum of the transition probabilities (4.30) does not seem to show any structure as that found experimentally.

B. Region $\omega_0 \sim 2\omega$

The transition of interest with initial states on the same energy shell are of the form

$$\begin{aligned}
&|n,\ m,\ -\tfrac{1}{2}\rangle \rightarrow |n-2,\ m+1,\ -\tfrac{1}{2}\rangle,\\
&|n,\ m-1,\ \tfrac{1}{2}\rangle \rightarrow |n-2,\ m,\ \tfrac{1}{2}\rangle,\\
&|n,\ m-1,\ \tfrac{1}{2}\rangle \rightarrow |n-2,\ m+1,\ -\tfrac{1}{2}\rangle.
\end{aligned} \tag{4.31}$$

Consequently the part of $\mathcal{H}_{\text{int}}$ which contains dangerous terms is

$$V = \tfrac{1}{2}\lambda_\perp(S_+\beta + S_-\beta^\dagger). \tag{4.32}$$

The eigenstates of $\mathcal{H}_0 + V$ are of the form

$$\begin{aligned}
|d_+\rangle &= (A^2+1)^{-1/2}\left(A|n,\ m,\ -\tfrac{1}{2}\rangle + |n,\ m-1,\ \tfrac{1}{2}\rangle\right),\\
|d_-\rangle &= (A^2+1)^{-1/2}\left(|n,\ m,\ -\tfrac{1}{2}\rangle - A|n,\ m-1,\ \tfrac{1}{2}\rangle\right),
\end{aligned} \tag{4.33}$$

corresponding to the eigenvalues

$$E_\pm = (n+2m)\,\omega - (\omega \mp \gamma), \tag{4.34}$$

where

$$A = \lambda_\perp\sqrt{m}/(\gamma-\delta), \quad \delta = 2\omega - \omega_0, \quad \gamma = (\delta^2 + \lambda_\perp^2 m)^{1/2}. \tag{4.35}$$

All doublets of form (4.33) coming from the states $|n-2i,\ m+i,\ -\frac{1}{2}\rangle$ and $|n-2i,\ m+i-1,\ \frac{1}{2}\rangle$ ($|i| \ll m$) have approximately the energy (4.34), and consequently must be included in the subspace relative to P and Q. The problem from now on is exactly analogous to the one we have solved in Sec. IV A, and we get the following formal equalities between the amplitudes $\mathfrak{B}$ for transitions (4.31) and those given by (4.30) at $\omega_0 \sim \omega$:

$$\begin{aligned}
&\mathfrak{B}^{n,m,-1/2}_{n-2,m+1,-1/2} = \mathfrak{A}^{n,m,-1/2}_{n-2,m+1,-1/2}, \quad \mathfrak{B}^{n,m-1,1/2}_{n-2,m,1/2} = \mathfrak{A}^{n-1,m,1/2}_{n-3,m+1,1/2},\\
&\mathfrak{B}^{n,m-1,1/2}_{n-2,m+1,-1/2} = \mathfrak{A}^{n,m,1/2}_{n-3,m+1,1/2}.
\end{aligned} \tag{4.36}$$

When using (4.36) however, one should remember that A and γ are now given by (4.35), that $\mathfrak{N}$ is the number of states of the form (4.33) which can be considered of the same energy, and that K must be calculated again from

$$\begin{aligned}
K_{++}(z) &\simeq \langle d_+|\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'|e_+\rangle\\
&= \langle d_+|\left(S_z\alpha^\dagger\frac{\epsilon_\parallel\epsilon_\perp/2}{z-\mathcal{H}_0-V}S_-\alpha^\dagger\right.\\
&\quad\left.+S_-\alpha^\dagger\frac{\epsilon_\parallel\epsilon_\perp/2}{z-\mathcal{H}_0-V}S_z\alpha^\dagger\right)|e_+\rangle.
\end{aligned} \tag{4.37}$$

Putting $z = (E_+ + E_-)/2$ in (4.37) with E_+ and E_- now given by (4.34), we finally get

$$K \sim \frac{\epsilon_\parallel\epsilon_\perp n}{2\omega}\frac{A}{A^2+1}$$

with A given by (4.35). Again we find that the power generated at double frequency is peaked at $\omega_0 \sim 2\omega$, this time in agreement with the experimental results which show no structure of this peak.

We may summarize the results of this section as follows. The theory predicts two peaks at $\omega_0 \sim \omega$ and $\omega_0 \sim 2\omega$, and this is observed experimentally. Moreover for reasonably short times, the transition amplitudes depend linearly on K as given by expressions (4.27) and (4.38), and consequently the transition probabilities depend on K^2. In particular, the transition probabilities at $\omega_0 \sim \omega$ depend on the occupation numbers like nm and those at ω_0

$\sim 2\omega$ like n^2. We do not wish here to undertake a self-consistent calculation of m as a function of n at $\omega_0 \sim \omega$, since this would necessarily involve consideration of the technical aspects of the experiment, and this would fall out of the scope of this paper. Experimentally,[2] the power dependence of the peak at $\omega_0 \sim 2\omega$ is like n^2, which agrees with our theory, while that of the peak at $\omega_0 \sim \omega$ is like $n^{1.7}$ which is in disagreement with our results even under the plausible assumption that the average value of m is essentially independent of n. Finally, since K depends quadratically on the coupling constants ϵ and λ, the intensity of the second-harmonic generation in DPPH should be intermediate between those of the two transitions of ruby for which we have calculated the coupling constants in Sec. II. This actually is only a qualitative prediction because of the $\mathfrak{N}$ factors appearing in the denominators of the transition amplitudes, but as such it is in agreement with the experiments when the absolute intensities of the peaks are measured in decibels above noise,[2] at least if the number of paramagnetic centers can be assumed about the same in different samples. The disagreement between theory and experiment, however, is evident in that the theory does not predict any structure of the peak at $\omega_0 \sim \omega$, while experimentally at high input power (large n), a hole develops at the center of that peak. Arguments can be brought to justify the presence of this dip,[3] but in the present framework they are of a rather artificial nature. We shall see that this peculiar feature of the second harmonic generation finds a natural explanation when the theory outlined here is extended to cover the mutual interaction of the paramagnetic spins induced by the electromagnetic field. We shall develop this theory in Secs. V and VI.

V. N SPINS: REGION $\omega_0 \sim \omega$

In this section we shall apply the general theory of Sec. III to the case of N equal spins $S^i = \frac{1}{2}$ placed in a uniform static magnetic field such that $\omega_0 \sim \omega$. The starting point for this case is again Hamiltonian (2.14) where the various spin operators are defined as in (2.13). We observe first that the total spin operator

$$|\vec{S}|^2 = \left| \sum_{i=1}^{N} \vec{S}^i \right|^2$$

is a constant of motion since it commutes with the Hamiltonian; hence the total Hilbert space of the system can be divided into subspaces each characterized by an eigenvalue of S. We shall develop our calculations in the subspace with the highest possible eigenvalue $S = N/2$, and for simplicity shall assume that N is even. This will simplify the notation, since we are now entitled to drop Γ, and it should not pose any serious limitation on the validity of final results. We shall also find it convenient to relabel the eigenstates of $\mathcal{H}_0$ in this subspace as $|n+x, m, -x\rangle$, where x is now the number of spin deexcitations counted from the state with $S_z = 0$. The range of x is therefore between $-S$ and S, while n is the number of ω photons present in the cavity when $S_z = 0$. The eigenvalue corresponding to this eigenstate of $\mathcal{H}_0$ is $(n + 2m - S)\omega + x\alpha$, where $\alpha = \omega - \omega_0$. Another assumption that we make is that the number of spins N is much smaller than n. This is indeed the case in the usual experimental setup where most of the work is performed under saturation conditions, and this fact will permit us to make some very useful approximations in the course of this paper.

A. Eigenstates of $\mathcal{H}_0 + V$

Like in Sec. IV A, the part of $\mathcal{H}_{\text{int}}$ which contains dangerous terms is obviously

$$V = \tfrac{1}{2}\epsilon_\perp (S_+ \alpha + S_- \alpha^\dagger), \tag{5.1}$$

where

$$S_\pm = \sum_{i=1}^{N} S_\pm^i. \tag{5.2}$$

V connects the state $|n+x, m, -x\rangle$ to $|n+x\pm 1, m, -x\mp 1\rangle$, and in order to diagonalize $\mathcal{H}_0 + V$ within this $2S+1$ manifold we have to solve the following system of equations for each μ ($\mu = 0, 1, \ldots, 2S$):

$$\begin{vmatrix} \cdots & & & \\ \cdots & & & \\ \cdots & & & \\ (n+2m-S)\omega + (x-1)\alpha - E_\mu & \tfrac{1}{2}\epsilon_\perp \sqrt{n}\,[(S+x)(S-x+1)]^{1/2} & 0 & \cdots \\ \tfrac{1}{2}\epsilon_\perp \sqrt{n}\,[(S+x)(S-x+1)]^{1/2} & (n+2m-S)\omega + x\alpha - E_\mu & \tfrac{1}{2}\epsilon_\perp \sqrt{n}\,[(S-x)(S+x+1)]^{1/2} & \cdots \\ 0 & \tfrac{1}{2}\epsilon_\perp \sqrt{n}\,[(S-x)(S+x+1)]^{1/2} & (n+2m-S)\omega + (x+1)\alpha - E_\mu & \cdots \\ & & & \end{vmatrix} \begin{vmatrix} \cdot \\ \cdot \\ \cdot \\ B^\mu_{S-x+1} \\ B^\mu_{S-x} \\ B^\mu_{S-x-1} \\ \cdots \\ \cdots \\ \cdots \end{vmatrix} = 0, \tag{5.3}$$

where we have approximated $(n+x)^{1/2} \sim \sqrt{n}$ and B^{μ}_{S-x} is the projection of the μth eigenvector of $\mathcal{H}_0 + V$ (which we shall indicate by $|d_\mu\rangle$) on the state $|n+x, m, -x\rangle$. From (5.3) we find immediately the system of difference equations for the B's:

$$\tfrac{1}{2}\epsilon_\perp\sqrt{n}[(S-x)(S+x+1)]^{1/2}B^{\mu}_{S-x-1} + [(n+2m-S)\omega + x\alpha - E_\mu]B^{\mu}_{S-x} + \tfrac{1}{2}\epsilon_\perp\sqrt{n}[(S+x)(S-x+1)]^{1/2}B^{\mu}_{S-x+1} = 0, \quad (5.4)$$

which can be regarded as an infinite system if we add the condition

$$B^{\mu}_{i} = 0, \quad 2S < i < 0. \quad (5.5)$$

We now transform the system (5.4) by putting

$$B^{\mu}_{S-x} = (-1)^{S-x}\left(\frac{(S-x)!\,(2S)!}{(S+x)!}\right)^{1/2} e^{\mu}_{S-x} \quad (5.6)$$

and (5.4) becomes

$$\tfrac{1}{2}\epsilon_\perp\sqrt{n}\,e^{\mu}_{S-x-1} - [(n+2m-S)\omega + x\alpha - E_\mu]e^{\mu}_{S-x} + \tfrac{1}{2}\epsilon_\perp\sqrt{n}\,(S+x)(S-x+1)\,e^{\mu}_{S-x+1} = 0 \quad (5.7)$$

with the conditions

$$e^{\mu}_{i} \text{ finite for } i \geq 0, \quad e^{\mu}_{i} = 0 \text{ for } i < 0. \quad (5.8)$$

We shall use a technique similar to that previously used by Scharf,[13,14] and introduce the set of characteristic functions

$$f^{\mu}(z) = \sum_{x=S}^{\infty} e^{\mu}_{S-x} z^{S-x}, \quad (5.9)$$

which can readily be seen to satisfy the differential equations

$$\frac{d^2 f^{\mu}}{dz^2} - \left(\frac{2S}{z} + \frac{2\alpha}{\epsilon_\perp\sqrt{n}}\right)\frac{df^{\mu}}{dz} - \left(1 - \frac{2}{\epsilon_\perp\sqrt{n}}\,\frac{E-E_\mu}{z}\right)f^{\mu} = 0, \quad (5.10)$$

where $E = (n+2m)\omega - S\omega_0$. Equations (5.10) must be solved together with the boundary condition which can be derived from (5.8)

$$\lim_{z\to 0} f^{\mu}(z) = e^{\mu}_{0} = \text{finite number}. \quad (5.11)$$

Putting

$$f^{\mu}(z) = e^{z(\alpha+\gamma)/\epsilon_\perp\sqrt{n}}F^{\mu}(z) \quad (5.12)$$

Eqs. (5.10) become

$$\frac{d^2F^{\mu}}{dz^2} + \left(-\frac{2S}{z} + \frac{2\gamma}{\epsilon_\perp\sqrt{n}}\right)\frac{dF^{\mu}}{dz} - \left(\frac{2S\gamma + 2S\alpha + 2(E_\mu - E)}{\epsilon_\perp\sqrt{n}Z}\right)F^{\mu} = 0. \quad (5.13)$$

A particular solution of Eq. (5.13) is given in terms of the confluent hypergeometric function[15]

$$F^{\mu}_{1}(z) = F\left(-S - \frac{E_\mu - E + S\alpha}{\gamma}, \; -2S; \; -\frac{2\gamma}{\epsilon_\perp\sqrt{n}}\,z\right). \quad (5.14)$$

Since $2S$ is a positive integer, solutions (5.14) would diverge unless

$$E_\mu = E - S\alpha + (S-\mu)\gamma \quad (\mu = 0, 1, \ldots, 2S), \quad (5.15)$$

and this set of solutions can be written

$$F^{\mu}_{1}(z) = F(\mu - 2S, \; -2S; \; -(2\gamma/\epsilon_\perp\sqrt{n})\,z) = e^{-2\gamma z/\epsilon_\perp\sqrt{n}}F(-\mu, \; -2S; \; (2\gamma/\epsilon_\perp\sqrt{n})z). \quad (5.16)$$

Another set of solutions of (5.13) linearly independent of (5.16) is of the logarithmic kind, since $-2S$ is an integer. This set is of the form

$$F^{\mu}_{2}(z) = F^{\mu}_{1}(z)\ln(2\gamma z/\epsilon_\perp\sqrt{n}) + z^{r}G(z),$$

where $G(z)$ is analytic at the origin and r is the second root of the indicial equation relative to the $z=0$ singularity. This second set of solutions however diverges for $z \to 0$ and is therefore to be excluded because of condition (5.11). From (5.16) and (5.12) we get

$$f^{\mu}(z) = e^{z(\alpha-\gamma)/\epsilon_\perp\sqrt{n}}F(-\mu, \; -2S; \; (2\gamma/\epsilon_\perp\sqrt{n})z). \quad (5.17)$$

Solutions (5.17) can be developed in a power series at $z=0$ as

$$f^{\mu}(z) = \sum_{n=0}^{\infty} c_n Z^n, \quad (5.18)$$

where

$$c_n = \left(\frac{\alpha-\gamma}{\epsilon_\perp\sqrt{n}}\right)^{n}\sum_{m=0}^{n,\mu}\frac{1}{m!\,(n-m)!}\,\frac{(-\mu)_m}{(-2S)_m}\left(\frac{2\gamma}{\alpha-\gamma}\right)^{m}.$$

In the last expression $(a)_m$ is the Pochammer's symbol

$$(a)_m = a(a+1)\cdots(a+m-1)$$

and $\sum_{m=0}^{n,\mu}$ indicates summation over m from 0 to the smallest of n and μ. Equating the coefficients of equal powers of z in (5.9) and (5.18) and substituting in (5.6), we finally find

$$B^{\mu}_{S-x} = (-1)^{S-x}\left[\frac{(S-x)!\,(2S)!}{(S+x)!}\right]^{1/2}\left(\frac{\alpha-\gamma}{\epsilon_\perp\sqrt{n}}\right)^{S-x} \times \sum_{m=0}^{S-x,\,\mu}\frac{(-1)^m}{m!\,(S-x-m)!}\,\frac{\mu!}{(\mu-m)!} \times \frac{1}{(-2S)_m}\left(\frac{2\gamma}{\alpha-\gamma}\right)^{m}. \quad (5.19)$$

Expressions (5.15) and (5.19) are the exact solutions of Eqs. (5.3). Expression (5.19), however, is rather complicated, and we shall devote the rest of this subsection to find approximations to B^{μ}_{S-x} of a manageable form. Rather than proceeding from (5.19) towards these approximations we shall find it more convenient to use our knowledge of the

exact eigenvalues (5.15) and convert approximately the difference equations (5.4) to a differential equation. We introduce the variable

$$\xi = x/S^{1/2} - S^{1/2}\alpha/\gamma$$

and approximate

$$B^{\mu}_{S-x-1} \simeq B^{\mu}_{S-x} + \dot{B}^{\mu}_{S-x} S^{1/2} + \tfrac{1}{2}\ddot{B}^{\mu}_{S-x} S, \quad \dot{B}^{\mu} \equiv \frac{dB^{\mu}}{d\xi}. \tag{5.20}$$

Substituting (5.20) in (5.4) we get approximately

$$\tfrac{1}{2}\epsilon_{\perp}\sqrt{n}\,(S^2 - x^2 + S)^{1/2}(B^{\mu} + \dot{B}^{\mu}/S^{1/2} + \ddot{B}^{\mu}/2S) + [x\alpha + (\mu - S)\gamma]B^{\mu} + \tfrac{1}{2}\epsilon_{\perp}\sqrt{n}\,(S^2 - x^2 + S)^{1/2} \times (B^{\mu} - \dot{B}^{\mu}/S^{1/2} + \ddot{B}^{\mu}/2S) = 0 \tag{5.21}$$

or

$$\ddot{B}^{\mu} + 2S\left(1 + \frac{x\alpha + (\mu - S)\gamma}{\epsilon_{\perp}\sqrt{n}\,(S^2 - x^2 + S)^{1/2}}\right)B^{\mu} = 0. \tag{5.22}$$

We now approximate for small α and x not too large:

$$\gamma \simeq \epsilon_{\perp}\sqrt{n}\,(1 + \alpha^2/2\epsilon_{\perp}^2 n), \quad (S^2 - x^2 + S)^{1/2} \simeq S + \tfrac{1}{2} - x^2/2S,$$

$$\frac{\mu\gamma}{\epsilon_{\perp}\sqrt{n}\,(S^2 - x^2 + S)^{1/2}} \simeq \frac{\mu}{S},$$

$$1 + \frac{x\alpha - S\gamma}{\epsilon_{\perp}\sqrt{n}\,(S^2 - x^2 + S)^{1/2}} \simeq \frac{1}{2S}\left[1 - \left(\frac{x}{S^{1/2}} - S^{1/2}\frac{\alpha}{\gamma}\right)^2\right],$$

and Eq. (5.22) becomes

$$\ddot{B}^{\mu} + \left[2\mu + 1 - \left(\frac{x}{S^{1/2}} - S^{1/2}\frac{\alpha}{\gamma}\right)^2\right]B^{\mu} = 0, \tag{5.23}$$

which is a Weber-Hermite equation whose solutions are

$$B^{\mu}_{S-x} = Ae^{-(S^{1/2}\alpha/\gamma - x/S^{1/2})^2/2} H_{\mu}\left(S^{1/2}\frac{\alpha}{\gamma} - \frac{x}{S^{1/2}}\right).$$

Here H_{μ} is the μth Hermite polynomial, and A is the normalization constant such that

$$\sum_{x=-S}^{S} B^{\mu}_{S-x} B^{\mu'}_{S-x} = \delta_{\mu\mu'}.$$

Since

$$\frac{1}{A^2}\sum_{x} B^{\mu}_{S-x} B^{\mu'}_{S-x} \simeq S^{1/2}\int_{-\infty}^{\infty} e^{-(S^{1/2}\alpha/\gamma - x/S^{1/2})^2} \times H_{\mu}\left(S^{1/2}\frac{\alpha}{\gamma} - \frac{x}{S^{1/2}}\right)H_{\mu'}\left(S^{1/2}\frac{\alpha}{\gamma} - \frac{x}{S^{1/2}}\right)\frac{dx}{S^{1/2}} = 2^{\mu}\mu!\,(\pi S)^{1/2}\delta_{\mu\mu'},$$

we find

$$B^{\mu}_{S-x} \simeq \frac{1}{(\pi S)^{1/4}}\frac{2^{-\mu/2}}{(\mu!)^{1/2}} e^{-(S^{1/2}\alpha/\gamma - x/S^{1/2})^2/2} \times H_{\mu}\left(S^{1/2}\frac{\alpha}{\gamma} - \frac{x}{S^{1/2}}\right). \tag{5.24}$$

We observe that (5.24) are good approximations to the real solutions for small μ (high energies), since then approximation (5.20) is a good one. As μ increases solutions (5.24) oscillate more and more rapidly as functions of x, and this eventually becomes inconsistent with (5.20). On the other hand, we may obtain the solutions for very high μ (low energy) if in (5.4) we change μ to $2S - \nu$ and B^{μ}_{S-x} to $(-1)^x B^{\nu}_{S-x}$. In this case, in fact, we obtain an equation similar to (5.21), but with $-x\alpha$ in place of $x\alpha$. It is then easy to see that the solutions for low energy (small ν) are

$$B^{\nu}_{S-x} \simeq \frac{1}{(\pi S)^{1/4}}\frac{2^{-\nu/2}}{(\nu!)^{1/2}}(-1)^x e^{-(S^{1/2}\alpha/\gamma + x/S^{1/2})^2/2} \times H_{\nu}\left(S^{1/2}\frac{\alpha}{\gamma} + \frac{x}{S^{1/2}}\right). \tag{5.25}$$

Approximate solutions (5.24) and (5.25) can also be obtained starting from (5.19), but this direct approach is more lengthy and boring than the one we have used here. These solutions reduce for $\alpha = 0$ to the approximate results by Tavis and Cummings,[16] and as we have seen are valid for low and high μ, for quite a large range of x and for a small region of $|\alpha| < \epsilon_{\perp}\sqrt{n}$. We may ask ourselves if their particularly simple form is susceptible to a physical interpretation. It is easy to convince oneself that this is so, since in the limit of large n the electromagnetic field tends to behave classically, and the problem of diagonalizing $\mathcal{H}_0 + V$ tends to become that of finding the motion of the spins in a frame of reference which rotates with frequency ω in a counterclockwise sense around its z axis parallel to the static magnetic field. As is well known, in this case the static field in the rotating frame reduces to $\alpha = \omega - \omega_0$, and this is to be added to the amplitude $\epsilon_{\perp}\sqrt{n}$ of the rotating field. The resulting field in the rotating frame is

$$\gamma = (\alpha^2 + \epsilon_{\perp}^2 n)^{1/2}$$

and the levels of the spin system shall be quantized in this field giving rise to the eigenvalues (5.15). Furthermore if S is large enough, the total magnetic moment $\vec{S}$ may be thought to precess with frequency γ around the resulting field in the rotating frame, and for small μ and $\alpha = 0$ the tip of the magnetization will describe a small circle with the same frequency. The projection of this motion on the z axis describes the time evolution of S_z, and it is obviously of the harmonic-oscillator kind with $S_z = 0$ as the center of oscillation. If the quantization of the system is taken into account, it is therefore to be expected that $B^{\mu}(x)$ is a parabolic cylinder function, since $x = -S_z$. When $\alpha \neq 0$, the magnetization shall precess around a direction slightly inclined on the x-y plane, and its projection on the z axis will again approximately behave like a harmonic oscillator if α is small; now however we

expect the center of oscillation to be displaced by a quantity which depends on α, and this again agrees with formulas (5.24) and (5.25).

We may conclude that we have found reasonable approximations for the eigenvalues and the eigenfunctions of $\mathcal{H}_0+V$ in the region $\omega_0\sim\omega$, belonging to the low- and high-energy ranges. The intermediate eigenfunctions however are not easily reducible to a simple and manageable form, and before proceeding to the calculation of the generation of second harmonic we shall show in Sec. V B that we really do not need them in order to explain the experimental results.

B. Initial States

As we have discussed, in the general theory, the transitions of interest in the new notation introduced at the beginning of this section, and in the present range of magnetic fields these are

$$\begin{aligned}&|n+x,\ m,\ -x\rangle \rightarrow |n+x-2,\ m+1,\ -x\rangle,\\ &|n+x,\ m,\ -x\rangle \rightarrow |n+x+1,\ m+1,\ -x+1\rangle,\\ &|n+x,\ m,\ -x\rangle \rightarrow |n+x-3,\ m+1,\ -x-1\rangle.\end{aligned} \tag{5.26}$$

Since we have calculated the eigenfunctions $|d_\mu\rangle$ and $|e_\mu\rangle$ of $\mathcal{H}_0+V$ in (5.1a), we might at this point proceed as before and develop the calculations for any x through steps (3.7) and (3.6) according to our general plan. A great simplification is possible however if we are able to select some value of x for which transitions (5.26) are more important, since the initial and final states relative to these transitions will turn out to have large components on the states of $\mathcal{H}_0+V$ for which we have found compact approximate expressions. This will permit a very effective simplification in the calculation of the double sum in (3.7), and in addition will ultimately allow us to give a simple physical picture of the generation of the second harmonic. In order to show this, we shall now make recourse to the theory of phenomenological Bloch's equations. We wish to emphasize that the use we make of Bloch's equations is limited to the selection of the initial and final states for our transition amplitudes, and that once this choice is made, the calculation is fully quantum mechanical and does not rely on relaxation times of any sort.

As is well known, the Bloch's equations for a magnetic moment $\vec{S}$ in a static external magnetic field ω_0 along the z axis and in a counter-rotating magnetic field h in the x-y plane with frequency ω can be written as

$$\begin{aligned}&\dot{S}_+ + i\omega_0 S_+ + S_+/\tau_2 = ihS_z e^{i\omega t},\\ &\dot{S}_- - i\omega_0 S_- + S_-/\tau_2 = -ihS_z e^{-i\omega t},\\ &\dot{S}_z + S_z/\tau_1 = \tfrac{1}{2}ih(S_+ e^{+i\omega t} - S_- e^{-i\omega t}) + |\vec{S}|/\tau_1,\end{aligned} \tag{5.27}$$

where $S_\pm = S_x \pm iS_y$ and τ_1 and τ_2 are the longitudinal and transverse relaxation times. A particular solution of (5.27) can be found for the case of slow passage, when the magnetic field ω_0 is swept very slowly through resonance, and consequently one can assume $\dot{S}_z = 0$. It can be shown[17] that in this solution the magnetic moment $\vec{S}$ precesses around the static field ω_0 at an angle φ_0 given by

$$\tan\varphi_0 = \frac{h\tau_2}{[1+(\omega-\omega_0)^2\tau_2^2]^{1/2}}. \tag{5.28}$$

In our formalism $h\sim\epsilon_\perp\sqrt{n}$. Assuming $n\sim 10^{21}$, which gives a real magnetic field at the sample of ~ 25 G, and using for $\epsilon_\perp$ the maximum value of 2.5×10^{-3} Hz that we have calculated in Sec. II for DPPH, we get $h\sim 8\times10^7$ Hz. For τ_2 we assume the value from phase measurements[2] of $\sim 9\times10^{-8}$ sec, and we find at resonance $\tan\varphi_0\sim 7.2$ or $\varphi_0\sim 82°$. This shows that in the neighborhood of resonance the magnetization is tilted to rotate practically in the x-y plane. Consequently, if we might neglect 1 in the denominator of (5.28), we would have

$$\tan\varphi_0 = \epsilon_\perp\sqrt{n}/|\alpha|,\quad S_z = S|\alpha|/\gamma,$$

and it should be very convenient in the calculations for the transition amplitudes to use initial and final states that behave in the way described above.

Let us now consider the average value of S_z on a state of high energy of the form (5.24). This is given by

$$\begin{aligned}\langle d_\mu|S_z|d_\mu\rangle \simeq &\left(\frac{S}{\pi}\right)^{1/2}\frac{2^{-\mu}}{\mu!}\int_{-\infty}^{\infty} e^{-(S^{1/2}\alpha/\gamma - x/S^{1/2})^2}\\ &\times H_\mu^2\left(S^{1/2}\frac{\alpha}{\gamma}-\frac{x}{S^{1/2}}\right)\frac{x}{S^{1/2}}\,d\left(\frac{x}{S^{1/2}}\right).\end{aligned} \tag{5.29}$$

Expression (5.29) is obviously equal to $S\alpha/\gamma$, since it is equivalent to the average value of the displacement of an eigenstate of a harmonic oscillator whose center of oscillation has been displaced by the amount $S^{1/2}\alpha/\gamma$, multiplied by the factor $S^{1/2}$ in front of the integral. By the same technique we find that the value of $\langle d_\mu|S_z^2|d_\mu\rangle$ is approximately equal to $S^2\alpha^2/\gamma^2$. Therefore we see that any eigenstate of $\mathcal{H}_0+V$ of the form (5.24) can adequately describe the physical situation for $\alpha<0$, and in this range of magnetic fields it can be used as an adequate initial and final state. Following the same criterion, for $\alpha>0$ we may choose as initial state any eigenstate of $\mathcal{H}_0+V$ of low energy that is of the form (5.25). This is approximately equivalent to using initial and final states of the form (5.26) in which $x\sim 0$, since these are the eigenstates of $\mathcal{H}_0$ with the largest components on the low- and high-energy states of $\mathcal{H}_0+V$.

C. Generation of Second Harmonic

We have seen in Sec. V B that the calculation of transition amplitudes can be reduced to the evalua-

tion of matrix elements of the resolvent operator such as

$$\langle d_\mu | G(z)_P | e_{\mu'} \rangle \quad (\alpha < 0), \quad \langle d_\nu | G(z)_P | e_{\nu'} \rangle \quad (\alpha > 0) .$$

We shall consider first the case $\alpha < 0$, where

$$|d_\mu\rangle = \sum_{x=-S}^{S} B^{\mu}_{S-x} |n+x,\ m,\ -x\rangle ,$$
$$|e_{\mu'}\rangle = \sum_{x=-S}^{S} B^{\mu'}_{S-x} |n+x-2,\ m+1,\ -x\rangle \quad (\mu, \mu' \ll S), \tag{5.30}$$

and the B's are approximately given by expression (5.24). We are now faced with the problem of the choice of the P and Q operators. In the case of the isolated spin this was solved by including in the P subspace all the eigenstates $|d_\pm\rangle$, $|e_\pm\rangle$, $|f_\pm\rangle$, ... of the same energy, and this entitled us to conveniently truncate the series expansion for $R(z)$. Now we cannot proceed in the same way for two reasons. First, as shown by formula (5.15) the splittings of the eigenvalues of $\mathcal{H}_0$ due to V are proportional to S, which is usually a very large number; consequently the energy region for the eigenstates of $\mathcal{H}_0 + V$ coming from states $|n+x,\ m,\ -x\rangle$ largely overlaps with the energy regions of other eigenstates of $\mathcal{H}_0 + V$ coming from states $|n+x+i,\ m+j,\ -x\rangle$, thus creating difficulties in identifying and enumerating the states to be included in the P subspace. Furthermore as we shall see later on, there is no guarantee that the shifts and the splittings of the eigenvalues of $\mathcal{H}_0 + V$ due to $\mathcal{H}'$ are small; hence the truncation of series (3.11) for $R(z)$ presents problems. From what we have said above, it follows that we have to resort to other approximations than those used in the case of the isolated spin. In order to find the most convenient approximations, we have to examine first the matrix elements of $\mathcal{H}'$ between eigenstates of $\mathcal{H}_0 + V$. As an example which shall be useful in the following we shall consider the matrix elements $\langle d_\mu | S_z \alpha^\dagger | f_{\mu''} \rangle$ and $\langle f_{\mu''} | S_+ \beta | e_{\mu'} \rangle$, with $|d_\mu\rangle$ and $|e_{\mu'}\rangle$ defined as in (5.30) and

$$|f_{\mu''}\rangle = \sum_{x=-S}^{S} B^{\mu''}_{S-x} |n+x-1,\ m,\ -x\rangle .$$

We immediately find, assuming $n,\ m \gg 1$,

$$\langle d_\mu | S_z \alpha^\dagger | f_{\mu''} \rangle = \sqrt{n} \sum_x (-x) B^{\mu}_{S-x} B^{\mu''}_{S-x},$$
$$\langle f_{\mu''} | S_+ \beta | e_{\mu'} \rangle = \sqrt{m} \sum_x [(S-x+1)(S+x)]^{1/2} \tag{5.31}$$
$$\times B^{\mu''}_{S-x+1} B^{\mu'}_{S-x} .$$

The two $\sum_x$ in (5.31) can be approximately evaluated by converting them to integrals as we did in (5.29). From (5.24) we see that B^{μ}_{S-x} as a function of x behaves like the μth eigenfunction of a harmonic oscillator whose center of oscillation is at $x = S\alpha/\gamma$. Therefore up to terms of $O(S)$ we have

$$\langle d_\mu | S_z \alpha^\dagger | f_{\mu''} \rangle = -\sqrt{n} S(\alpha/\gamma)\, \delta_{\mu\mu''} ,$$
$$\langle f_{\mu''} | S_+ \beta | e_{\mu'} \rangle = \sqrt{m} S(1 - \alpha^2/\gamma^2)^{1/2} \delta_{\mu'\mu''} , \tag{5.32a}$$

where we have approximated

$$[(S-x+1)(S+x)]^{1/2} \simeq S(1 - x^2/S^2)^{1/2}$$

and where terms $O(S^{1/2})$ have been discarded.

With the same approximations we find

$$\langle d_\mu | S_+ \beta | f_{\mu''} \rangle = \sqrt{m} S(1 - \alpha^2/\gamma^2)^{1/2} \delta_{\mu\mu''} ,$$
$$\langle f_{\mu''} | S_z \alpha^\dagger | e_{\mu'} \rangle = -\sqrt{n} S(\alpha/\gamma)\, \delta_{\mu'\mu''} , \tag{5.32b}$$

where

$$|f_{\mu''}\rangle = \sum_x B^{\mu''}_{S-x} |n+x-1,\ m+1,\ -x\rangle .$$

Furthermore,

$$\langle d_\mu | S_+ \alpha^\dagger | f_{\mu''} \rangle = \sqrt{n} S(1 - \alpha^2/\gamma^2)^{1/2} \delta_{\mu\mu''} ,$$
$$\langle f_{\mu''} | S_z \beta | e_{\mu'} \rangle = -\sqrt{m} S(\alpha/\gamma) \delta_{\mu'\mu''} , \tag{5.32c}$$

where

$$|f_{\mu''}\rangle = \sum_x B^{\mu''}_{S-x} |n+x-2,\ m,\ -x\rangle$$

and finally

$$\langle d_\mu | S_z \beta | f_{\mu''} \rangle = -\sqrt{m} S(\alpha/\gamma) \delta_{\mu\mu'} ,$$
$$\langle f_{\mu''} | S_+ \alpha^\dagger | e_{\mu'} \rangle = \sqrt{n} S(1 - \alpha^2/\gamma^2)^{1/2} \delta_{\mu'\mu''} , \tag{5.32d}$$

where

$$|f_{\mu''}\rangle = \sum_x B^{\mu''}_{S-x} |n+x,\ m+1,\ -x\rangle .$$

We now turn to the evaluation of

$$\langle d_\mu | G(z)_P^{-1} | e_{\mu'} \rangle = \langle d_\mu | [z - (\mathcal{H}_0 + V)_P - R(z)_P] | e_{\mu'} \rangle$$
$$= -\langle d_\mu | R(z)_P | e_{\mu'} \rangle \equiv K_{\mu\mu'} ,$$

where we choose the P operator to project on the 2×2 subspace spanned by $|d_\mu\rangle$ and $|e_{\mu'}\rangle$ defined in (5.30). We have

$$K_{\mu\mu'} = -\langle d_\mu | \mathcal{H}' \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} \mathcal{H}' | e_{\mu'} \rangle = -\langle d_\mu | \mathcal{H}' Q \Big(\frac{1}{z - \mathcal{H}_0 - V} + \frac{1}{z - \mathcal{H}_0 - V} Q\mathcal{H}'Q \frac{1}{z - \mathcal{H}_0 - V}$$
$$+ \frac{1}{z - \mathcal{H}_0 - V} Q\mathcal{H}'Q \frac{1}{z - \mathcal{H}_0 - V} Q\mathcal{H}'Q \frac{1}{z - \mathcal{H}_0 - V} + \cdots \Big) Q\mathcal{H}' | e_{\mu'} \rangle . \tag{5.33}$$

As we have said before, we cannot truncate the series in (5.33), because in view of (5.32) we have no guarantee that the neglected terms give small contributions, and also because in so doing we neglect poles whose

residues may be large. We may use results (5.32) however in order to select a partial summation from (5.33). We observe that the first term is

$$-\langle d_\mu|\mathcal{H}'\frac{Q}{z-\mathcal{H}_0-V}\mathcal{H}'|e_{\mu'}\rangle=-\tfrac{1}{2}\epsilon_\parallel\lambda_\perp\langle d_\mu|\left(S_z\alpha^\dagger\frac{1}{z-\mathcal{H}_0-V}S_+\beta+S_+\beta\frac{1}{z-\mathcal{H}_0-V}S_z\alpha^\dagger\right)|e_{\mu'}\rangle$$
$$-\tfrac{1}{2}\epsilon_\perp\lambda_\parallel\langle d_\mu|\left(S_+\alpha^\dagger\frac{1}{z-\mathcal{H}_0-V}S_z\beta+S_z\beta\frac{1}{z-\mathcal{H}_0-V}S_+\alpha^\dagger\right)|e_{\mu'}\rangle. \quad (5.34)$$

We are thus led to consider the matrix elements of the four operators

$$S_z\alpha^\dagger g(z)S_+\beta,\quad S_+\beta g(z)S_z\alpha^\dagger,\quad S_+\alpha^\dagger g(z)S_z\beta,\quad S_z\beta g(z)S_+\alpha^\dagger$$

between $|d_\mu\rangle$ and $|e_{\mu'}\rangle$, where

$$g(z)=\frac{1}{z-\mathcal{H}_0-V}+\frac{1}{z-\mathcal{H}_0-V}Q\mathcal{H}'Q\frac{1}{z-\mathcal{H}_0-V}+\frac{1}{z-\mathcal{H}_0-V}Q\mathcal{H}'Q\frac{1}{z-\mathcal{H}_0-V}Q\mathcal{H}'Q\frac{1}{z-\mathcal{H}_0-V}+\cdots, \quad (5.35)$$

and in view of (5.32) the problem is reduced to the evaluation of $\langle f_\mu|g(z)|f_{\mu'}\rangle$ for each of the four. The following propositions are now based on relationships (5.32) and make possible an approximate evaluation of $\langle f_\mu|g(z)|f_{\mu'}\rangle$. (i) Among all the possible terms of $\langle f_\mu|g(z)|f_{\mu'}\rangle$, the largest are those with $\mu=\mu'$, the rest of them being smaller by a factor $S^{-1/2}$ at least. (ii) In each term in the series for $\langle f_\mu|g(z)|f_\mu\rangle$ which is obtained from (5.35), the most important contribution comes from terms in which $\mathcal{H}'$ is represented by $(S_+\alpha^\dagger+S_-\alpha)$, and in these terms one must have an equal number of $S_+\alpha^\dagger$ and $S_-\alpha$. (iii) Once the terms discussed in (ii) are selected, we observe that the most important are those in which the $S_+\alpha^\dagger$ operators alternate with the $S_-\alpha$ ones. It is easy to convince oneself however, that all the other terms obtained by permutating the $S_+\alpha^\dagger$ and $S_-\alpha$ operators are of the same order of magnitude in S and α, and give rise to a set of new poles in $\langle f_\mu|g(z)|f_\mu\rangle$. We shall try to take them approximately into account by introducing a parameter C as a factor in this matrix element, and by reducing all the energy denominators to $z-E_{f_\mu}$, where E_{f_μ} is the energy of $|f_\mu\rangle$.

Coherently with what we have said above we shall approximate

$$\langle f_\mu|g(z)|f_{\mu'}\rangle\simeq C\langle f_\mu|\left(\frac{1}{z-E_{f_\mu}}+\frac{\epsilon_\perp^2/4}{(z-E_{f_\mu})^3}S_-\alpha S_+\alpha^\dagger+\frac{(\epsilon_\perp^2/4)^2}{(z-E_{f_\mu})^5}(S_-\alpha S_+\alpha^\dagger)^2+\cdots\right)|f_\mu\rangle\delta_{\mu\mu'}$$
$$\simeq\frac{C}{z-E_{f_\mu}}\left(1+\frac{1}{4}\frac{\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)}{(z-E_{f_\mu})^2}+\frac{1}{16}\frac{\epsilon_\perp^4n^2S^4(1-\alpha^2/\gamma^2)^2}{(z-E_{f_\mu})^4}+\cdots\right)\delta_{\mu\mu'}$$
$$=\frac{C}{z-E_{f_\mu}}\left(\frac{1}{1-\frac{1}{4}[\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)/(z-E_{f_\mu})^2]}\right)\delta_{\mu\mu'}. \quad (5.36)$$

From (5.36) and (5.32) we get

$$\langle d_\mu|S_z\alpha^\dagger g(z)S_+\beta|e_{\mu'}\rangle\simeq-\frac{B(\alpha)}{z-E_\mu+\omega}\left(\frac{1}{1-\frac{1}{4}[\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)/(z-E_\mu+\omega)^2]}\right)\delta_{\mu\mu'}$$
$$=-B(\alpha)\frac{z-E_\mu+\omega}{(z-E_\mu+\omega)^2-\frac{1}{4}\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)}\delta_{\mu\mu'},$$

$$\langle d_\mu|S_+\beta g(z)S_z\alpha^\dagger|e_{\mu'}\rangle\simeq-B(\alpha)\frac{z-E_\mu-\omega}{(z-E_\mu-\omega)^2-\frac{1}{4}\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)}\delta_{\mu\mu'}, \quad (5.37)$$

$$\langle d_\mu|S_+\alpha^\dagger g(z)S_z\beta|e_{\mu'}\rangle\simeq-B(\alpha)\frac{z-E_\mu+2\omega}{(z-E_\mu+2\omega)^2-\frac{1}{4}\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)}\delta_{\mu\mu'},$$

$$\langle d_\mu|S_z\beta g(z)S_+\alpha^\dagger|e_{\mu'}\rangle\simeq-B(\alpha)\frac{z-E_\mu-2\omega}{(z-E_\mu-2\omega)^2-\frac{1}{4}\epsilon_\perp^2nS^2(1-\alpha^2/\gamma^2)}\delta_{\mu\mu'},$$

where

$$B(\alpha)=C(nm)^{1/2}S^2(\alpha/\gamma)(1-\alpha^2/\gamma^2)^{1/2}$$

is a function of ω_0 which is zero at resonance. We wish to emphasize that other contributions to $K_{\mu\mu'}$ exist, which originate from chains of operators $S_-\alpha$ and $S_+\alpha^\dagger$ containing the terms $S_+\alpha^\dagger$ and $S_z\beta$ or $S_z\alpha^\dagger$ and $S_+\beta$ somewhere in the middle of the chain rather than at the extremes. These contributions, however, should be of the same form as (5.37), and we may tacitly renormalize parameter C in order to take them into ac-

count. Using (5.37) in (5.35), we find

$$K_{\mu\mu'} \simeq \tfrac{1}{2} B(\alpha)\Big[\epsilon_{\parallel}\lambda_{\perp}\Big(\frac{z-E_\mu+\omega}{(z-E_\mu+\omega)^2-\frac{1}{4}\epsilon_\perp^2 nS^2(1-\alpha^2/\gamma^2)}+\frac{z-E_\mu-\omega}{(z-E_\mu-\omega)^2-\frac{1}{4}\epsilon_\perp^2 nS^2(1-\alpha^2/\gamma^2)}\Big)$$
$$+\epsilon_{\perp}\lambda_{\parallel}\Big(\frac{z-E_\mu+2\omega}{(z-E_\mu+2\omega)^2-\frac{1}{4}\epsilon_\perp^2 nS^2(1-\alpha^2/\gamma^2)}+\frac{z-E_\mu-2\omega}{(z-E_\mu-2\omega)^2-\frac{1}{4}\epsilon_\perp^2 nS^2(1-\alpha^2/\gamma^2)}\Big)\Big]\delta_{\mu\mu'}, \quad (5.38)$$

With the same approximations as above, one can use result (5.36) to calculate $R_{\mu\mu}$, the contribution of $R(z)_P$ to the diagonal matrix element $\langle d_\mu | G(z)_P^{-1} | d_\mu \rangle$, obtaining

$$R_{\mu\mu} \simeq \tfrac{1}{4} CS^2\Big(1-\frac{\alpha^2}{\gamma^2}\Big)n\epsilon_\perp^2\Big(\frac{z-E_\mu+2\omega}{(z-E_\mu+2\omega)^2-\frac{1}{4}\epsilon_\perp^2 nS^2(1-\alpha^2/\gamma^2)}+\frac{z-E_\mu-2\omega}{(z-E_\mu-2\omega)^2-\frac{1}{4}\epsilon_\perp^2 nS^2(1-\alpha^2/\gamma^2)}\Big). \quad (5.39)$$

Neglecting α^2/γ^2 with respect to 1 and the various ω shifts as small quantities as compared to $\epsilon_\perp\sqrt{n}S$, we can further simplify expressions (5.38) and (5.39) and obtain

$$\langle d_\mu | G(z)_P^{-1} | e_\mu \rangle \simeq C(\epsilon_{\parallel}\lambda_{\perp}+\epsilon_{\perp}\lambda_{\parallel})(nm)^{1/2}S^2\frac{\alpha}{\gamma}\frac{z-E_\mu}{(z-E_\mu)^2-\frac{1}{4}\epsilon_\perp^2 nS^2},$$
$$\langle d_\mu | G(z)_P^{-1} | d_\mu \rangle = \langle e_\mu | G(z)_P^{-1} | e_\mu \rangle \simeq z-E_\mu-\tfrac{1}{2}C\epsilon_\perp^2 nS^2\frac{z-E_\mu}{(z-E_\mu)^2-\frac{1}{4}\epsilon_\perp^2 nS^2}. \quad (5.40)$$

The 2×2 matrix whose elements are given by (5.40) can easily be inverted. The off-diagonal matrix element that is relevant to the generation of the second harmonic is of the form

$$\langle d_\mu | G(z)_P | e_\mu \rangle = \frac{F(z-E)/[(z-E)^2-A]}{\{z-E-B(z-E)/[(z-E)^2-A]\}^2-\{F(z-E)/[(z-E)^2-A]\}^2}, \quad (5.41)$$

where we have put

$$F = C(\epsilon_{\parallel}\lambda_{\perp}+\epsilon_{\perp}\lambda_{\parallel})(nm)^{1/2}S^2\alpha/\gamma, \quad A=\epsilon_\perp^2 nS^2/4, \quad B=C\epsilon_\perp^2 nS^2/2, \quad E=E_\mu. \quad (5.42)$$

Matrix element (5.41) can be put into the form

$$\langle d_\mu | G(z)_P | e_\mu \rangle = F\frac{1}{(z-E)^2-A-B-F}\times\frac{1}{(z-E)^2-A-B+F}\frac{(z-E)^2-A}{z-E},$$

which is a convenient one to show that it has five simple poles along the real axis. One of them is at $z=E$, two are at $z=E\pm(A+B+F)^{1/2}$, and the other two are at $z=E\pm(A+B-F)^{1/2}$. A straightforward calculation yields the five residues

$$\mathrm{Res}(z=E) = -FA/[(A+B)^2-F^2],$$
$$\mathrm{Res}(z=E\pm(A+B+F)^{1/2}) = (F+B)/4(A+B+F), \quad (5.43)$$
$$\mathrm{Res}(z=E\pm(A+B-F)^{1/2}) = (F-B)/4(A+B-F).$$

We can now calculate the transition amplitude as

$$\frac{1}{2\pi i}\oint \langle d_\mu | G(z)_P | e_\mu \rangle e^{-izt}\,dz$$
$$\simeq \frac{FA}{(A+B)^2}\{\cos[(A+B)^{1/2}t]\cos[(F/2(A+B)^{1/2})t]-1\}$$
$$-\frac{B}{A+B}\sin[(A+B)^{1/2}t]\sin[(F/2(A+B)^{1/2})t], \quad (5.44)$$

where we have neglected terms of $O(F^2)$. In the neighborhood of $\omega_0 \sim \omega$, and for sufficiently short times, transitions amplitude (5.44) can be approximated to

$$\alpha_{e_\mu}^{d_\mu} \simeq \tfrac{1}{2}C(\epsilon_{\parallel}\lambda_{\perp}+\epsilon_{\perp}\lambda_{\parallel})(nm)^{1/2}S^2(\alpha^2/\gamma^2)t^2. \quad (5.45)$$

We see that this transition amplitude vanishes as we approach the resonance from the above. A symmetrical result would be obtained when the resonance is approached from below, if we would use states $|d_\nu\rangle$ and $|e_\nu\rangle$ in (5.25), as discussed in Sec. V B. The vanishing of the transition amplitude at $\omega=\omega_0$ could have been predicted directly by the vanishing of the off-diagonal matrix elements in (5.40) at $\alpha=0$. This can be easily seen from the obvious relationship

$$\langle d_\mu | G(z)_P | e_\mu \rangle = -\frac{\langle d_\mu | G(z)_P^{-1} | e_\mu \rangle}{(\langle d_\mu | G(z)_P^{-1} | d_\mu \rangle)^2}.$$

The appearance of this peculiar feature of the sec-

ond-harmonic generation in our calculations is one of the successes of the present theory; it should be considered an effect of the interactions of the various spins among themselves via the electromagnetic field, since no trace of this feature can be found in the results that we have obtained for the isolated spin; in this sense it may be thought of as a many-body effect. In Sec. V D we shall see that our theory enables us to give a modellistic explanation of this effect.

D. A Physical Model

From a mathematical point of view the vanishing of the off-diagonal matrix elements of $G(z)_P$, and hence the appearance of the dip in the middle of the $\omega_0 \sim \omega$ resonance is related to the presence in every term of the development for $R(z)_P$ of the terms $S_z\alpha^\dagger$ or $S_z\beta$. This fact is most evident in Eqs. (5.32), and it is related to the choice that we have made for our initial and final states. As we have already pointed out $|d_\mu\rangle$ and $|e_\mu\rangle$ describe states in which at resonance the total magnetic moment is tilted to rotate in the x-y plane, and its component along the z axis vanishes. We therefore expect that the angle at which the magnetic moment precesses about the z axis is going to be an important parameter in our physical model. Moreover, it is possible to see that contributions (5.37) to $\langle d_\mu | G(z)_P | e_\mu \rangle$ fall into two classes. The first class of matrix elements which contain the operators $S_z\alpha^\dagger$ and $S_+\beta$ should describe processes in which the ω field dresses the z component of the spin system which then emits a 2ω photon by a process in which the transverse component of the magnetization is involved. We may picture this situation as follows. In the rotating system the magnetic moment precesses about the resultant field $\vec{\gamma}$ with a small amplitude and frequency γ. Therefore the phase of the transverse component of the magnetization varies like $\eta \sin\gamma t$, where η is the (small) amplitude. Therefore in the laboratory system the phase ψ of the transverse magnetization varies like

$$\psi(t) = \omega t + \eta \sin\gamma t .$$

On the other hand, defining φ_0 as the time-averaged angle between the magnetization and the z axis, the intensity of the field γ is modulated by the z component of the microwave field h_z as

$$\gamma = \gamma_0 + h_z \cos\varphi_0 \sin\omega t .$$

Therefore

$$\psi(t) = \omega t + \eta \sin[\gamma_0 + h_z \cos\varphi_0 \sin\omega t]\, t$$

$$\sim \omega t + \eta\tau(\gamma_0 + h_z \cos\varphi_0 \sin\omega t), \qquad (5.46)$$

where we have taken into account the fact that γ is a very small quantity with respect to ω at $\omega_0 \sim \omega$. Consequently τ plays the role of a characteristic time which ultimately depends on the relaxation times. Expression (5.46) can now be used to evaluate the x component of the magnetization M_x in the laboratory frame. One has

$$M_x = S \sin\varphi_0 \cos\psi \simeq S \sin\varphi_0 \cos[\omega t + \eta\gamma_0\tau + \eta h_z \tau \cos\varphi_0 \sin\omega t]$$

$$\sim S \sin\varphi_0 [J_0(\eta h_z \tau \cos\varphi_0) \cos\omega t + J_1(\eta h_z \tau \cos\varphi_0) \cos 2\omega t + \cdots], \qquad (5.47)$$

where we have expanded in the usual series of Bessel functions and we have neglected the phase $\eta\gamma_0\tau$. From (5.47) we see that the magnetization along the x axis has components which vary at 2ω frequency with an amplitude $S \sin\varphi_0 J_1(\eta h_z \tau \cos\varphi_0)$. This amplitude vanishes when $\varphi_0 = \frac{1}{2}\pi$ and the magnetization rotates in the x-y plane. As we have seen, in our model this happens when $\omega_0 \sim \omega$, and this accounts for the vanishing of the generation of the second harmonic at resonance. Another source for 2ω components of M_x is the modulation of η itself by the z component of the microwave field. We shall not consider it here in detail since it would also give a vanishing effect at $\omega_0 \sim \omega$.

Let us now consider the second class of matrix elements containing $S_+\alpha^\dagger$ and $S_z\beta$. They should describe processes in which the transverse component of the magnetization is dressed by the ω field, and then a 2ω photon is emitted via a variation in the z component of the magnetization. Let us go back to our rotating frame of reference in which the magnetization precesses around $\vec{\gamma}$ with a small amplitude and frequency γ. In this system the magnetization is acted upon also by the counter-rotating field at frequency 2ω. The component of this field perpendicular to $\vec{\gamma}$ causes the magnetization to vary the angle φ at frequency 2ω according to

$$\varphi = \varphi_0 + \rho \cos\varphi_0 \sin 2\omega t , \qquad (5.48)$$

where the amplitude ρ is small, since the counter-rotating field is out of resonance with the spin system, and where $\cos\varphi_0$ takes into account the fact that this high-frequency tilting of the magnetization cannot take place when the magnetization rotates in the x-y plane. Using (5.48) we now calculate the time variation of the z component M_z of the magnetization as

$$M_z = S \cos\varphi = S \cos(\varphi_0 + \rho \cos\varphi_0 \sin 2\omega t)$$

$$= S[\cos\varphi_0 \cos(\rho \cos\varphi_0 \sin 2\omega t) - \sin\varphi_0 \sin(\rho \cos\varphi_0 \sin 2\omega t)]$$

$$= S\Big[\cos\varphi_0\Big(J_0(\rho\cos\varphi_0) + 2\sum_{k=1}^{\infty} J_{2k}(\rho\cos\varphi_0)\cos(4k\omega t)\Big) - 2\sin\varphi_0 \sum_{k=0}^{\infty} J_{2k+1}(\rho\cos\varphi_0)\sin[(4k+2)\omega t]\Big]. \tag{5.49}$$

Since $\cos\varphi_0 = |\alpha|/\gamma$ from (5.47) and (5.49), it is possible to see that the amplitudes of the 2ω Fourier components of M_z and M_x vanish when $\omega_0 = \omega$. We therefore conclude that the model we have studied may be considered as the classical counterpart of the processes that we have studied quantum mechanically in Secs. V A–C, since the above-mentioned components are responsible for the emission of radiation at frequency 2ω.

VI. N SPINS: REGION $\omega_0 \sim 2\omega$

It is convenient also in this region of magnetic fields to divide the total Hilbert space of the system into many subspaces each characterized by an eigenvalue of S. As we have done before, we shall develop our calculations in the subspace with the highest possible eigenvalue S; moreover, we shall relabel the eigenstates of $\mathcal{H}_0$ in (3.1) as $|n,\ m+x,\ -S+m-x\rangle$, where $-S+m-x$ is the value of the z component of the total spin $\vec{S}$. The eigenvalue corresponding to this eigenstate of $\mathcal{H}_0$ is obviously given by $(n+2m)\omega - (S-m)\omega_0 + x\delta$, where $\delta = 2\omega - \omega_0$. It should be stressed that the average number m of photons at frequency 2ω is always much smaller than S, so that the limits of x are given by $-m$ and m. With this notation we are picking up only the eigenstates of $\mathcal{H}_0$ in which the sum of the spin excitations plus the number of 2ω photons is even. The other set of eigenstates is of the form $|n,\ m+1+x,\ -S+m-x\rangle$, and since $m \gg 1$ we shall treat it analogously to the first set, neglecting the small differences in their properties.

A. Eigenstates of $\mathcal{H}_0 + V$

When $\omega_0 \sim 2\omega$, the part of $\mathcal{H}_{\text{int}}$ which contains dangerous terms is

$$V = \tfrac{1}{2}\lambda_\perp(S_+\beta + S_-\beta^\dagger), \tag{6.1}$$

which connects the state $|n,\ m+x,\ -S+m-x\rangle$ to $|n,\ m+x\pm 1,\ -S+m-x\mp 1\rangle$. The secular equation within our $2m+1$ manifold associated with $\mathcal{H}_0 + V$ for each $\mu = 0, 1, \ldots, 2m$ is

$$\begin{array}{c|ccccc|c}
 & \cdots & B^{\mu}_{m-x+1} & B^{\mu}_{m-x} & B^{\mu}_{m-x-1} & \cdots & \\
\hline
 & \vdots & \vdots & \vdots & \vdots & & \\
\cdots & E_0+(x-1)\delta - E_\mu & \tfrac{1}{2}\lambda_\perp[(m+x)(2S-m+x)(m-x+1)]^{1/2} & 0 & \cdots & & \\
\cdots & \tfrac{1}{2}\lambda_\perp[(m+x)(2S-m+x)(m-x+1)]^{1/2} & E_0+x\delta - E_\mu & \tfrac{1}{2}\lambda_\perp[(m+x+1)(2S-m+x+1)(m-x)]^{1/2} & \cdots & & = 0, \quad (6.2)\\
\cdots & 0 & \tfrac{1}{2}\lambda_\perp[(m+x+1)(2S-m+x+1)(m-x)]^{1/2} & E_0+(x+1)\delta - E_\mu & \cdots & & \\
 & \vdots & \vdots & \vdots & \vdots & &
\end{array}$$

where

$$E_0 = (n+2m)\omega - (S-m)\omega_0$$

and B^{μ}_{m-x} is the projection of the μth eigenvector of $\mathcal{H}_0 + V$ (which we shall indicate by $|d_\mu\rangle$) on the state $|n,\ m+x,\ -S+m-x\rangle$. We shall now simplify Eq. (6.2) by approximating $2S-m+x \sim 2S$. This is justified by m being much smaller than S.[16] When this is done, we obtain from (6.2) the following system of coupled difference equations:

$$\tfrac{1}{2}\lambda_\perp(2S)^{1/2}[(m-x)(m+x+1)]^{1/2}B^{\mu}_{m-x-1} + [(n+2m)\omega - (S-m)\omega_0 + x\delta - E_\mu]B^{\mu}_{m-x} + \tfrac{1}{2}\lambda_\perp(2S)^{1/2}[(m+x)(m-x+1)]^{1/2}B^{\mu}_{m-x+1} = 0 \quad (6.3)$$

with the boundary conditions

$$B^{\mu}_{i} = 0, \quad 2m < i < 0. \quad (6.4)$$

System (6.3) and (6.4) becomes identical to system (5.4) and (5.5) when the following substitutions are done:

$$\lambda_\perp(2S)^{1/2} \to \epsilon_\perp\sqrt{n}, \quad m \to S, \qquad [(n+2m)\omega - (S-m)\omega_0] \to [(n+2m-S)\omega]. \quad (6.5)$$

Taking this analogy into account, one immediately finds the high eigenvalues of $\mathcal{H}_0 + V$ (small μ) as

$$E_\mu = E - m\delta + (m-\mu)\gamma, \quad (6.6)$$

where

$$E = (n+4m)\omega - S\omega_0, \quad \gamma = (\delta^2 + 2\lambda_\perp^2 S)^{1/2}$$

and the expansion coefficients for $|d_\mu\rangle$ are

$$B^{\mu}_{m-x} \simeq \frac{1}{(\pi m)^{1/4}} \frac{2^{-\mu/2}}{(\mu!)^{1/2}} e^{-(\sqrt{m}\,\delta/\gamma - x/\sqrt{m})^2/2} \times H_\mu\left(\sqrt{m}\,\frac{\delta}{\gamma} - \frac{x}{\sqrt{m}}\right) \quad (6.7)$$

On the other hand, the low eigenvalues (small ν) are given by

$$E_\nu = E - m\delta + (\nu - m)\gamma \quad (6.8)$$

and the corresponding expansion coefficients by

$$B^{\nu}_{m-x} \simeq \frac{1}{(\pi m)^{1/4}} \frac{2^{-\nu/2}}{(\nu!)^{1/2}} (-1)^x e^{-(\sqrt{m}\delta/\gamma + x/\sqrt{m})^2/2} \times H_\nu\left(\sqrt{m}\,\frac{\delta}{\gamma} + \frac{x}{\sqrt{m}}\right). \quad (6.9)$$

It can be seen from (6.7) and (6.9) that even at resonance in the rotating frame of reference the spins are not precessing around the field $\lambda_\perp\sqrt{m}$, since the value of $\langle d_\mu|S_z|d_\mu\rangle$ is approximately $-S+m(1-\delta/\gamma)$ and that of $\langle d_\nu|S_z|d_\nu\rangle$ approximately $-S+m(1+\delta/\gamma)$. The reason for this is, of course, that $m \ll S$, and in these conditions the quasiclassical approximation breaks down, since a reversal of the total spin up to positive values of S_z could not be paid for by the 2ω photons. The total spin in states $|d_\mu\rangle$ can rather be described as precessing about a direction which makes an angle φ_0 given by

$$\cos\varphi_0 \sim 1 - \frac{m(1-\delta/\gamma)}{S}$$

with the negative z axis. We see that as we approach the resonance from below ($\delta > 0$) the angle increases until $\cos\varphi_0$ reaches the minimum value of $1 - m/S$. In states $|d_\nu\rangle$ on the other hand, the angle is given by

$$\cos\varphi_0 \sim 1 - \frac{m(1+\delta/\gamma)}{S}$$

and when we proceed from resonance toward higher magnetic fields φ_0 decreases again towards zero.

B. Initial States

Formula (5.28) shows that if the field h is small, the effect of the relaxation times is such that the total spin shall precess about a direction whose angle with the static external field is quite small. When the resonance is approached this angle will increase slightly, always remaining small, and it will successively decrease as we get out of resonance. In the present situation we may assume $h \sim \lambda_\perp\sqrt{m}$. Assuming $m \sim 10^{14}$, we have a real magnetic field at the sample of $\sim 1.2\times10^{-2}$ G, and an equivalent magnetic field $h \sim 3.7\times10^{4}$ Hz, where we have used the maximum value calculated in Sec. II for DPPH. For τ_2 we take the value 5.5×10^{-9} sec measured[2] on DPPH at $\omega_0 \sim 2\omega$, and we get the very small value $\tan\varphi \sim 2\times10^{-4}$ at resonance. Similarly, small values are obtained for the corresponding transitions in ruby. This fact permits us to use the states $|d_\mu\rangle$ of Sec. VI A as initial and final states for $\delta > 0$, and the states $|d_\nu\rangle$ for $\delta < 0$.

C. Generation of Second Harmonic

On the basis of what we have said above, we have to calculate the matrix elements

$$\langle d_\mu|G(z)_P|e_{\mu'}\rangle \ (\delta<0), \quad \langle d_\nu|G(z)_P|e_{\nu'}\rangle \ (\delta>0). \quad (6.10)$$

Let us consider the case $\delta < 0$. Then

$$|d_\mu\rangle = \sum_{x=-m}^{m} B^{\mu}_{m-x}|n,\ m+x,\ -S+m-x\rangle, \qquad |e_{\mu'}\rangle = \sum_{x=-m}^{m} B^{\mu'}_{m-x}|n-2,\ m+x+1,\ -S+m-x\rangle, \quad (6.11)$$

where $\mu,\ \mu' \ll m$ and the B's are given by formula (6.7). Naturally we shall meet here the same difficulties as in the case $\omega_0 \sim \omega$, and we shall have to take P as projecting on the 2×2 subspace spanned by $|d_\mu\rangle$ and $|e_{\mu'}\rangle$, and to resort to partial summations. We now follow the development of

Sec. V, and we obtain, to the highest possible order in S and neglecting terms in δ/γ for simplicity,

$$\langle d_\mu | S_- \alpha^\dagger | f_{\mu''} \rangle \simeq \sqrt{n} \sum_{x=-m}^{m} [(m+x)(2S-m+x)]^{1/2} \times B^{\mu}_{m-x} B^{\mu''}_{m-x} \simeq (2Snm)^{1/2} \delta_{\mu\mu''}, \tag{6.12a}$$

$$\langle f_{\mu''} | S_z \alpha^\dagger | e_{\mu'} \rangle \simeq \sqrt{n} \sum_{x=-m}^{m} (-S+m-x) B^{\mu'}_{m-x} B^{\mu''}_{m-x} \simeq -\sqrt{n} S \delta_{\mu'\mu''},$$

where

$$| f_{\mu''} \rangle \simeq \sum_{x=-m}^{m} B^{\mu''}_{m-x} | n-1,\ m+x+1,\ -S+m-x \rangle$$

and

$$\langle d_\mu | S_z \alpha^\dagger | f_{\mu''} \rangle \simeq \sqrt{n} \sum_x (-S+m-x) B^{\mu}_{m-x} B^{\mu''}_{m-x} \simeq -\sqrt{n} S \delta_{\mu\mu''}, \tag{6.12b}$$

$$\langle f_{\mu''} | S_- \alpha^\dagger | e_{\mu'} \rangle \simeq \sqrt{n} \sum_x [(m-x)(2S-m+x+1)]^{1/2} \times B^{\mu'}_{m-x} B^{\mu''}_{m-x} \simeq (2Snm)^{1/2} \delta_{\mu'\mu''},$$

where

$$| f_{\mu''} \rangle \simeq \sum_x B^{\mu''}_{m-x} | n-1,\ m+x,\ -S+m-x \rangle .$$

For $K_{\mu\mu'}$ we shall consider the expression

$$K_{\mu\mu'} = -\tfrac{1}{2} \epsilon_\parallel \epsilon_\perp \langle d_\mu | \left[S_- \alpha^\dagger \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} S_z \alpha^\dagger + S_z \alpha^\dagger \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} S_- \alpha^\dagger \right] | e_{\mu'} \rangle \tag{6.13}$$

and on the basis of arguments similar to those used in Sec. V we select chains containing alternatively the terms $S_z\alpha$ and $S_z\alpha^\dagger$ in the development (5.33) for $(z - \mathcal{H}_0 - V - Q\mathcal{H}'Q)^{-1}$, and perform a partial summation. With the same approximations as in (5.36) and using (6.12) we find

$$\langle d_\mu | S_- \alpha^\dagger \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} S_z \alpha^\dagger | e_{\mu'} \rangle \simeq -C(2S^3 m)^{1/2} n \frac{z - E_\mu - \omega}{(z - E_\mu - \omega)^2 - \epsilon_\parallel^2 n S^2} \delta_{\mu\mu'},$$

$$\langle d_{\mu'} | S_z \alpha^\dagger \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} S_- \alpha^\dagger | e_{\mu'} \rangle \simeq -C(2S^3 m)^{1/2} n \frac{z - E_\mu + \omega}{(z - E_\mu + \omega)^2 - \epsilon_\parallel^2 n S^2} \delta_{\mu\mu'}, \tag{6.14}$$

where E_μ is the unperturbed energy of $|d_\mu\rangle$ and $|e_\mu\rangle$, while C is a parameter analogous to that of (5.36), by which we try to take into account the contributions of all the neglected chains of operators which are obtainable from those considered by means of permutations. We then find

$$K_{\mu\mu'} \simeq C \frac{\epsilon_\parallel \epsilon_\perp}{2} (2S^3 m)^{1/2} n \left(\frac{z - E_\mu - \omega}{(z - E_\mu - \omega)^2 - \epsilon_\parallel^2 n S^2} + \frac{z - E_\mu - \omega}{(z - E_\mu + \omega)^2 - \epsilon_\parallel^2 n S^2} \right) \delta_{\mu\mu'}. \tag{6.15}$$

Within the same approximations as above, we also find for the diagonal matrix elements of $G(z)_P^{-1}$

$$R_{\mu\mu} \simeq \epsilon_\parallel^2 \left(\langle d_\mu | S_z \alpha \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} S_z \alpha^\dagger | d_\mu \rangle + \langle d_\mu | S_z \alpha^\dagger \frac{Q}{z - (\mathcal{H}_0 + V) - Q\mathcal{H}'Q} S_z \alpha | d_\mu \rangle \right) \simeq C \epsilon_\parallel^2 n S^2 \left(\frac{z - E_\mu - \omega}{(z - E_\mu - \omega)^2 - \epsilon_\parallel^2 n S^2} + \frac{z - E_\mu + \omega}{(z - E_\mu + \omega)^2 - \epsilon_\parallel^2 n S^2} \right). \tag{6.16}$$

We shall now simplify expressions (6.15) and (6.16) as we did for the corresponding ones of Sec. V. We then obtain

$$\langle d_\mu | G(z)_P^{-1} | e_\mu \rangle \simeq C \epsilon_\parallel \epsilon_\perp (2S^3 m)^{1/2} n \frac{z - E_\mu}{(z - E_\mu)^2 - \epsilon_\parallel^2 n S^2},$$

$$\langle d_\mu | G(z)_P^{-1} | d_\mu \rangle = \langle e_\mu | G(z)_P^{-1} | e_\mu \rangle \simeq z - E_\mu - C 2S^2 \epsilon_\parallel^2 n \frac{z - E_\mu}{(z - E_\mu)^2 - \epsilon_\parallel^2 n S^2}. \tag{6.17}$$

Since (6.17) are formally equal to (5.40), inversion of the matrix of $G(z)_P^{-1}$ leads to the same formula (5.41), where

$$F = C \epsilon_\parallel \epsilon_\perp (2S^3 m)^{1/2} n, \quad A = \epsilon_\parallel^2 n S^2, \quad B = C 2S^2 \epsilon_\parallel^2 n. \tag{6.18}$$

The residues of $\langle d_\mu | G(z)_P | e_\mu \rangle$ are given by expressions (5.43), and the approximate transition amplitudes for the generation of the second harmonic by expression (5.44). This time F does not vanish at resonance as it can be seen from (6.18). On the contrary, if we had not neglected the terms in δ/γ in (6.12) in order to simplify the notation, the factor $(2S^3 m)^{1/2}$ in F would have been replaced by $S^2 \sin\varphi_0$, so that we would have found a maximum for $\delta = 0$ as it is observed experimentally.

D. A Physical Model

A plausible physical interpretation of the formulas we have found for the transition amplitudes in this region of magnetic fields can be obtained along the same lines as in Sec. V D. Consider in

fact, a reference frame rotating at frequency 2ω around its z axis parallel to the external static magnetic field. From what we have seen in Secs. VI A and VI B, it is evident that the x component of the total magnetization will have components varying at 2ω frequency. The goal is now to show that M_x develops also components at ω in the laboratory reference frame, so that an interaction can take place between the ω and 2ω fields via the magnetic moment. This can be seen in the following way. As we have said, the motion of total magnetic moment in the rotating frame can be described as a precession around $\vec{\gamma}$ at a small angle φ_0 from the z axis. In this frame the phase of the transverse component of the magnetization varies like $\eta \sin\gamma t$ and in the laboratory frame this becomes

$$\psi(t) = 2\omega t + \eta \sin\gamma t .$$

On the other hand, γ is modulated by the component $h_z \sin\omega t$ of the ω field oscillating along the z axis, so that

$$\gamma = \gamma_0 + h \cos\varphi_0 \sin\omega t$$

and

$$\psi(t) = 2\omega t + \eta \sin(\gamma_0 + h_z \cos\varphi_0 \sin\omega t)t$$
$$\simeq 2\omega t + \eta\tau(\gamma_0 + h_z \cos\varphi_0 \sin\omega t),$$

with the same approximations as in Sec. V D. Passing now to the x component of the magnetization, one has

$$M_x = S \sin\varphi_0 \cos\psi \simeq S \sin\varphi_0 \cos[2\omega t + \eta\gamma_0\tau + (\eta h_z \tau \cos\varphi_0) \sin\omega t]$$
$$= S \sin\varphi_0 [J_2(\eta h_z \tau \cos\varphi_0) - J_1(\eta h_z \tau \cos\varphi_0) \cos\omega t + \cdots], \quad (6.19)$$

where the J's are Bessel functions and where we have neglected the phase $\eta\gamma_0\tau$. Expression (6.19) shows that $M_x(\omega_0)$ has a maximum at $\omega_0 \sim 2\omega$, since φ_0 as a function of $\delta = 2\omega - \omega_0$ behaves as described in Sec. VI A, and consequently that the interaction between the ω and 2ω fields has a maximum there.

VII. DISCUSSION AND CONCLUSIONS

The first part of this section shall be devoted to compare the results of the theory for the isolated spin with those for the N-spin system. We shall begin as usual from the lines at $\omega_0 \sim \omega$. In this region the isolated-spin transition amplitudes for sufficiently short times are proportional to K given by (4.38), and since this quantity does not vanish at resonance, rather artificial assumption have to be done[3] in order to get a minimum at resonance rather than a maximum. For the N-spin system, on the other hand, the corresponding expression varies like $(\omega - \omega_0)/\gamma$ as is apparent from (5.38), and it may be instructive to investigate what the reason is for this different behavior. It is not difficult to see from expression (5.32) that the average value of S_z and S_z^2 in the initial, final, and intermediate states used in the calculations for $K_{\mu\mu'}$ in the case of N spins is close to zero near resonance; consequently, the orientation of the total magnetization does not change very much during the various steps in the generation of second harmonic, remaining nearly perpendicular to the z axis. This causes the α/γ dependence of $K_{\mu\mu'}$. To put it in another way, all the relevant intermediate states available to the system display a noticeable stability in the total-spin orientation relative to the z axis. On the contrary, for any state in the case of the isolated spin the value of S_z^2 is a constant, even in those for which the average value of S_z is zero. This is due to the fact that in order to build a state with $\langle S_z \rangle = 0$ one has at one's disposal only the states $|\pm\frac{1}{2}\rangle$, in each of which the value of S_z is relatively large. It follows that for the isolated spin each step of the frequency conversion process shall actually find the spin "up" or "down" with respect to the z direction, and the value of K will not show any dramatic α dependence. In other words, the isolated spin fluctuates quite strongly between the two opposite orientations with respect to the z axis, and this spoils any effect related to its perpendicularity to the z axis itself. Since the structure of the $\omega_0 \sim \omega$ line is indeed an effect of this sort, in the case of the isolated spin it is washed out by these fluctuations.

Another point which should be mentioned is the following. If we add incoherently the emission of N "isolated" spins, we obviously get a probability for the transitions which generate second harmonic which varies like N. On the contrary, the probability for the generation of second harmonic we have calculated in Sec. V varies like N^4 as is obvious from (5.45). It is evident that some coherency mechanism which phases the emission from the various spins is playing an active role in the second case. This mechanism was first studied by Dicke[9] and is commonly known as superradiance. As we have already pointed out, when the electromagnetic fields are uniform over the volume occupied by the N spins as in our case; the total spin is a constant of motion. This means that the motion of the various spins are correlated, and so are also their interaction processes with the field. As shown by Dicke, this fact causes the matrix elements for the single acts of emission or absorption of photons to be proportional to N when the total spin precesses in the x-y plane. Since two such acts are involved in the generation of second harmonic, we get matrix elements proportional to N^2 and transition probabilities proportional to N^4. The coherency which leads to this "super-second-harmonic-generation" may be thought to be in-

duced by the interactions among the various spins caused by the presence of the uniform electromagnetic field. On the other hand, adding the transition probabilities for the isolated spins is equivalent to neglecting these interactions, and now we see that these play a very important role.

In the other region $\omega_0 \sim 2\omega$ the same way of reasoning applies, mutatis mutandis. In fact we find the same stability of S_z and S_z^2 in the case of N spins which we have been discussing for the region $\omega_0 \sim \omega$. In this case however, this stability does not cause the appearance of any structure in the peak of the second-harmonic generation, since the average values of both S_z and S_z^2 remain about their maximum value when the magnetic field is swept through $\omega_0 \sim 2\omega$. Therefore at least apparently, the peak at $\omega_0 \sim 2\omega$ which we have calculated for the case of N spins is similar to the corresponding one for the isolated spin. From a quantitative point of view however, the S^3 dependence of the transition probability should be remarked for the N-spin system; this is in relation to the fact that, due to the unfavorable orientation of the total magnetic moment relative to the x-y plane, the interaction with the electromagnetic fields in this plane is not superradiant. Formally this is characterized by the appearance of the $S^{1/2}$ factors in the relevant matrix elements (6.12).

We now turn to a comparison of our results with those of the theory by Ciccarello *et al.*,[2] who use a density matrix approach to the problem. Such an approach is of a phenomenological nature in that it relies on the introduction of the relaxation times τ_1 and τ_2 and it can be shown to be equivalent to a Bloch-equations approach. Its success in presenting a unified picture of the most relevant experimental features of the phenomenon of second-harmonic generation, however, makes the comparison particularly desirable. The main result of the density matrix approach[2] is that the power radiated at double frequency by a system of N spins is proportional to, using our notation,

$$\frac{(\epsilon^2 n \sin\theta \cos^2\theta N)^2(\alpha^2 + 1/\tau_2^2)}{(\alpha^2 + 1/\tau_2^2 + S^2)^2} \tag{7.1}$$

when $\omega_0 \sim \omega$ and where the saturation factor is given by

$$S^2 = \epsilon^2 n \cos^2\theta \, \tau_1/\tau_2 \tag{7.2}$$

and to

$$\frac{(\epsilon^2 n \cos\theta \cos^2\theta N)^2}{\delta^2 + 1/\tau_2^2} \tag{7.3}$$

when $\omega_0 \sim 2\omega$. On the other hand, we have shown that for sufficiently short times the transition amplitude given by our theory in the neighborhood of $\omega_0 \sim \omega$ is proportional to

$$(\epsilon_\parallel \lambda_\perp + \epsilon_\perp \lambda_\parallel)(nm)^{1/2} \epsilon_\perp \sqrt{n}\alpha/\gamma^2, \tag{7.4}$$

where we have reintroduced the factor $\epsilon_\perp\sqrt{n}/\gamma$ which we had neglected for $\alpha \ll \gamma$. Our transition probability is therefore proportional to

$$\frac{\lambda^2 m(\epsilon^2 n \sin\theta \cos^2\theta N^2)^2 \alpha^2}{(\alpha^2 + \epsilon^2 n \cos^2\theta)^2}. \tag{7.5}$$

The factor $\lambda^2 m$, which is the squared amplitude of the 2ω field, appears in (7.5) because we take explicitly into account the interaction of the spin system with the field that it generates, while the N^4 dependence has been previously discussed and it is related to the fact that we do not neglect coherence effects in the intermediate steps of the process. Apart from these two differences, it is seen that (7.5) can be obtained from (7.1) by letting $\tau_1 = \tau_2 \to \infty$. In the neighborhood of $\omega_0 \sim 2\omega$ our theory gives a transition amplitude proportional to

$$\epsilon_\parallel \epsilon_\perp n N^2 \sin\varphi_0. \tag{7.6}$$

In order to make the comparison with the density matrix approach, it is necessary to introduce in (7.6) the relaxation times. From (6.28) we get

$$\sin\varphi_0 \sim \tan\varphi_0 \sim \lambda_\perp \sqrt{m}\, \tau_2/(1 + \delta^2\tau_2^2)^{1/2}$$

and hence a transition probability proportional to

$$\frac{\lambda^2 m(\epsilon^2 n \sin\theta \cos^2\theta N^2)^2 \tau_2^2}{1 + \delta^2\tau_2^2} \tag{7.7}$$

which is the counterpart of (7.3). We conclude that there is a close analogy between the results of our theory and those obtained by the density-matrix approach. We wish to mention however a physical feature of the phenomenon under study which cannot be reproduced by our quantum-mechanical approach. Since $|\vec{S}|^2$ commutes with the total Hamiltonian of the system, it is a constant of motion so that pictorially speaking if we represent $\vec{S}$ by a stick, we can turn it around at our will, but its length is to remain constant. Relaxation times, however, break this conservation law, allowing for a certain shortening or lengthening of the total magnetic moment under particularly intense radiation. It is in fact well known[15] that the solution of the Bloch equations (5.27) for slow passage entails that at resonance

$$\frac{|\vec{S}|}{S_0} = \frac{(1 + h^2\tau_2^2)^{1/2}}{1 + h^2\tau_1\tau_2}, \tag{7.8}$$

where S_0 is the total magnetic moment far from resonance. If we use in (7.8) the values previously calculated for DPPH, $h \sim 8\times10^7$ Hz, $\tau_2 \sim 9\times10^{-8}$ sec, $\tau_1 \sim 10^{-3}$ sec, we easily obtain a very substantial reduction of $|\vec{S}|$ at $\alpha = 0$. In our picture this would correspond to moving to subspaces of $\mathcal{H}$ characterized by a smaller value of $|\vec{S}|$. This, of course, should mean a further reduction of the

ability of the system to generate second harmonic at resonance, and thereby a further deepening of the antiresonance at the center of the $\omega_0 \sim \omega$ line. We emphasize however that this reduction of $|\vec{S}|$ is by no means conceptually essential in order to have the antiresonance, as we have shown by our theory.

We wish now to spend a few words to connect our theory to the present and future experimental developments. We have seen how our final formulas for the transition probabilities which generate second harmonic are obtainable from those of the density-matrix approach by letting the relaxation times go to infinity. Therefore we do not need a detailed comparison of our theory with the experimental results, since this has been done quite successfully in the paper by Boscaino *et al.*[2] A conceptual point which should be worthy of further experimental investigations, however, is the N dependence of the probability for the processes we have calculated. As mentioned earlier, internal coherence of the spin system in the intermediate steps is essential in order to observe superradiant effects, whose occurrence has also been recently predicted in scattering phenomena.[18] Experiments of the kind discussed in the present work should be particularly suited to investigate these coherence properties by measuring the dependence of the second-harmonic power on the concentration of two-level systems, when a reliable method to compare the intensities of 2ω lines in different samples is found.

In conclusion, we have discussed a purely quantum-mechanical theory of second-harmonic generation at microwave frequency by a system of two-level objects. The predictions of the present theory are in agreement with the experiments, and they also agree qualitatively with the density-matrix approach, when relaxation times are introduced. Furthermore, we have presented a qualitative picture of the phenomenon, by which insight into the physical features of the process can be gained. As a by-product of our investigation, we have also obtained an approximate solution in analytical form for a canonical problem, that is the eigenvalue problem of a set of two-level systems coupled to a strong monochromatic radiation field. Finally we have pointed out the role of superradiance in the second-harmonic generation processes, and we have suggested experiments by which the importance of this role could be further investigated.

ACKNOWLEDGMENTS

We are indebted to Dr. R. Boscaino, Professor I. Ciccarello, and Dr. C. Cusumano for communication of unpublished results and for many stimulating conversations. We also wish to thank Professor M. W. P. Strandberg for his interest in the present work. One of the authors (F. P.) wishes to acknowledge the hospitality received during one of his visits at the International Center for Theoretical Physics in Trieste where part of this paper was written.

[1] R. Boscaino, I. Ciccarello, and C. Cusumano, Phys. Rev. Lett. **20**, 421 (1968).
[2] R. Boscaino, I. Ciccarello, C. Cusumano, and M. W. P. Strandberg, Phys. Rev. B **3**, 2675 (1971).
[3] F. Persico and G. Vetri, Solid State Commun. **8**, 1509 (1970).
[4] F. Persico and G. Vetri, Solid State Commun. **11**, 69 (1972).
[5] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, England, 1970), p. 430.
[6] E. O. Schulz-duBois, Bell Syst. Tech. J. **38**, 271 (1959).
[7] D. J. E. Ingram, *Spectroscopy at Radio and Microwave Frequencies* (Butterworths, London, 1955), p. 203.
[8] *Technique of Microwave Measurements*, edited by G. C. Montgomery (McGraw-Hill, New York, 1947), p. 305.
[9] R. M. Dicke, Phys. Rev. **93**, 439 (1954).
[10] G. Vetri, Phys. Lett. A **33**, 249 (1970).
[11] C. Cohen-Tannoudji, *Cargese Lectures in Physics* (Gordon and Breach, New York, 1967), Vol. 2, p. 347.
[12] T. Muir, *Theory of Determinants* (Dover, New York, 1960), Vol. 4, p. 401.
[13] G. Sharf, Phys. Lett. A **31**, 497 (1970).
[14] G. Sharf, Helv. Phys. Acta **43**, 806 (1970).
[15] P. M. Morse and H. Feschbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. 1, p. 551.
[16] M. Tavis and F. W. Cummings, Phys. Rev. **188**, 692 (1969).
[17] A. Abragam and B. Bleaney, Phys. Rev. **188**, 116 (1969).
[18] O. N. Gadomsky and V. R. Nagibarov, Phys. Lett. A **38**, 249 (1972).