# Beyond linear response: Line shapes for coupled spins or oscillators via direct calculation of dissipated power

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Absorption spectra are calculated for four model systems using two different methods for the calculation: The first is the standard linear response technique, while the second involves direct calculation of the energy dissipated in the sample interacting with the applied field, thus corresponding exactly to what is in fact measured experimentally. This latter technique, which we call the direct method, agrees with a linear response (as it must) for weakly applied fields for which the first-order perturbation analysis underlying linear response is in fact valid. For cases in which the system/field interaction is stronger, the linear approximation becomes poor, and the direct method, which includes the field-induced dynamics and in itself contains no approximations, is far better. The four systems considered consist of either single or coupled pairs of harmonic oscillators or two-level systems (spins) each in a thermal bath and coupled to the field by a displacement coupling. For both linear-response and direct calculations the system/field dynamics is solved exactly and the system/bath dynamics treated using a semigroup technique. For the harmonic oscillators, for which the population in any single excited state can never become large, the nonlinear effects (those present in the direct but not in the linear response) are quite minor. For the two-level/spin/systems, however, substantial corrections to the linear-response result are found in the direct calculation. These include power (or saturation) broadening and the appearance, when the two spins are coupled strongly to each other and one is coupled strongly to the field, of a new line at the averaged frequency of the two spins. For even stronger coupling, the line shape becomes very complex (corresponding to the full 15$D$ algebra of the two spins plus the field), exhibiting several peaks and Fano antiresonances. The direct method, which is based on work of Lebowitz, seems to offer substantial advantages for the analysis of systems in which the applied field interactions are strong: This situation, common in microwave and magnetic resonance spectroscopy, is also relevant to high-energy laser studies.

## I. INTRODUCTION

The standard approach to calculation of transport and response phenomena is the linear response theory developed by Kubo in 1957.[1-3] This is based on the assumption that the perturbed density matrix for the system in the presence of an external field can be treated by a first-order correction of the unperturbed density matrix: i.e., it corresponds, in a sense, to first-order time dependent perturbation theory. The assumption of weak system-probe interaction is valid for nearly all transport and spectroscopic measurements, since the field strengths involved are very small compared to the internal forces within the system (atom, molecule, and solid) being probed. There are, however, some conditions under which the assumptions of linear response theory may become invalid. These might include spectroscopy with very high intensity lasers, where the system is driven far from its unperturbed state. It can also occur in magnetic resonance spectroscopy, when the applied resonance power is great enough to lead to saturation (as occurs, for instance, in the ENDOR experiment).[4] Several important physical phenomena, including power broadening of the observed spectra and relaxation-limited absorption and broadening, can then occur, whose description within a linear-response picture can become difficult. Under these conditions, an alternative description of the spectroscopy, one which directly calculates the actually measured quantity, power dissipated in the system when it interacts with the probe, is probably more convenient. Such a scheme has been outlined by Spohn and Lebowitz,[5] based on a direct calculation of the time dependence of the operators of the composite (system plus probe). The aim of the present paper is to apply this Lebowitz scheme to calculate the spectra for two important model systems; one corresponding to vibrational spectroscopy of two coupled modes, the other to the magnetic spectroscopy of two coupled spins or the optical spectroscopy of two coupled two-level systems. We will study these spectra using both linear-response and direct methods, and from comparison of the calculated spectra, will be able to indicate specific deficiencies of the linear-response prescription.

Previous studies of optical response in the nonlinear regime have appeared for a single system, either two-level[6] or harmonic oscillator.[7] Several extra features of interest appear in the extension to pairs of systems which is our subject here. These include the efficiency of transfer from pumped to unpumped mode, the effects of slow relaxation (in the optically uncoupled mode) in broadening the line and fast relaxation in narrowing it, and in the appearance of new, joint features not present in either single system. These should be of use in describing any of several physically important situations (a four-level laser system can be seen as a pair of two-level situations, V→V energy transfer can be thought

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of, to a rough approximation, in terms of coupled oscillators). There are four chief advantages of the algebraic technique which we employ: It is exact in the system dynamics, it treats relaxation (given the system/bath coupling) in a rigorous way, it makes no assumptions of linearity, and it does not depend on any perturbation expansion. The same general approach is also useful in more complex systems, in which exact solution is impossible and consistent and higher-order approximations are required.

The Spohn and Lebowitz method, which we will refer to as the direct method (DM), calculates the power dissipated from the applied field as it interacts with the system under illumination; this is a direct reflection of the experimental situation, in which the energy lost by the field is measured. We outline in Sec. II the linear-response (LR) and direct methods for calculation of spectra. In Sec. III, we define our model systems (two coupled oscillators and two coupled spins), and present the formal solutions for their spectra. In Sec. IV, we consider the limiting uncoupled cases (single spin or single oscillator). Then we present calculated spectra for several values of the parameters of the models (interaction strength between systems, applied field strength, temperature and relaxation rates, and unperturbed system frequencies), and study the specific effects, such as power broadening, saturation, and relaxation narrowing, which occur in these systems. Finally, we present in Sec. V some general remarks about these calculations.

## II. THE LINEAR RESPONSE AND DIRECT METHODS FOR CALCULATING LINE SHAPES

In ordinary absorption spectra (vibrational, optical, or magnetic resonance), one measures the absorption of incident energy by the system. The power dissipated is then the time derivative of the energy change of the radiation on passing through the sample. Following Flygare,[8] we can write for $\Delta I$, the change in intensity of incident radiation, a limiting case of Beer's Law:

$$\Delta I = \frac{d(\Delta E)/dt}{A} \cong \gamma y I_0 \ . \tag{1}$$

Here $A$ is the sample area, $y$ the sample thickness, $I_0$ the incident intensity, $\Delta E$ the energy change in the beam, and $\gamma$ the absorption coefficient. Then for unit volume equal to $V_0$,

$$\text{power} = d(\Delta E)/dt = V_0 I_0 \gamma \ . \tag{2}$$

The absorption coefficient $\gamma$ is, in turn, related to the line shape function by[9]

$$\gamma(u) = \left(\frac{4\pi u}{c}\right) L(u) \ , \tag{3}$$

where $L(u)$ is the line shape function, $c$ is the speed of light, and $u$ is the electromagnetic frequency. The intensity $I_0$ is simply

$$I_0 = cE_0^2/8\pi \ , \tag{4}$$

where $E_0^2$ is the electric field intensity. By combining Eqs. (3), (2), and (4) we find

$$(\text{power}) = \frac{E_0^2 u}{2} V_0 L(u) \ , \tag{5a}$$

or, taking $V_0$ as $4\pi$, we find

$$(\text{power}) = 2\pi E_0^2 u L(u) \ . \tag{5b}$$

Equation (5) relates the power dissipated in the sample, which is calculated from the direct method, with the line shape $L(u)$, usually found from linear response theory.[1-3] Having the relationship between power and line shape, we now examine the calculation of each. Consider, then, a molecular species coupled to a bath, as well as to an external field. The system Hamiltonian is then written

$$H = H_0 + h(t) \ , \tag{6}$$

where $H_0$ includes the energies of the bare system and of the system-bath interaction, while $h(t)$ is the field-system coupling. We can then write the total power as

$$dE/dt = d\langle H\rangle/dt = \left\langle \frac{\partial h(t)}{\partial t} \right\rangle + \langle \mathcal{L} \cdot H \rangle \ , \tag{7a}$$

with $\mathcal{L}$ the Liouville operator for the overall dynamics. Then we take

$$\mathcal{L} = \mathcal{L}_D + \mathcal{L}_H \ , \tag{7b}$$

where $\mathcal{L}_H$ denotes the evolution due to the system Hamiltonian while $\mathcal{L}_D$ is the dissipative part arising from the bath coupling. Then, since

$$\mathcal{L}_H \cdot H = 0 \tag{7c}$$

(since $H$ commutes with itself), we have

$$\frac{dE}{dt} = \left\langle \frac{\partial H}{\partial t} \right\rangle + \langle \mathcal{L}_D \cdot H \rangle = \frac{dW}{dt} + \frac{dQ}{dt} \ . \tag{8}$$

Here the last equality is simply the first law of thermodynamics, which is valid since there is a system/bath coupling. The one-to-one correspondence

$$\langle \partial h(t)/\partial t \rangle \rightarrow dW/dt \ , \tag{9}$$

$$\langle \mathcal{L}_D \cdot H \rangle \rightarrow dQ/dt \tag{10}$$

is straightforward, since work is defined by the coupling of the thermodynamic system to the external world, and such coupling is available only through the $h(t)$ term. The Liouville term $\langle \mathcal{L}_D \cdot H \rangle$ describes the internal dynamics of the field/system/bath composite, and results in production of heat (by degradation of applied field energy via the field-system and system-bath couplings). The quantity we wish to calculate is the power dissipated in the system under illumination, which is given by Eq. (9) and is in fact directly measured in a spectroscopic experiment; calculation of Eq. (9) is the essence of the direct method.

Linear response theory is based on the idea of weak system/field interaction; i.e.,[3] "The major conclusion of this theory is that it is only necessary to know how both systems [molecule and field] behave in the absence of coupling in order to describe the way one reacts to another." This is equivalent to saying that by study of the spontaneous correlations in the unperturbed molecule, one can study the dissipation of energy in that molecule when it is exposed to an external field (fluctua-

tion dissipation theorem).[10] Operationally, this means that if the system/field interaction is written

$$h(t) = \epsilon\{\exp(-iut)a^* + \exp(iut)a\} , \tag{11}$$

where $\epsilon$ is an interaction strength, $u$ is the frequency of the field, and $a^*$ is a dimensionless creation operator for some generalized displacement in the molecule, then the vibrational line shape function $I(u)$ can be written (in the classical limit)

$$I(u) = \frac{m_0^2}{4\pi}\int_0^\infty e^{-iut}\langle(a^*+a)(0)\cdot(a^*+a)(t)\rangle_0\, dt . \tag{12}$$

Here $m_0$ is the proportionality coefficient between the dipole moment $M$ and the generalized displacement:

$$(a^*+a)m_0 \equiv M . \tag{13}$$

The ensemble average in Eq. (12) is, as indicated by the notation, to be performed over the system described by $H_0$: no field perturbations at all are present in the linear response line shape. Since the field is absent in Eq. (12), the linear response formulation clearly cannot describe phenomena such as power broadening or field-induced mixing. The relative importance of such effects clearly depends on the size of $\epsilon$: linear response should be correct when $\epsilon$ becomes very small.

When the radiative power applied to the system is large, the linear response approximation is expected to break down. Within the confines of standard theory, this is often dealt with[11] by introduction of Bloch equations,[12] with phenomenological relaxation terms. The calculation of power dissipated, via Eq. (9), provides an alternative approach.

## III. MODEL SYSTEMS: COUPLED SPINS AND COUPLED OSCILLATORS

In most spectroscopic studies, a particular transition is strongly favored by the experimental conditions selected; e.g., in $CO_2$ the asymmetric stretch will be strongly pumped by light polarized along the molecular axis, while the other two normal modes will not absorb. The other states of the species are, however, coupled to the pumped state pair, since, generally, the states prepared by optical (or magnetic resonance) interaction are not molecular eigenstates. Thus energy can flow between the states prepared by excitation and other molecular states (throughout this discussion, "state" means eigenfunctions of effective separable Hamiltonian, not molecular eigenstates). That is to say that the excited state reached by electromagnetic excitation can decay. We wish to consider two model situations for such situations: The first describes two coupled two-level systems (for example a pair of spins), and the second two coupled oscillators (a model for vibrational energy transfer).

The system evolution can then be described by time-dependent Hamiltonian; energy is not a constant of the motion, since it will flow into (or out of) the molecule via the electromagnetic field. The Hamiltonian is then written

$$H = H_0 + h(t) . \tag{6}$$

The system described by $H$ exists in the presence of a heat bath (which can influence its dynamics and can exchange energy) and a field (which can exchange energy).

For the familiar case of two coupled oscillators, we have

$$H_0 = \omega_1 a^* a + \omega_2 b^* b + \mu(a^* b + b^* a) , \tag{14}$$

$$h(t) = \epsilon(a\, e^{iut} + a^*\, e^{-iut}) . \tag{15}$$

Here $a^*$ creates a quantum of energy with frequency $\omega_1$ in mode 1, and $b^*$ creates one of the frequency $\omega_2$ in mode 2. The two modes are coupled by an energy-exchange term with strength $\mu$. The electromagnetic field, of frequency $u$, couples only to mode 1, and the coupling strength is $\epsilon$ [for dipole radiative coupling, $\epsilon = \mathbf{E}_0 \cdot \mathbf{M}$, where the molecular dipole is $(a^*+a)\mathbf{M}$ and $\mathbf{E}_0$ is the electric field]. We have chosen atomic units ($\hbar = 1$) and neglected the (unimportant) zero-point energy.

For the case of a pair of two level systems, we take

$$H_0 = \omega_1\sigma_1^z + \omega_2\sigma_2^z + \mu\{\sigma_1^+\sigma_2^- + \sigma_2^+\sigma_1^-\} , \tag{16}$$

$$h(t) = \epsilon(\sigma_1^+\, e^{-iut} + \sigma_1^-\, e^{iut}) . \tag{17}$$

Here the $\sigma$ are the Pauli spin matrices, with normalization defined by

$$\sigma_x\sigma_y = \tfrac{1}{2}i\sigma_z , \tag{18}$$

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \tfrac{1}{4} . \tag{19}$$

Thus $\sigma_1^z$ measures the excitation state of spin of mode 1, while $\sigma_1^+$ excites and $\sigma_1^-$ deexcites spin of mode 1. The two-level system described by Eqs. (16) and (17) is term-by-term comparable to the coupled oscillators described by Eqs. (14) and (15). The only formal difference comes in the commutation relations

$$[a_i, a_j^*] = \delta_{ij} , \tag{20}$$

$$[\sigma_i^+, \sigma_j^-] = \delta_{ij}\sigma_i^z , \tag{21}$$

$$\sigma_+^2 = \sigma_-^2 = 0 \tag{22}$$

physically, this simply means that one can put any number of quanta into the oscillator, but at most one quantum into the spin.

We are now interested in solving for the spectra expected for the model systems (14) and (15) or (16) and (17). For the linear response calculation, we simply take

$$I(u) = \frac{m^2}{\pi}\int_0^\infty e^{-iut}\langle(a^*+a)(t)(a^*+a)(0)\rangle_0\, dt \tag{23}$$

for the oscillators, and

$$I(u) = \frac{M^2}{\pi}\int_0^\infty \langle(\sigma_1^+ + \sigma_1^-)(t)(\sigma_1^+ + \sigma_1^-)(0)\rangle_0\, e^{-iut}\, dt \tag{24}$$

for the coupled spins, where $M$ is the spin transition dipole. These expressions are simply Laplace transforms. To find the correlation functions, for the field free case, we write the Heisenberg motion equations, generalized to include the effects of heat-bath relationships calculated (rigorously) using a semigroup technique,[13-16] as

$$d\Omega/dt = i[H_0, \Omega] + (\dot{\Omega})_R , \tag{25}$$

where $\Omega$ is any system operator (particularly $a$ or $a^+$) and $(\dot{\Omega})_R$ is the relaxation contribution to the evolution. If the system/heat bath coupling is written

$$H_{S-B}=\sum_i B_i V_i \ , \tag{26}$$

where $V_i$ is an operator of the system, and $B_i$ a bath variable, then

$$(\dot{\Omega}_i)_R=2\sum_\lambda \gamma_\lambda \{V_\lambda \Omega_i V_\lambda^+ - [V_\lambda V_\lambda^+, \Omega_i]_+/2\} \ . \tag{27}$$

The phenomenological constants $\gamma_\lambda$ of Eq. (27) [completely unrelated to the $\gamma$ of Eqs. (1)–(3)] are rigorously nonnegative; they can be evaluated in the weak-coupling limits. The form (27) is rigorous and exact for the coupling Eq. (26). For the present sample case, we assume that

$$V_i = \begin{cases} \begin{Bmatrix} a^+ \\ a \end{Bmatrix} & i=1 \\ \begin{Bmatrix} b^+ \\ b \end{Bmatrix} & i=2 \end{cases} \tag{28}$$

for oscillators, and

$$V_i = \begin{cases} \begin{Bmatrix} \sigma_1^+ \\ \sigma_1^- \end{Bmatrix} & i=1 \\ \begin{Bmatrix} \sigma_2^+ \\ \sigma_2^- \end{Bmatrix} & i=2 \end{cases} \tag{29}$$

for the spins, then Eq. (27) becomes simply

$$(\dot{b}^+)_R=-\Gamma_a b^+ \ , \tag{30}$$

$$(\dot{a})_R=-\Gamma_a a \ , \tag{31}$$

$$(\dot{\sigma}_i^\pm)_R=-\Gamma_i\sigma^\pm \ , \quad i=1,2 \ , \tag{32}$$

$$(\dot{\sigma}_i^z)_R=-2\Gamma_i\sigma^z+K_i \ , \tag{33}$$

where $\Gamma$ is a relaxation lifetime, and $K$ in Eq. (33) is needed to assure a proper thermal average spin excitation: in the absence of a field or spin–spin coupling

$$\dot{\sigma}_Z=-2\Gamma\sigma^z+K=0 \ . \tag{34}$$

The identification of $K$ is then made by averaging Eq. (34) over an ensemble: in steady state $\langle\dot{\sigma}_Z\rangle$ must be zero, so that we obtain, from Eq. (34),

$$\langle\sigma^z\rangle=K/2\Gamma \ . \tag{35}$$

From comparison with the Fermi distribution, then

$$K=2\Gamma\langle\sigma^z\rangle=\Gamma\frac{1-e^{-\beta\omega_1}}{1+e^{-\beta\omega_1}} \tag{36}$$

for $\beta^{-1}=k_BT$.

By using Eqs. (30) and (32) in connecting with $H_0$ of Eqs. (14) or (16), an exact solution to the linear-response line shape can be obtained. It is rather complicated, and arises from the form

$$\mathrm{Re}\int_0^\infty e^{-iut}a(t)dt=\frac{-a^0\Gamma_2\{(u-\omega_1)(u-\omega_2)-\mu^2\Gamma_1\Gamma_2\}+\{b^0\mu+a^0(u-\omega_2)\}\{\Gamma_1(u-\omega_2)+\Gamma_2(u-\omega_1)\}}{[(u-\omega_1)(u-\omega_2)-\mu^2-\Gamma_1\Gamma_2]^2+[\Gamma_1(u-\omega_2)+\Gamma_2(u-\omega_1)]^2} \ . \tag{37}$$

Here $a^0$ and $b^0$ are the initial-time values of $a$, $b$. The analogous expression for the coupled spins is

$$\int_0^\infty e^{-iut}\sigma_1^+(t)dt=\frac{(iu+i\omega_2+2\Gamma_1+\Gamma_2)\sigma_1^+(0)}{-u^2+iu(i\omega_2+i\omega_1+\Gamma_2+3\Gamma_1)+(i\omega_1+\Gamma_1)(i\omega_2+2\Gamma_1+\Gamma_2)+i\mu K_1+\mu^2/4} \ . \tag{38}$$

(There is an additional term, proportional to $\sigma_2^+(0)$, which is unimportant, as it will vanish in the correlation function.)

Thus the linear-response forms are straightforward, but complex. They may be made clearer by consideration of limiting cases, as will be given in Sec. IV, below.

For the direct method, we require the evaluation of $\langle h(t)\rangle$. This is most easily accomplished by transforming $H$ into the rotating frame, rewriting Eqs. (14)–(17) in terms of

$$\bar{a}\equiv e^{iut}a \ , \tag{39}$$

$$\bar{b}^+\equiv e^{-iut}b^+ \ , \tag{40}$$

$$\bar{\sigma}_1^+\equiv\sigma_1^+e^{-iut} \ , \tag{41}$$

$$\bar{\sigma}_2^-\equiv\sigma_2^-e^{iut} \ . \tag{42}$$

Then Eqs. (14) and (16) are unchanged, except that $\bar{\sigma}$ replaces $\sigma$, $\bar{a}$ replaces $a$, and $\bar{b}$ replaces $b$, while Eqs. (15) and (17) become

$$h(t)=\epsilon(\bar{a}^+ + \bar{a}) \ \text{(oscillators)} \ , \tag{43}$$

$$h(t)=\epsilon(\bar{\sigma}_1^+ + \bar{\sigma}_1^-) \ \text{(spins)} \ . \tag{44}$$

Then we wish to calculate the power dissipated in the steady state, or $\langle h(t)\rangle$. This is quite easy: we just write the equations for the operators as

$$\frac{d\Omega}{dt}=i[H,\Omega]+(\dot{\Omega})_R \ . \tag{45}$$

Note the significant difference between Eqs. (12) and (45): in the linear-response case, the spectrum [from Eq. (12)] is calculated from the behavior of the system in the absence of the field coupling, while for the direct calculation, the driving term $h(t)$ is included in the evolution. Clearly, in the appropriate limit of very small $\epsilon$, the two will become the same.

The formula for the power is, from Eqs. (15) and (17):

$$-\langle \dot{h}(t)\rangle = iu\epsilon(\bar{\sigma}_1^+ - \bar{\sigma}_1^-) \quad \text{(spins)}, \tag{46}$$

$$= iu\epsilon(\bar{a}^+ - \bar{a}) \quad \text{(oscillators)}, \tag{47}$$

equivalently,

$$\text{power} = \begin{cases} 2u\epsilon\,\mathrm{Im}(\bar{\sigma}_1^+) & \text{(spins)} \quad (48) \\ 2u\epsilon\,\mathrm{Im}(\bar{a}^+) & \text{(oscillators)}. \quad (49) \end{cases}$$

Here the rotating frame operators $\bar{a}$ and $\bar{\sigma}$ are to be evaluated in the steady state.

The equations of motion arising from Eqs. (48) and (49) using Eqs. (14)–(17) can become quite complex. There are two relevant operators (two coupled equations) for the oscillator case Eqs. (14) and (15) and then the solution for steady state is simply found from the pair of coupled equations

$$\dot{\bar{a}} = 0 = -i(\omega_1 - u)\bar{a} - i\mu\bar{b} - \Gamma_1\bar{a} - i\epsilon, \tag{50}$$

$$\dot{\bar{b}} = 0 = -i(\omega_2 - u)\bar{b} - i\mu\bar{a} - \Gamma_2\bar{b}. \tag{51}$$

This solution is

$$\mathrm{Im}(a)\,\text{(steady state)} = \frac{\epsilon\Gamma_2\{\Gamma_1\Gamma_2 - \tilde{\omega}_1\tilde{\omega}_2 + \mu^2\} + \epsilon\tilde{\omega}_2(\tilde{\omega}_1\Gamma_2 + \tilde{\omega}_2\Gamma_1)}{(\mu^2 + \Gamma_1\Gamma_2 - \tilde{\omega}_1\tilde{\omega}_2)^2 + (\tilde{\omega}_1\Gamma_2 + \tilde{\omega}_2\Gamma_1)^2}, \tag{52}$$

where $\tilde{\omega}_1 = \omega_1 - u$ and $\tilde{\omega}_2 = \omega_2 - u$.

The solution for Eqs. (16) and (17), with two coupled spins, is more complex. There are then a total of 15 separate operators, and 15 operator equations of type (50). Fortunately, these 15 equations form a linear system, and one can write

$$\frac{d\Omega}{dt} = A\Omega + C = 0, \tag{53}$$

where $\Omega$ is a column vector of the 15 operators, $A$ is a coefficient matrix and $C$ is the inhomogeneous part. The 15 operators are conveniently chosen as $\sigma_1^+ + \sigma_1^-$, $\sigma_1^+ - \sigma_1^-$, $\sigma_1^z(\sigma_2^+ + \sigma_2^-)$, $\sigma_1^z(\sigma_2^+ - \sigma_2^-)$, $\sigma_1^+\sigma_2^- - \sigma_2^+\sigma_1^-$, $\sigma_1^+\sigma_2^- + \sigma_2^+\sigma_1^-$, $\sigma_1^z$, $\sigma_1^+\sigma_2^+ + \sigma_1^-\sigma_2^-$, $\sigma_1^+\sigma_2^+ - \sigma_1^-\sigma_2^-$, $\sigma_2^z$, $\sigma_2^+ + \sigma_2^-$, $\sigma_2^+ - \sigma_2^-$, $\sigma_2^z(\sigma_1^+ + \sigma_1^-)$, $\sigma_2^z(\sigma_1^+ - \sigma_1^-)$, $\sigma_1^z\sigma_2^z$. Of these 15, only $\sigma_1^z$ and $\sigma_2^z$ have inhomogeneous parts, which are $-K_1$ and $-K_2$ [from Eq. (33)], respectively.

The 15 simultaneous equations cannot be easily solved in closed form, but for any choice of the parameters $(\omega_1, \omega_2, T, \mu, \epsilon, \Gamma)$, the linear equation set (53) can be solved numerically. Some limiting cases, particularly the $\mu \to 0$ limit corresponding to a single pumped oscillator or spin, can be compared with simpler systems. More generally, the linear response result can be directly compared with the direct calculation from Eq. (53); for such a comparison it is merely necessary to divide by $u$.

## IV. RESULTS

Having solved the equations of motion exactly, we can find the spectra for any of the models considered using either linear response or direct calculation of the dissipated power.

### A. Uncoupled oscillator

We start by consideration of the simplest case of a single harmonic oscillator linearly coupled to the field. This is just the $\mu \to 0$ limit of Eq. (14). The linear response form is then simply

$$L(u)\big|_{\text{l.r.}} = \frac{m^2}{\pi}\Big[\langle a^+ a\rangle_0 \times \Big\{\frac{\Gamma}{\Gamma^2 + (\omega - u)^2} + \frac{\Gamma}{\Gamma^2 + (\omega + u)^2}\Big\} + \frac{\Gamma}{\Gamma^2 + (\omega - u)^2}\Big], \tag{54a}$$

where $\langle a^+ a\rangle_0$ is the thermal oscillator population and $\Gamma$ is a relaxation rate (inverse relaxation time) arising from the coupling to the heat bath. To compare with the direct method, we go to the rotating wave, and drop the (nonresonant) terms involving $\omega + u$, obtaining

$$L(u) = \frac{m^2}{\pi}[\langle a^+ a\rangle_0 + 1]\frac{\Gamma}{\Gamma^2 + (\omega - u)^2}. \tag{54b}$$

In the direct method, we find from Eq. (19) that $\bar{a}^+$ is required. This can be found from the steady-state condition in the rotating frame:

$$\dot{\bar{a}} = iu\bar{a} - i\omega\bar{a} - \Gamma\bar{a} - i\epsilon \tag{55}$$

or

$$\bar{a} = \frac{-i\epsilon}{\Gamma + i(\omega - u)}.$$

Then

$$\text{power} = \frac{2u\epsilon^2\Gamma}{\Gamma^2 + (u - \omega)^2}. \tag{56}$$

The $\Gamma$ in Eq. (56) arises from the semigroup formalism of Eq. (27); in the case of weak system-heat bath coupling, it is exactly the phenomenological $\Gamma$ of Eq. (54).

The results Eqs. (56) and (54) appear different. However Eq. (56) applies to the steady state, and in steady state the occupation number of oscillator excitations $\langle a^+ a\rangle$ should really be taken as small (compared to unity) at low temperatures. Thus in steady state we find, by using Eqs. (56), (55), and (5) with the dipole radiation coupling

$$\epsilon = -mE_0, \tag{57}$$

that the ratio of calculated line shapes using linear response and direct methods:

$$L(\omega)\big|_{LR}/L(\omega)\big|_{DM} = 1. \tag{58}$$

Thus for the driven oscillator, at steady state, both linear response and direct methods agree, and both [compare Eq. (54)] yield a simple Lorentzian line of width $\Gamma$ centered at $u = \omega$. No power broadening is observed. This is easily understood: As the harmonic oscillator is pumped ever harder, the system can climb up the energy ladder to higher oscillator state; thus the first excited state does not build up enough population to inhibit absorption and cause broadening. For this case, the direct method enjoys no advantage over linear response (that is, the spectrum should be independent of field strength).

### B. Uncoupled two-level system

The exact solution to the single driven two-level system of Eqs. (16) and (17), $\mu \to 0$ is of interest in both

magnetic resonance and laser contexts, and is given in several places.[6] Again, the power dissipation is simply obtained from the condition of steady state in the rotating frame:

$$0=\dot{\bar{\sigma}}_+=\dot{\bar{\sigma}}_-=\dot{\bar{\sigma}}_z \ . \tag{59}$$

Solving the three equations of motion for the spin operators gives, in steady state,

$$\bar{\sigma}_+=\frac{-i\epsilon K[\Gamma+i(u-\omega)]}{-2\Gamma^3-2\Gamma(\omega-u)^2-2\epsilon^2\Gamma} \ . \tag{60}$$

Here $K$, which arises from the semigroup Eq. (27), is related to the steady-state excitation level [compare Eq. (35)]

$$\langle\sigma_z\rangle=\frac{K}{2\Gamma} \quad (\epsilon\to 0) \ . \tag{61}$$

[It enters the equation of motion for $\dot{\bar{\sigma}}_z$ as:

$$\dot{\bar{\sigma}}_z=\dot{\sigma}_z=-i\epsilon(\bar{\sigma}_+-\bar{\sigma}_-)-2\Gamma\bar{\sigma}_z+K.] \tag{62}$$

The power is obtained then, as

$$(\text{power})=2u\epsilon\ \mathrm{Im}\,\bar{\sigma}_+ \ , \tag{63}$$

$$=\epsilon^2 uK/[\Gamma^2+\epsilon^2+(u-\omega)^2] \ . \tag{64}$$

Or, from Eq. (5), the direct calculation gives the line shape as

$$L(u)\big|_{\text{Direct}}=\Gamma\langle\sigma_z\rangle\hat{M}^2/[\Gamma^2+\epsilon^2+(\omega-u)^2]\pi \ , \tag{65}$$

where $\hat{M}$ is the magnetic dipole moment (or spin moment), and

$$\epsilon=-\hat{M}\mathbf{H}_0 \ , \tag{66}$$

with $\mathbf{H}_0$ the magnetic field.

The linear response result for a single two-level system is simply

$$\begin{aligned} L(u)\big|_{\text{Lin. R.}} &= \frac{\hat{M}^2}{4\pi}\int_0^\infty e^{-iut}\langle(\sigma_+ +\sigma_-)(t)(\sigma_+ +\sigma_-)\rangle\, dt \\ &= \frac{\hat{M}^2}{4\pi}\left\{(\langle\sigma_+\sigma_-\rangle+\langle\sigma_+\sigma_+\rangle)\frac{\Gamma}{\Gamma^2+(u-\omega)^2}\right. \\ &\quad \left.+(\langle\sigma_-\sigma_+\rangle+\langle\sigma_-\sigma_-\rangle)\frac{\Gamma}{\Gamma^2+(\omega+u)^2}\right\} . \end{aligned} \tag{67}$$

Using the identities

$$\sigma_+^2=\sigma_-^2=0 \ , \tag{68}$$

$$\sigma_+\sigma_-=\tfrac{1}{4}(1+2\sigma_z) \ , \tag{69}$$

$$\sigma_-\sigma_+=\tfrac{1}{4}(1-2\sigma_z) \ , \tag{70}$$

this becomes

$$L(u)\big|_{\text{Lin. R.}}=\frac{\hat{M}^2\Gamma}{16\pi^2}\left\{\frac{\langle 1+2\sigma_z\rangle}{\Gamma^2+(\omega+u)^2}+\frac{\langle 1-2\sigma_z\rangle}{\Gamma^2+(\omega-u)^2}\right\} . \tag{71}$$

Then once more taking the ratio of the predicted line shapes in the rotating wave system, we obtain for

$$\frac{L(u)|_{\text{Lin. R.}}}{L(u)|_{\text{Dir}}}=\frac{\langle 1-2\sigma_z\rangle}{4\langle\sigma_z\rangle}\frac{\Gamma^2+\epsilon^2+(u-\omega)^2}{\Gamma^2+(u-\omega)^2} \ . \tag{72}$$

Thus, except for a numerical factor and a thermodynamic average, the difference is due to an $\epsilon^2$ term in the calculated power dissipation Eq. (65) which is absent in linear response. Note that the $\epsilon^2$ appears additively with $\Gamma^2$ in Eq. (65)! Thus it is a broadening effect. It is referred to as power broadening, and really amounts to an increasing of the frequency interval which is effectively pumped from being a delta function of $\omega$ to a broader situation. This is due to system-field interaction causing a splitting of the energy levels of the bare system; these split levels are then probed by the field. Such a term cannot appear in linear response, in which the approximation is made that the field probes the fluctuations of the *unperturbed* system. The numerical factor

$$\frac{\langle 1-2\sigma_z\rangle}{4\langle\sigma_z\rangle}$$

which occurs in Eq. (72) is of some interest in understanding the difference between linear response and direct methods. For the two-level system, $2\langle\sigma_z\rangle$ is the population difference between upper and lower levels, while $\frac{1}{2}\langle 1-2\sigma_z\rangle$ is simply the population in the lower level. Thus for the transition near resonance ($u\cong\omega$), linear response, which is rigorous only at very weak fields, and therefore for small upper-state population, gives a signal proportional to the lower-level population, while the direct method (more correctly) gives a signal proportional to the population difference between upper and lower levels.

For both of the simple systems, harmonic oscillator and single spin, the differences between direct power dissipation and linear response are straightforward: For the oscillator, there is no difference, while for the single spin the differences are power broadening, not found for the linear response approximation, but present in the true system dynamics and final-state counting.

### C. Two coupled oscillators

Since the single driven oscillator does not show power broadening, we do not anticipate power broadening for the coupled-oscillator model of Eqs. (14) and (15). From the simple coupled oscillator expression without relaxation or driving, we expect resonance at

$$u=\tfrac{1}{2}\{\omega_1+\omega_2\pm\sqrt{(\omega_1-\omega_2)^2+4\mu^2}\} \ . \tag{73}$$

This is, essentially, just what is observed. The line shape is independent of $\epsilon$, and the linear response and direct power dissipation calculations agree for all values of the field strength. Additionally, the signal is predicted to depend on temperature only through the dependence of the relaxation constants $\Gamma$ on $T$ [compare Eq. (52)]. The only features of interest come from the relative sizes of $\mu$ and $(\omega_1-\omega_2)$, which will determine how strongly the modes mix, and the effects of relaxation.

On comparing, for instance, the power dissipation in Figs. 1 and 2, we see that for weak damping, if $\mu/(\omega_1-\omega_2)=\frac{1}{5}$, the resonances appear very near the unperturbed frequencies [Eq. (73) predicts 598 and 652 $\text{cm}^{-1}$], and because the coupling is weak, energy from the field is absorbed only very weakly at $\omega_2\cong u$. When $\mu$ becomes equal to $(\omega_1-\omega_2)$, the splitting is much larger (Fig. 2; predicted frequencies of 681 and 569) from Eq. (72), and the absorption is rather strong at $u=681$.

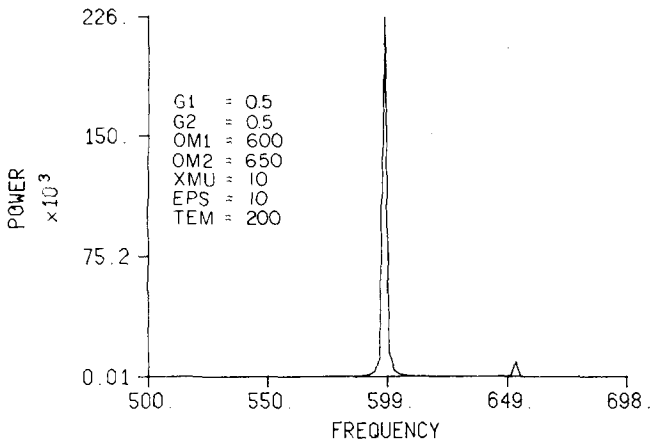


FIG. 1. Direct method (DM) calculation of the power dissipation for a two-oscillator system [Eqs. (14) and (15)]; only the first oscillator is coupled to the field. The parameters are indicated: $\Gamma_2 = \Gamma_2 = 0.5$ cm$^{-1}$, $\omega_1 = 600$ cm$^{-1}$, $\omega_2 = 650$ cm$^{-1}$, $\mu = 10$ cm$^{-1}$, $\epsilon = 10$ cm$^{-1}$, and $T = 200$ cm$^{-1}$. The linear response (LR) and DM results for Figs. 1–5 are in agreement.

It is interesting to note that unless energy is dissipated into the bath (i.e., unless $\Gamma \neq 0$), there is no absorption of power from the field. This is reasonable thermodynamically, since we are in a steady-state situation, and no energy can be absorbed by the system at steady state unless there is also an energy dissipation channel.

When the coupling between the "silent" modes (not directly field coupled) and the heat bath increases, the effective coupling between mode 2 and the field decreases, and the absorption near $\omega_2$ goes away (Figs. 3–5). This may be understood semiclassically in terms of an interaction time: The decrease of lifetime as $\Gamma_2$ increases means that there is no time for the coupling between modes 1 and 2 to be effective. The result is that, as $\Gamma_2$ increases with fixed values of the other parameters, one passes from weak, narrow absorption at $\omega_2$ to a strong wide peak near the resonances of Eq.

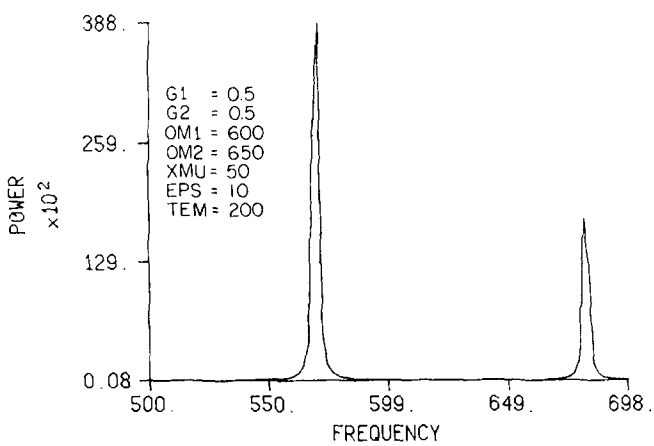


FIG. 2. As in Fig. 1, but the oscillator coupling $\mu$ has been increased, leading to larger splitting and a stronger relative absorption at the high-frequency peak.

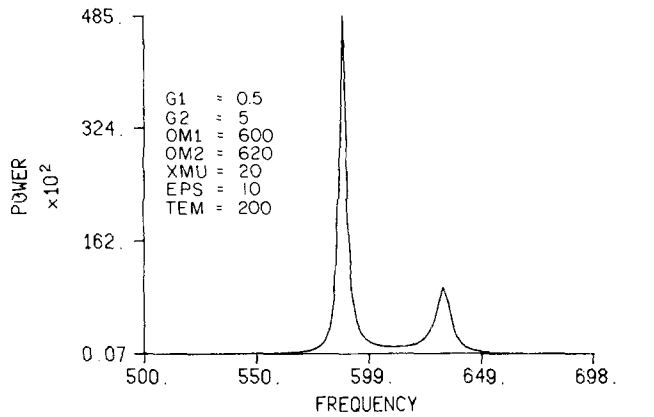


FIG. 3. As in Fig. 2, but with oscillators closer in frequency and stronger damping in the second oscillator.

(72) (Fig. 3) to a shoulder on the side of the main peak near $\omega_1$ (Fig. 4) to, finally, a narrow line $\omega_1$ (Fig. 5) when $\Gamma_2$ exceeds $\mu$.

The behavior of the coupled harmonic oscillators is straightforward. It shows no special effects due to strong fields both because the spectrum is unbounded from above so that no population congestion occurs, and because the levels are all evenly spaced, so that no strong resonances or localization of energy in specific states, can occur. The last feature disappears when more realistic models (such as coupled Morse oscillators) are considered.

### D. Two coupled two-level systems

Both the linear response result Eq. (38) and direct calculation (simultaneous solution of the 15 steady-state equations described at the end of Sec. III) are rather complex in this case, and features are best discerned by actual comparison of calculated power dissipation. When the coupling to the field $\epsilon$ is weak, one expects the linear-response and direct calculations to yield the same results. We have therefore renormalized the constants out of the linear response result; Fig. 6 shows the two predicted power dissipation spectra for the weak-field case; they are, indeed, nearly identical.

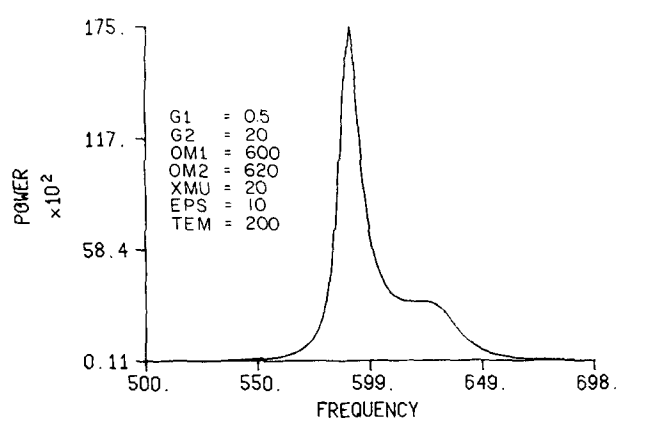


FIG. 4. As in Fig. 3, but even stronger damping of $\omega_2$.

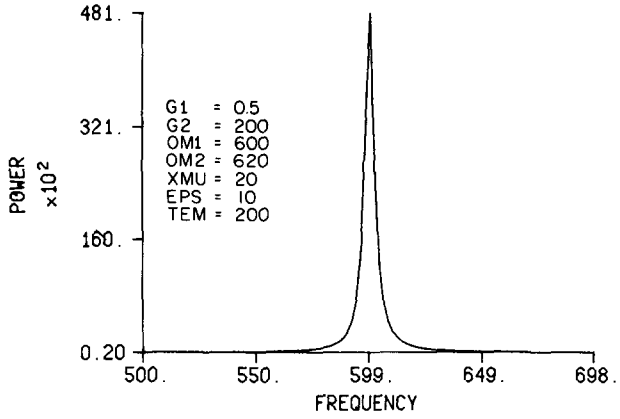


FIG. 5. As in Fig. 4, but strongly overdamped second oscillator leads to narrowing of peak at $\omega_1$ (relaxation decoupling).

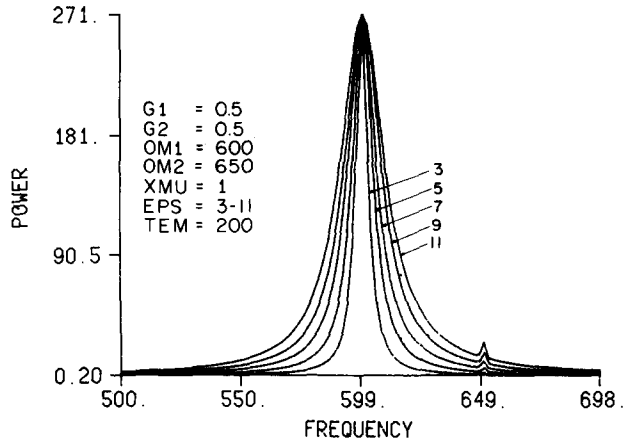


FIG. 7. As in Fig. 6, but only DM curves, showing increase of power broadening with increasing field coupling $\epsilon$, in $\epsilon > \Gamma$ limit.

Some of the coupled-spin behavior can be fairly simply understood by comparison with either uncoupled spins on the one hand or with coupled oscillators on the other. When the mode–mode coupling $\mu$ is fairly weak, the dominant effect of increased $\epsilon$ is just to broaden the absorption near $u=\omega_1$; this is simple power broadening, just as occurred for the single spin (Fig. 7). We also observe for coupled two-level systems, just as for coupled oscillators, that decoupling between the modes can be induced by making the lifetime $(\Gamma_2)^{-1}$ short; this is shown (for coupled modes) in Fig. 8. The effect of temperature is simple: the constant $K$ is related to the steady-state excitation value by Eq. (61), and therefore (for weak fields) the Fermion population at equilibrium requires

$$K_i=\Gamma_i(1-e^{\omega_i/kT})/(1+e^{\omega_i kT})\ , \quad i=1,2\ . \tag{74}$$

This (rather weak) dependence can be seen by comparison of Figs. 9 and 10.

If the coupling $\mu$ is decreased no oscillator strength is transferred to $\omega_2$, which therefore loses the absorption peak (compare Figs. 11 and 12).

Although increasing the relaxation rates $\Gamma_1$ and $\Gamma_2$ normally would be expected to broaden the absorption line, there are ways in which increase of the relaxation rate can apparently decrease the linewidth. The first of these is the effective decoupling of the two modes, which is shown in Fig. 8, and which truly is a narrowing and has already been discussed. The second is simpler, occurs even for a single spin, is of some historical interest, and is only an apparent narrowing. If the relaxation $\Gamma$ is very small, there is no way for the system to dissipate power into the heat bath. Then the two-level system will reach a steady state in the applied field, but no further energy will be dissipated and no signal will be observed; the line is not narrowed, but it is not seen. This simple situation occurs both in the linear response and direct calculations, and it was the choice of sample with extremely long relaxation time (small $\Gamma$) which prevented Gorter from discovering nuclear magnetic resonance.[17]

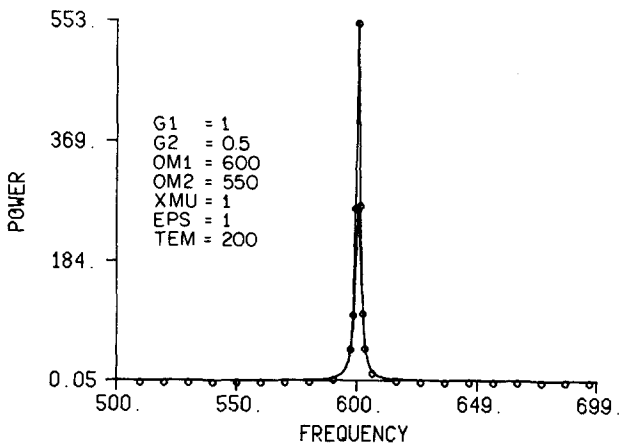


FIG. 6. DM (no circles) and LR (circled curve) power dissipation for two coupled two-level systems [Eqs. (16) and (17)], with only the first coupled to the field. The field coupling $\epsilon$ is small, so that the two calculations agree.

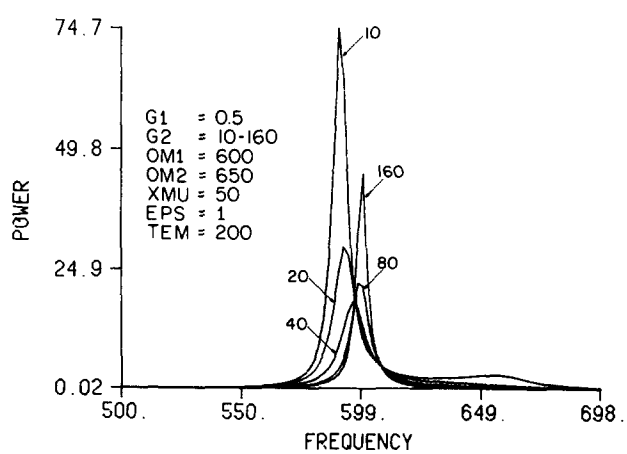


FIG. 8. As in Fig. 7, but showing effects of relaxation decoupling. As $\Gamma_2$ goes from $\ll\mu$ to $\cong\mu$ to $\gg\mu$, the line starts narrow, then broadens and shifts toward $\omega_1$, finally narrowing again for $\Gamma_2\gg\mu$.

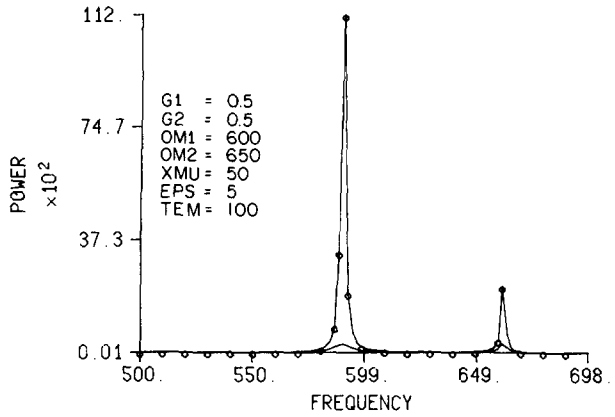


FIG. 9. As in Fig. 6, but with stronger field and intersystem coupling. Note broadening of DM response.

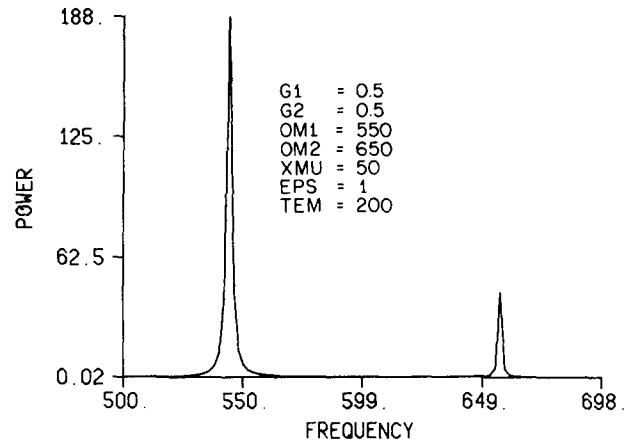


FIG. 11. As in Fig. 7, but smaller field coupling and greater $\omega_2-\omega_1$.

As expected, the behavior of the linear response results diverge strongly from the correct direct result when $\epsilon$ is fairly large (compare Figs. 13–16). Therefore we now focus on the direct calculation to examine the behavior of a strongly pumped situation. There is one rather striking observation which is, really, quite unexpected; this is the central peak which occurs close to the average of $\omega_1$ and $\omega_2$. This central peak requires both large $\mu$ (compared to $\omega_1-\omega_2$) and large $\epsilon$ to occur; if $\mu$ is too small or $\epsilon$ is too small it is absent. Formally, this behavior comes about from the coupling of three of the 15 equations for the operators at the end of Sec. III. These three equations of motion (in the rotating frame) are

$$\partial/\partial t(\sigma_1^+ + \sigma_1^-) = i(u+\omega)[\sigma_1^+ - \sigma_1^-] - i\mu\sigma_1^z[\sigma_2^+ - \sigma_2^-] - \Gamma_1(\sigma_1^+ + \sigma_1^-)\,, \tag{75}$$

$$\partial/\partial t[\sigma_1^z(\sigma_2^+ - \sigma_2^-)] = i(u+\omega_2)[\sigma_1^z(\sigma_2^+ + \sigma_2^-)] - i\epsilon\sigma_1^+\sigma_2^+ - i\epsilon\sigma_2^-\sigma_1^- + i\epsilon(\sigma_2^+\sigma_1^- + \sigma_2^-\sigma_1^+) - i\mu/4(\sigma_1^+ + \sigma_1^-) + K_1(\sigma_2^+ - \sigma_2^-) - (2\Gamma_1 + \Gamma_2)\sigma^z(\sigma_2^+ - \sigma_2^-)\,, \tag{76}$$

$$\partial/\partial t\sigma_1^+\sigma_2^+ = i(2u+\omega_1+\omega_2)\sigma_1^+\sigma_2^+ - i\epsilon\sigma_1^z\sigma_2^+ - (\Gamma_1+\Gamma_2)\sigma_1^+\sigma_2^+\,. \tag{77}$$

The operator $(\sigma_1^+ + \sigma_2^-)$ itself enters into the power (or line shape) expressions. It is coupled via $\mu$ to $\sigma_1^z(\sigma_2^+ - \sigma_2^-)$, which in turn is coupled via $\epsilon$ to $\sigma_1^+\sigma_2^+$. The equation for $\sigma_1^+\sigma_2^+$ contains a factor $(2u+\omega_1+\omega_2)$, and this goes to zero, resulting in strong absorption, for $|u| = (\omega_1+\omega_2)/2$, the averaged frequency. Physically, if the two spins are strongly coupled (via $\mu$) and at the same time coupled to the radiation field (via $\epsilon$), the photon is apparently in some way split between the spins. We are not aware of any experimental situation in which such a central peak has been seen, though it would seem that the magnetic resonance situation (in which the power broadening is easier to bring about) would be a reasonable place to look for it (see below). Such a central line cannot occur in the linear response calculation since only two equations are coupled, hence only two resonance frequencies can emerge.

The central peak is (from 75–77 and 44) second order in $\epsilon$, first order in $\mu$, while the overall line is first order in $\epsilon$. Thus for small $\epsilon$ (linear limit), the central peak cannot appear. On the other hand, when even larger values of $\epsilon$ are considered, the effective opera-

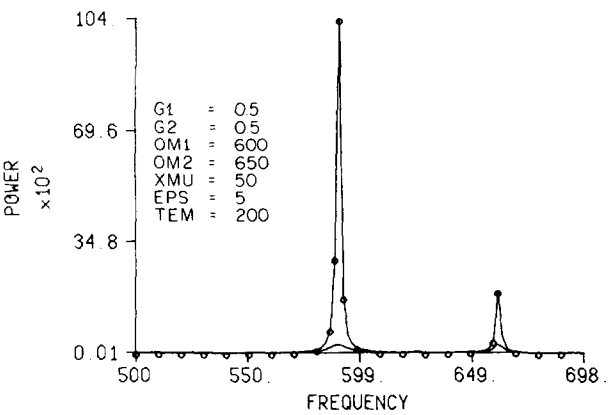


FIG. 10. As in Fig. 9, but for lower temperature; note very small influence of $T$ in this regime.

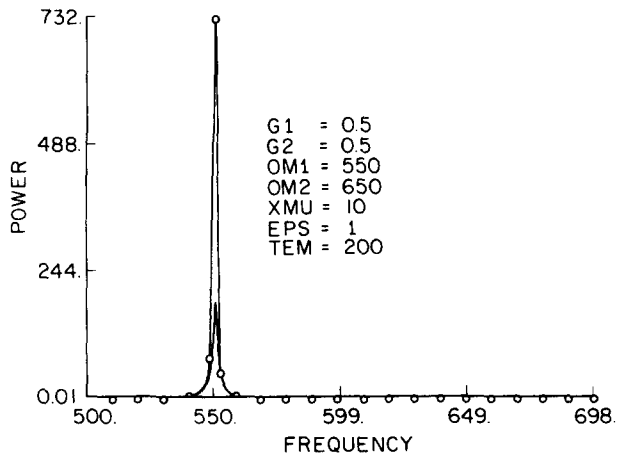


FIG. 12. As in Fig. 11, but with much decreased intersystem coupling $\mu$—the second spin is now not seen, since it cannot effectively take oscillator strength from system 1 via $\mu$.

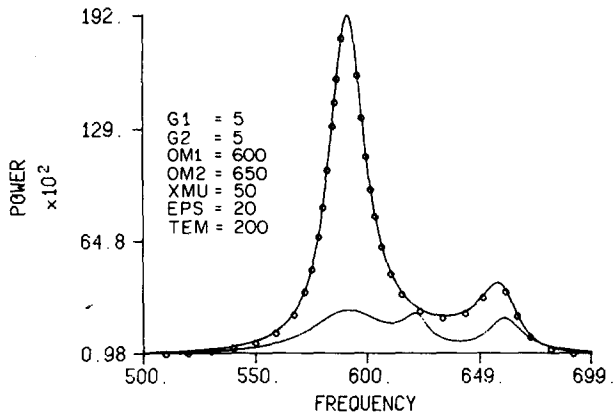


FIG. 13. As in Fig. 6, but now both $\mu$ and $\epsilon$ are large. Note significant difference between LR curve (with circles) and DM curve (line), particularly the appearance of the third, central peak in the latter. This central peak is second order in $\epsilon$ and first order in $\mu$, so it requires significant values of both to be seen.

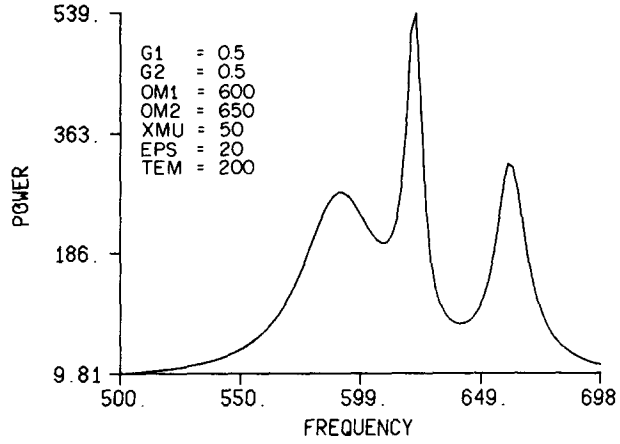


FIG. 15. As in Fig. 14, but showing more power broadening.

tor algebra which is coupled to the field becomes closer to the full 15-function system. Then the number of excitations coupled to the field gets large, with concomitant complex line shapes (Fig. 16), including features which strongly resemble Fano antiresonances.[18]

## V. REMARKS

The importance of nonlinear response to applied fields has long been recognized; in the simplest form of power broadening or saturation broadening it occurs in standard texts on microwave spectroscopy,[19] laser physics,[16] and magnetic resonance.[4] Generally, however, spectroscopy is described from the viewpoint of perturbation theory: this leads, in the density matrix formalism, to linear-response theory.[1-3] Using this approach, the line shape is linearly proportional to the field strength $\epsilon$. Extensions beyond the validity range of linear response theory are generally of three types: most commonly, Bloch-type equations are employed to describe non-Hamiltonian evolution of the system variables; for certain cases, restricted sets of motion equations are studied; for optical excitations, a power series in the field is developed[20] in which the coefficients are the higher order polarizabilities. In the particularly important case of microwave saturation, a solution is obtained by calculation of the power dissipated in the photostationary state[19]; it is precisely this latter approach which underlies the calculations presented here.

There are many advantages to the linear-response formalism[2]: it is fairly easy to use for nonthermal perturbations, it is well defined in both quantal and classical systems, and it is easily understood in fluctuation/dissipation terms[10]: the dissipated energy in a perturbation experiment is proportional to the spontaneous fluctuations in the unperturbed system (at identical frequency). On the other hand, linear response will fail for the situation in which the system-field coupling, which we have characterized by $\epsilon$, approaches in value the other characteristic energies of any given system. This situation, common in microwave studies and magnetic resonance, is also relevant for modern experiments with high-energy lasers. Linear response will also fail when considering any of the nonlinear spec-

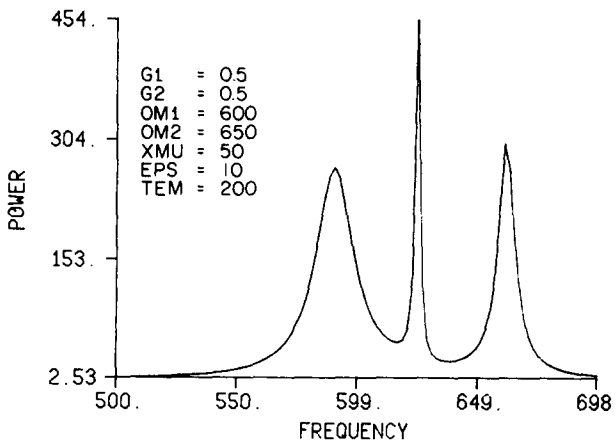


FIG. 14. As in Fig. 13, but only DM shown, with weaker damping. Note strong, sharp central peak.

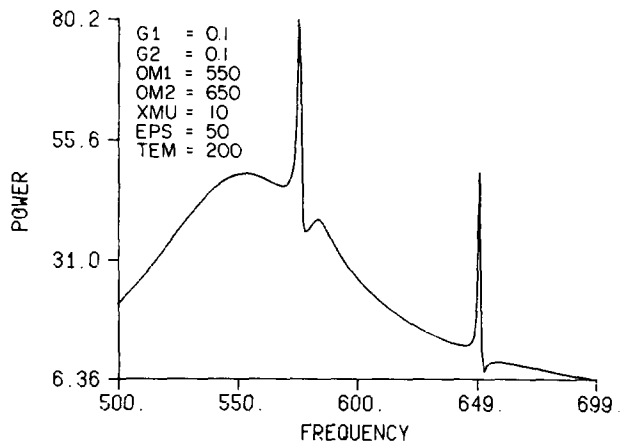


FIG. 16. As in Fig. 15, but for weak damping (small $\Gamma$). Note Fano-type (antiresonance) line shape, with very rounded shape near primary frequency $\omega_1$.

troscopic techniques (CARS, four-wave mixing, CSRS, and coherent Rayleigh scattering) in which several photons are in fact involved. The direct calculation of the dissipated power, which was proposed by Spohn and Lebowitz[5] and is expanded upon and pursued here, offers several important advantages for calculating the absorption spectrum: It calculates the very same data (power dissipated) which is measured experimentally, it is not based on any perturbation expansion, and therefore can be extended to arbitrary values of the system and bath coupling parameters. It is as easy to implement calculationally as the linear-response method, and it can be combined with the semigroup analysis[13–15] of the system-bath Hamiltonian and self-consistent decouplings of the operator algebra as generated by a selected equilibrium density matrix[16,21] to handle even very strongly coupled situations. Further applications, notably to the important model system of an oscillator coupled to a spin, are in progress in our laboratories and will be reported soon.

Of the particular features observed in the present calculations but not in linear response, some (power broadening) are experimentally well known, while others (notably the predicted central peak for the coupled-spin system) have not, to our knowledge been observed. In the case of microwave or magnetic resonance spectra, for which the field interaction can be quite strong (as evidenced by the power broadening), we expect that this peak can easily be found.

Dick and Hochstrasser[22] have recently developed a density operator technique for calculation of nonlinear spectra, and have even included the effects of several Fourier components, rather than simply a single one [at frequency $u$ as in Eqs. (15) and (17)]. Their technique differs in several details from that presented here, notably in being based on Liouville, rather than Heisenberg, equations of motion; also bath coupling terms and the semigroup formalism are not included in their treatment, which finds density matrix elements of the molecule/field system. Each approach has its advantages; both should be of real use in the nonlinear regime.

## ACKNOWLEDGMENTS

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