that the configuration of the $4f$ electrons is different in the two materials.

VIII. SUMMARY

Using the Mössbauer effect, the hyperfine structure of Tm^{169} in Fe_2Tm has been studied as a function of temperature. The results have been adequately explained by a relatively simple treatment of the Tm-ion energy levels and straightforward evaluation of the hyperfine interaction. Using the measured value of Tm^{169} nuclear ground-state moment, various nuclear and electronic quantities have been derived and found in general to be in satisfactory agreement with previous results.

Theory of Spin Resonance and Relaxation

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A quantum-statistical-mechanical theory of spin resonance and relaxation is presented, which avoids the assumptions of earlier theories, is capable of extension to other than the lowest Born approximation for the strength of the relaxation mechanism, and is applicable over a broader range of physical situations. From the Liouville equation for the combined system of spin+bath, the theory yields a non-Markoffian equation for the time development of the statistical density operator for the spin system alone. Detailed consideration is given to the response of the spin system linear in the driving field, and an equation for the steady-state spin density operator is deduced. A simple application exemplifies the new features of the theory and it is shown that it describes the phenomenon of "motional" narrowing. The response to an arbitrary external field is studied with particular reference to the problem of approach to thermal equilibrium and the phenomenon of spin resonance saturation. The latter is considered in some detail for a system of independent spins, for which an equation for the steady-state magnetization is derived and discussed.

1. INTRODUCTION

EQUATIONS of motion for the macroscopic magnetization of a sample under the combined action of external magnetic fields and a "heat bath" have been very useful in the study of magnetic resonance and relaxation. Bloch's[1] equations and later modifications[2,3] were the first ones to be suggested on phenomenological grounds, where the main assumption was made that the effects of the bath can be described by means of two constants, the so-called relaxation times, to be determined from experiment. Microscopic theories of the relaxation of the spin system were presented soon afterwards, beginning with the well-known work of Bloembergen, Purcell, and Pound,[4] where the bath was approximated to be an external fluctuating field. This latter semiclassical approximation was eliminated and a quantum-mechanical treatment of the problem was presented in the pioneering work of Wangsness and Bloch[5] and Bloch.[6,7] Redfield,[8] Fano,[9] and other authors[10–12] have subsequently given similar theories. In all these theories, the bath was considered as a quantum-mechanical system, that remained in thermodynamic equilibrium, while its exchange of energy with the spin system was taken into account. These theories have provided a derivation of the phenomenological equations while they pointed out the limits of their validity, and have given a microscopic determination of the relaxation times. They have also yielded much more general equations[7,8,10,11] of motion for the statistical-mechanical density operator of the spin system, which determines all its observable properties.

In the theories mentioned above, some assumptions were made, which were clearly stated in the works of Bloch,[5–7] Fano[9] and Abragam.[2] In particular, the sta-

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tistical-mechanical assumptions were made at a certain strategic point of the calculation, that the spin and bath systems are uncorrelated and that the bath remains in thermodynamic equilibrium. Both of these assumptions are unsatisfactory. The first one is clearly wrong if made for all times, for it amounts to ignoring the interaction between the system of interest and the bath. It can, however, yield valid results if made, as was the case with these theories, at the appropriate stage of the calculation. Even then, however, it entails a certain approximation as to the strength of the spin-bath interaction. In particular, all the theories mentioned above treat the interaction only in the lowest Born approximation. It is not clear that the method of derivation of the equation of motion for the spin density operator which was adopted in these works, apart from its mathematical complexity, is capable of extension to stronger interactions. The second assumption amounts to the repeated random phase assumption for the bath, the unsatisfactory nature of which has been pointed out recently by Van Hove.[13] In addition, on account of the method of derivation, which bases its considerations on the short time development of the system, these theories are valid only if the bath provides a sufficiently rapidly fluctuating environment for the spin, i.e., only if $\tau_c/\tau_r \ll 1$, where $\tau_c =$ correlation time for the bath and $\tau_r = $ a measure of the relaxation time. Thus, important physical phenomena are left out of the range of validity of these theories.

In this paper we are concerned with the same problem, which in its generality is that of obtaining an equation of motion for a subsystem from the Liouville equation of motion for the whole, isolated system. A method for the derivation of equations of motion of subsystems has recently been proposed,[14,15] which avoids these assumptions and restrictions. This method was arrived at[16] as a generalization of the work of one of us.[17] We have, however, profited from the elegant work of Zwanzig,[18] who clearly and concisely stated the essence of this point of view, in connection with the derivation of the master equation for approach to equilibrium and the generalization of Onsager's theory of irreversible processes.

We have applied here this method to the problem of spin resonance and relaxation.[19] The main characteristic

of the theory is that, in contrast to the earlier theories, it yields a non-Markoffian equation of motion for the spin system which is valid for all times. This enables the equation of motion to be valid for arbitrary τ_c/τ_r. In addition, it can in principle describe the effects of the spin-bath interaction to arbitrary order. Although the method can be applied equally well to the study of the bath and its evolution in time, we have restricted our attention here to the spin system only, characterizing mathematically the dissipative behavior of the bath by the existence of the correlation time τ_c. In the study of the driven steady state, whenever it exists, the non-Markoffian character of the equation of motion results in a description of the effects of the spin-bath interaction that involves the frequency of the driving field. Thus, this theory predicts in general non-Lorentzian absorption line shapes. The exact shape is determined by the frequency spectrum of the bath correlation functions. The results of the previous theories[5–12] are obtained from this theory in the lowest Born approximation for the strength of the relaxation mechanism and for $\tau_c/\tau_r \ll 1$, while the statistical assumptions mentioned above are avoided.

In the first three sections we consider the response of the spin system, linear in an external, time-varying driving field, a problem of considerable interest.[20] The general formalism is applied and the equation for the steady state is obtained in the lowest Born approximation for the spin-bath interaction. This equation is applied to the simple system of independent spins with the bath taken to be a randomly fluctuating magnetic field, where it is demonstrated that an equation for the steady-state magnetization exists and which describes a phenomenon that may be considered as the prototype of "motional" narrowing. A macroscopic, classical derivation of this particular result is discussed in the Appendix. Finally, a general discussion of the linear response for arbitrary spin-bath interaction is given and it is indicated how approximations other than the lowest Born approximation can be obtained. The important question of the quantitative criterion for the validity of the lowest Born approximation is not discussed in general.

In the following section the equation of motion for a general spin system is obtained. This includes the description of the approach of the spin system toward equilibrium and of the phenomenon of spin resonance saturation. Although no comparison with experiments is attempted, in the last section the general results of the theory are demonstrated in the case of a system of independent spins in a bath of a certain range of finite temperatures in a typical spin-resonance experiment for driving fields of arbitrary strengths. An equation for the steady-state magnetization is obtained with four relaxation times, all dependent in general on the frequency

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and strength of the driving field. Some of the consequences of this equation are discussed in special cases. In particular, it is pointed out that a qualitative description of the various aspects of the phenomenon of resonance saturation with increasing strength of the driving field, e.g., the difference in the saturation behaviors of the absorption and dispersion signals, is included in this equation.

The applicability of the general formalism to more realistic models is obvious and will be reported in other publications.

2. EQUATION OF MOTION FOR THE LINEAR RESPONSE OF THE SPIN SYSTEM

We consider an arbitrary spin system in interaction with external fields and another system, to be taken eventually to act as a heat bath. From the Liouville equation of motion of the combined system, we derive an equation of motion for the spin system alone. Only the response linear in the driving field is considered in this section.

Let the Hamiltonian of the total system be

$$H_T(t) = A_0 + B + V + A_1(t)$$
$$= H_0 + V + A_1(t) = H + A_1(t), \quad (2.1)$$

where A_0 is the Hamiltonian of the spin system in any external static fields of force, $A_1(t)$ its interaction energy with a weak driving field, B the Hamiltonian for the bath, and V the interaction between the two systems. The Liouville equation for the density operator $\rho(t)$ of the total system is ($\hbar = 1$)

$$i(d/dt)\rho(t) = [H_T(t), \rho(t)] \equiv \mathfrak{IC}_T(t)\rho(t). \quad (2.2)$$

Here we introduce the Liouville-operator $\mathfrak{IC}_T$ corresponding to the operator H_T. Since we shall make extensive use of this formalism in the following, we point out that we shall denote a Liouville-operator corresponding to an operator, say A, by the same letter in script form, i.e., $\mathfrak{C}$. Liouville-operators operate in the space of operators rather than states of a system.

The density operator for the spin system may be taken as

$$\sigma(t) = \mathrm{tr}_b \rho(t), \quad (2.3)$$

where tr_b denotes the trace operation over the bath variables only. Clearly, the expectation value of an observable Q of the spin system alone is given by

$$\langle Q \rangle = \mathrm{Tr} Q\rho(t) = \mathrm{tr} Q\sigma(t). \quad (2.4)$$

tr is the trace operation over the spin variables only and $\mathrm{Tr} = \mathrm{tr}\, \mathrm{tr}_b$. Furthermore, it can easily be verified that $\sigma(t)$, as defined in (2.3), has all the properties of a density operator: it is Hermitian, i.e., $\sigma^\dagger(t) = \sigma(t)$; it is normalized, $\mathrm{tr}\sigma(t) = 1$; and its diagonal matrix elements in any representation for the spin system are nonnegative.

In order to obtain the response of the system to the first order in the driving perturbation $A_1(t)$, we assume that before the disturbance is turned on, say at $t=0$, the system is in thermodynamic equilibrium at temperature $T = (k\beta)^{-1}$, i.e.,

$$\rho(0) = f(H) \equiv \exp(-\beta H)/\mathrm{Tr}\{\exp(-\beta H)\}, \quad (2.5)$$

where $H = H_0 + V$. It is then clear that the linear response is described by $\rho_1(t)$, the linear part of $\rho(t) - f(H)$, that satisfies the inhomogeneous equation

$$i\frac{d}{dt}\rho_1(t) = \mathfrak{IC}\rho_1(t) + \mathfrak{C}_1(t)f(H), \quad \rho_1(0) = 0. \quad (2.6)$$

The linear response of the spin system is then completely determined by $\sigma_1(t) = \mathrm{tr}_b \rho_1(t)$, which has the properties $\sigma_1^\dagger(t) = \sigma_1(t)$, $\mathrm{tr}\sigma_1(t) = 0$.

In order to derive an equation of motion for $\sigma_1(t)$, we separate the density operator $\rho_1(t)$ into two parts, the part we are interested in and the remainder. Thus, it proves convenient to write[14]

$$\rho_1(t) = f(B)\sigma_1(t) + \eta_1(t). \quad (2.7)$$

Clearly $\eta_1(t) = \mathcal{O}\rho_1(t)$, where

$$\mathcal{O} = 1 - f(B)\,\mathrm{tr}_b \quad (2.8)$$

is a projection operator ($\mathcal{O}^2 = \mathcal{O}$) in the space of operators for the total system. In terms of $\sigma_1(t)$ and $\eta_1(t)$, Eq. (2.6) for $\rho_1(t)$ becomes a system of coupled linear differential equations, namely,

$$i\frac{d}{dt}\sigma_1(t) = [\mathfrak{C}_0 + \mathrm{tr}_b \mathcal{V} f(B)]\sigma_1(t)$$
$$+ \mathrm{tr}_b \mathcal{V}\eta_1(t) + \mathrm{tr}_b \mathfrak{C}_1(t)f(H), \quad (2.9)$$

$$i\frac{d}{dt}\eta_1(t) = (\mathfrak{IC}_0 + \mathcal{O}\mathcal{V})\eta_1(t)$$
$$+ \mathcal{O}\mathcal{V} f(B)\sigma_1(t) + \mathcal{O}\mathfrak{C}_1(t)f(H). \quad (2.10)$$

Here we have made use of a number of relations that are direct consequences of the definitions; e.g., $\mathrm{tr}_b \eta_1(t) = 0$, $\mathcal{O}\mathfrak{IC}_0 = \mathfrak{IC}_0\mathcal{O}$, $\mathcal{O}\eta_1(t) = \eta_1(t)$, $\mathcal{O}f(B)\sigma_1(t) = 0$. An equation for $\sigma_1(t)$ is then obtained by solving Eq. (2.10) for $\eta_1(t)$ in terms of $\sigma_1(t)$ with the initial condition $\eta_1(0) = \mathcal{O}\rho_1(0) = 0$, and substituting into Eq. (2.9) for $\sigma_1(t)$. A formal solution of Eq. (2.10) is obtained by the standard method of "variation of constants." Since the solution to the homogeneous equation is $\mathcal{S}(t)\eta_1(0)$ with

$$\mathcal{S}(t) = \exp\{-i(\mathfrak{IC}_0 + \mathcal{O}\mathcal{V})t\}, \quad (2.11)$$

we have

$$\eta_1(t) = -i\int_0^t d\tau \mathcal{S}(t-\tau)$$
$$\times \mathcal{O}\{\mathcal{V} f(B)\sigma_1(\tau) + \mathfrak{C}_1(\tau)f(H)\}. \quad (2.12)$$

Substitution of this expression for $\eta_1(t)$ into (2.9) yields

the linear equation for $\sigma_1(t)$

$$\frac{d}{dt}\sigma_1(t) = -i\mathcal{Q}_0\sigma_1(t) + \mathcal{C}(t,\{\sigma_1\})$$
$$-i\mathcal{Q}_1(t)\sigma(0) + D(t), \quad (2.13)$$

where

$$\mathcal{C}(t,\{\sigma_1\}) = -\operatorname{tr}_b\left\{ i\mathcal{U}f(B)\sigma_1(t) \right.$$

$$\left. +\mathcal{U}\int_0^t d\tau S(t-\tau)\mathcal{P}\mathcal{U}f(B)\sigma_1(\tau) \right\}, \quad (2.13a)$$

$$D(t) = -\operatorname{tr}_b\mathcal{U}\int_0^t d\tau S(t-\tau)\mathcal{P}\mathcal{Q}_1(\tau)f(H), \quad (2.13b)$$

and $\sigma(0) = \operatorname{tr}_b f(H)$.

Equation (2.13) in conjunction with the initial condition $\sigma_1(0) = \operatorname{tr}_b\rho_1(0) = 0$ determines completely the time evolution of the linear response of the spin system. It is clear from its derivation that this equation is exact and valid for all times t. The first term in (2.13) describes the unperturbed motion of the spin system. $\mathcal{C}(t,\{\sigma_1\})$ describes the effects of the bath alone on the dynamics of the spin system. The first term of $\mathcal{C}$ in (2.13a) gives the first-order effects of the interaction V. It can always be absorbed into $\mathcal{Q}_0$ without any loss of generality; a simple renormalization of the unperturbed energies of the spin system and the interaction V will give $\operatorname{tr}_b f(B)V = 0$. We shall adopt this renormalization in the following. The second term of $\mathcal{C}$ may be considered as a generalized collision operator, correct to all orders in V. It is clear that this term shows "memory," i.e., the rate of change of $\sigma_1(t)$ at time t due to collisions depends on all earlier values of $\sigma_1(t)$. The third term of (2.13) gives the effects of the driving field, while $D(t)$ describes the effects of interference of the driving field and the interaction with the bath. It is clear that in both $\mathcal{C}$ and D the collisions are described formally without any approximations.

In order to see more explicitly the nature of the equation of motion for $\sigma_1(t)$, Eq. (2.13), we consider here the case of a spin system interacting weakly with the bath. In the lowest Born approximation the operators $\mathcal{C}$ and D are of order V^2 and are obtained from (2.13a) and (2.13b) by replacing $S(t)$ by $\exp(-i\mathcal{JC}_0t)$. Thus, after the first-order renormalization,

$$\frac{d}{dt}\sigma_1(t) = -i\mathcal{Q}_0\sigma_1(t) + \mathcal{C}_0(t,\{\sigma_1\})$$
$$-i\mathcal{Q}_1(t)\sigma(0) + D_0(t), \quad (2.14)$$

where

$$\mathcal{C}_0(t,\{\sigma_1\}) = -\operatorname{tr}_b\mathcal{U}\int_0^t d\tau$$

$$\times \exp(-i\mathcal{JC}_0\tau)\mathcal{U}f(B)\sigma_1(t-\tau), \quad (2.14a)$$

$$D_0(t) = -\operatorname{tr}_b\mathcal{U}\int_0^t d\tau$$

$$\times \exp(-i\mathcal{JC}_0\tau)\mathcal{Q}_1(t-\tau)f^{(1)}. \quad (2.14b)$$

$f^{(1)}$ is the term of order V in the expansion of $f(H) = f(A_0 + B + V)$ in power series in V; the zeroth-order term makes no contribution, since $\mathcal{P}\mathcal{Q}_1f(A_0 + B) = 0$. In (2.14) $\sigma(0) = \operatorname{tr}_b f(H)$ should be taken for consistency up to second order in V, i.e., $\sigma(0) = f(A_0) + \operatorname{tr}_b f^{(2)}$.

In order to be able to analyze these expressions in terms of the separate properties of the bath, it is useful to expand V in a complete set of operators $u_\kappa v_\kappa$, i.e.,

$$V = \sum_\kappa u_\kappa v_\kappa, \quad (2.15)$$

where u_κ and v_κ operate in the spaces of the bath and the spin system, respectively. Bearing in mind that $\exp(-i\mathcal{JC}_0t)V = \exp(-iH_0t)V\exp(iH_0t)$, we find from (2.15), (2.14a), and (2.14b)

$$\mathcal{C}_0(t,\{\sigma_1\})$$

$$= -\sum_{\kappa\lambda}\int_0^t d\tau\{c_{\kappa\lambda}(\tau)[v_\kappa, \exp(-i\mathcal{Q}_0\tau)v_\lambda\sigma_1(t-\tau)]$$

$$-c_{\lambda\kappa}(-\tau)[v_\kappa, \exp(-i\mathcal{Q}_0\tau)\sigma_1(t-\tau)v_\lambda]\}, \quad (2.16a)$$

$$D_0(t) = \sum_{\kappa\lambda}\int_0^t d\tau\int_0^\beta d\beta' c_{\lambda\kappa}(-\tau-i\beta')[v_\kappa, \exp(-i\mathcal{Q}_0\tau)$$

$$\times \mathcal{Q}_1(t-\tau)f(A_0)\exp(\beta'\mathcal{Q}_0)v_\lambda]. \quad (2.16b)$$

We note that in these expressions, all reference to the bath has been concentrated in the quantities $c_{\kappa\lambda}(\tau)$, which are the thermodynamic (nonsymmetrized) correlation functions for the Heisenberg operators $u_\kappa(t) = \exp(i\mathcal{B}t)u_\kappa$ of the bath, defined by

$$c_{\kappa\lambda}(\tau) = \operatorname{tr}_b f(B)u_\kappa(t+\tau)u_\lambda(t) = \operatorname{tr}_b f(B)u_\kappa(\tau)u_\lambda. \quad (2.17)$$

We suppose now that the bath can be characterized mathematically by the fact that there exists a time τ_c, called the correlation time for the bath, such that for *all* the thermodynamic correlation functions $c_{\kappa\lambda}(\tau)$ and all temperatures higher than $(k\beta)^{-1}$ we have

$$c_{\kappa\lambda}(\tau) = 0 \quad \text{for} \quad |\tau| > \tau_c. \quad (2.18)$$

One condition that is necessary for this to be true for arbitrarily long times is that the energy spectrum of the bath be continuous, otherwise $c_{\kappa\lambda}(\tau)$ are quasiperiodic functions of τ, as it is evident from their definitions. Thus, we effectively deal with the bath in the limiting case of an infinite Poincaré period. Of course, condition (2.18) is more stringent than the qualitative requirement of the continuity of the energy spectrum and provides a mathematical characterization of the dissipative behavior of the bath.

The solution of Eq. (2.14) describes the complete time development of $\sigma_1(t)$ from $t=0$ to very long times, where presumably a steady state is attained. An equation for the steady state itself, when it exists, can be obtained from (2.14) with the help of the assumption (2.18) for

the bath on the basis of the following argument. We take $A_1(t)$ to be given quite generally by

$$A_1(t) = \sum_\omega e^{-i\omega t} A_1(\omega),\qquad (2.19)$$

where for each ω the summation goes over ω and $-\omega$. Now we seek a solution of (2.14) of the form

$$\sigma_1(t) = \sum_\omega e^{-i\omega t}\sigma_1(\omega,t);\quad \sigma_1(\omega,t)\underset{t\to\infty}{\longrightarrow}\sigma_1(\omega),\quad (2.20)$$

where $\sum_\omega$ goes over the same frequencies as in (2.19). Thus, (2.20) describes for very long times a steady state $\sigma_1{}^{(s)}(t) = \sum_\omega e^{-i\omega t}\sigma_1(\omega)$. In order to find an equation for $\sigma_1(\omega)$, we substitute (2.20) and (2.19) into (2.14) and study it in the limit $t\to\infty$. The expression (2.16a) for the collision term for long times is evaluated by noting that for $t>\tau_c$ the upper limit of the integral can be put equal to τ_c, due to the condition (2.18). Thus, the values of $\sigma_1(\omega,t)$ that enter the integral are from $\sigma_1(\omega,\,t-\tau_c)$ to $\sigma_1(\omega,t)$, which for $t\to\infty$ can be taken, in accordance with (2.20), to be equal to $\sigma_1(\omega)$. The evaluation of the other terms of (2.14) is straightforward. We thus find that if a steady-state solution $\sigma_1{}^{(s)}(t) = \sum_\omega e^{-i\omega t}\sigma_1(\omega)$ of (2.14) exists for long times, $\sigma_1(\omega)$ satisfies the equation

$$-i\omega\sigma_1(\omega) = -i\mathcal{Q}_0\sigma_1(\omega) + \mathcal{C}_0(\omega)\sigma_1(\omega)$$
$$-i\mathcal{Q}_1(\omega)\sigma(0) + D_0(\omega),\quad (2.21)$$

where

$$\mathcal{C}_0(\omega)\sigma_1(\omega) = -\sum_{\kappa\lambda}\,[v_\kappa,\, j_{\kappa\lambda}{}^+(\omega-\mathcal{Q}_0)[v_\lambda,\sigma_1(\omega)]$$

$$+ j_{\kappa\lambda}{}^-(\omega-\mathcal{Q}_0)[v_\lambda,\sigma_1(\omega)]_+],\quad (2.21a)$$

$$D_0(\omega) = \sum_{\kappa\lambda}\left[v_\kappa,\,\int_0^\beta d\beta'\,j_{\kappa\lambda}(\beta';\omega-\mathcal{Q}_0)\right.$$

$$\left.\times\,\mathcal{Q}_1(\omega)f(A_0)\exp(\beta'\mathcal{Q}_0)v_\lambda\right].\quad (2.21b)$$

Here $[a,b]_+ = ab+ba$ and

$$j_{\kappa\lambda}{}^\pm(\omega) = \int_0^\infty d\tau e^{i\omega\tau}c_{\kappa\lambda}{}^\pm(\tau)\qquad (2.22a)$$

[and similarly for $j_{\kappa\lambda}(\omega)$] are the one-sided Fourier transforms of the symmetrized and antisymmetrized correlation functions $c_{\kappa\lambda}{}^\pm(\tau) = (\tfrac{1}{2})[c_{\kappa\lambda}(\tau)\pm c_{\lambda\kappa}(-\tau)]$ $= \pm c_{\lambda\kappa}{}^\pm(-\tau)$ [and of the nonsymmetrized $c_{\kappa\lambda}(\tau)$], while

$$j_{\kappa\lambda}(\beta';\omega) = \int_0^\infty d\tau e^{i\omega\tau}c_{\lambda\kappa}(-\tau-i\beta'),\quad (2.22b)$$

which has the property $j_{\kappa\lambda}(\beta;\omega) = j_{\kappa\lambda}(\omega)$. In terms of the more usual Fourier transforms

$$J_{\kappa\lambda}{}^\pm(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\tau e^{i\omega\tau}c_{\kappa\lambda}{}^\pm(\tau),\qquad (2.23)$$

which have the property $J_{\kappa\lambda}{}^-(\omega) = J_{\kappa\lambda}{}^+(\omega)\tanh(\beta\omega/2)$, it is seen that

$$j_{\kappa\lambda}{}^\pm(\omega) = \int_{-\infty}^{+\infty} d\omega' J_{\kappa\lambda}{}^\pm(\omega')\theta(\omega-\omega'),\quad (2.23a)$$

where

$$\theta(x) = \int_0^\infty d\tau e^{ix\tau} = \pi\delta(x) + i(1/x)_p.\quad (2.23b)$$

Usually the parts of (2.21a) arising from $(1/x)_p$ can be combined with $-i\mathcal{Q}_0\sigma_1(\omega)$ of (2.21) and may be viewed as giving the renormalization of the spin energy spectrum due to the interaction with the bath, to second order in V. Since, however, they depend on ω, they are not simply shifts of the resonant frequency; they also affect the shape of the resonance line. The parts associated with the $\delta(x)$ may be viewed as describing the relaxation of the spin system through energy conserving processes. For a more general derivation and discussion of the equation for the steady state see Sec. 4.

More explicit forms of (2.21) are obtained by recognizing that for an arbitrary function $\phi(\mathcal{Q}_0)$ we have $\langle s|\phi(\mathcal{Q}_0)Q|s'\rangle = \phi(\omega_s-\omega_{s'})\langle s|Q|s'\rangle$, where $A_0|s\rangle = \omega_s|s\rangle$ and Q is any spin operator.

In a semiclassical treatment where the bath is treated classically but the temperature effects are described correctly, we must identify the classical bath correlation functions with the symmetrized quantum-mechanical correlation functions $c_{\kappa\lambda}{}^+(\tau) = \mathrm{tr}_b f(B)(\tfrac{1}{2})\{u_\kappa(\tau)u_\lambda + u_\lambda u_\kappa(\tau)\}$. j^- can be expressed in terms of j^+ by use of (2.23a) and the aforementioned relation between J^- and J^+.

If the bath can be approximated as a random field of force, then $\beta=0$ and $\mathcal{C}_0(\omega)$ and $D_0(\omega)$ have the particularly simple form

$$\mathcal{C}_0(\omega)\sigma_1(\omega) = -\sum_{\kappa\lambda}\,[v_\kappa,\, j_{\kappa\lambda}(\omega-\mathcal{Q}_0)[v_\lambda,\sigma_1(\omega)]],\quad (2.24a)$$

$$D_0(\omega) = 0.\qquad (2.24b)$$

An application of these equations will be made in the next section. For this case of a classical bath, a derivation of (2.21) with $\mathcal{C}_0(\omega)$ and $D_0(\omega)$ as given by (2.24) can be obtained directly, as is shown and discussed in the Appendix.

It must be observed that in Eq. (2.21) for the steady state, the description of the effects of the spin-bath interaction includes the driving frequency ω. This is clearly a result of the "memory" of the collision operator. It is quite important, as we shall demonstrate in the next section, because the absorption line shape is no longer Lorentzian, but it depends on the frequency spectrum of the bath correlation functions.

In order to make connection with earlier theories, we show now that the "memory" effects can be approximated in a way that leads to a Markoffian equation of motion for the spin system valid only for long times,

i.e., $t > \tau_c$, and under an additional restriction for the strength of the spin-bath interaction. We note that for $t > \tau_c$, due to condition (2.18) the upper limit in the integrals (2.16) can be put equal to infinity and thus $\mathcal{C}_0(t,\{\sigma_1\})$ and $D_0(t)$ are of order V^2. We may then use (2.14) to write for $t > \tau_c$:

$$\exp(-i\mathcal{Q}_0\tau)\sigma(t-\tau)$$

$$= \sigma(t) + i\int_0^\tau d\tau' \exp(-i\mathcal{Q}_0\tau')$$
$$\times \mathcal{Q}_1(t-\tau')f(A_0) + O(\tau_c/\tau_r), \quad (2.25)$$

where τ_r is a measure of the relaxation time and is of order V^{-2}. Substituting this into expression (2.16a) for the collision term, we find, for $t > \tau_c$ and $\tau_c/\tau_r \ll 1$, the Markoffian equation of motion

$$\frac{d}{dt}\sigma_1^{(m)}(t) = -i\mathcal{Q}_0\sigma_1^{(m)}(t) + \mathcal{C}_0^{(m)}\sigma_1^{(m)}(t)$$
$$- i\mathcal{Q}_1(t)\sigma(0) + D_0(t) + E(t), \quad (2.26)$$

where

$$\mathcal{C}_0^{(m)}\sigma_1^{(m)}(t) = -\sum_{\kappa\lambda}[v_\kappa, [j_{\kappa\lambda}{}^+(-\mathcal{Q}_0)v_\lambda, \sigma_1^{(m)}(t)]$$
$$+ [j_{\kappa\lambda}{}^-(-\mathcal{Q}_0)v_\lambda, \sigma_1^{(m)}(t)]_+], \quad (2.26a)$$

$$E(t) = \sum_\omega e^{-i\omega t}E(\omega)$$
$$= \sum_\omega e^{-i\omega t}[\mathcal{C}_0(\omega) - \mathcal{C}_0^{(m)}]\sigma_1^{(0)}(\omega), \quad (2.26b)$$

for $A_1(t)$ given by (2.19). Here

$$\sigma_1^{(0)}(\omega) = (\omega - \mathcal{Q}_0)^{-1}\mathcal{Q}_1(\omega)f(A_0) \quad (2.26c)$$

is the steady-state $\sigma_1(\omega)$ in the absence of any collisions; in the case of direct resonance, i.e., for $\omega = \omega_s - \omega_{s'}$ with $\langle s|\mathcal{Q}_1(\omega)f(A_0)|s'\rangle \neq 0$, $\sigma_1^{(0)}(\omega)$ does not exist, but $E(\omega)$ is well defined and is equal to its limiting value as ω approaches $\omega_s - \omega_{s'}$ smoothly in (2.26b), as can be verified directly.

The equation for the steady state can now be found immediately to be

$$-i\omega\sigma_1^{(m)}(\omega) = -i\mathcal{Q}_0\sigma_1^{(m)}(\omega) + \mathcal{C}_0^{(m)}\sigma_1^{(m)}(\omega)$$
$$- i\mathcal{Q}_1(\omega)\sigma(0) + D_0(\omega) + E(\omega), \quad (2.27)$$

where $\mathcal{C}_0^{(m)}$ and $E(\omega)$ are given by (2.26a) and (2.26b). We note that $\mathcal{C}_0^{(m)}$ is independent of ω, leading eventually to a Lorentzian resonance line shape, as a function of ω. This method of derivation of Eqs. (2.26) and (2.27) indicates that they are valid only if $\tau_c/\tau_r \ll 1$. More quantitative criteria are obtained by comparing the solution of (2.27) with that of (2.21). An example will be given in the next section.

For the case $\beta = 0$, the collision operator in the Markoffian approximation becomes simply

$$\mathcal{C}_0^{(m)}\sigma_1^{(m)} = -\sum_{\kappa\lambda}[v_\kappa, [j_{\kappa\lambda}(-\mathcal{Q}_0)v_\lambda, \sigma_1^{(m)}]]. \quad (2.28)$$

This should be compared with (2.24a).

3. SIMPLE APPLICATION—THE PHENOMENON OF MOTIONAL NARROWING

In order to make some of the results of the previous section more concrete and to demonstrate their new content, we study below a simple illustrative example. We consider the case of a collection of independent spins in a typical spin resonance arrangement and in a bath taken as a randomly fluctuating magnetic field $\mathbf{h}_b(t)$.

Since the spins are independent, it suffices to consider only one spin, with magnetomechanical ratio γ. If the external magnetic field consists of a static part $\mathbf{h}_0$ in the z direction and a transverse, circularly polarized one of frequency ω, $\mathbf{h}_1(t) = h_1(\mathbf{i}\cos\omega t - \mathbf{j}\sin\omega t)$, we have

$$A_0 = -\omega_0 I_z, \quad (3.1)$$

$$A_1(t) = -\tfrac{1}{2}\omega_1(I_-e^{-i\omega t} + I_+e^{i\omega t}), \quad (3.2)$$

where $\mathbf{I}$ is the spin operator with $I_\pm = I_x \pm iI_y$, $\omega_0 = \gamma h_0$ is the Larmor precession frequency, and $\omega_1 = \gamma h_1$. The interaction with the bath is

$$V = -\gamma\mathbf{h}_b(t)\cdot\mathbf{I}. \quad (3.3)$$

For simplicity we shall further assume a cylindrically symmetric environment, i.e., $j_{zz} = j_z$, $j_{xx} = j_{yy} = j_t$, $j_{xy} = j_{yz} = j_{zx} = 0$.

The steady-state magnetization,

$$\mathbf{M}(t) = \mathbf{M}(\omega)\exp(-i\omega t) + \text{c.c.},$$

of this system, linear in h_1, can be found by first constructing an equation for it with the use of (2.21) and $\mathbf{M}(\omega) = n\gamma\,\text{tr}\{\mathbf{I}\sigma_1(\omega)\}$, where n is the density of the spins. In this case of a bath characterized by a given random field, the infinite temperature expressions (2.24) for $\mathcal{C}_0(\omega)$ and $D_0(\omega)$ are applicable. Since we are interested only in the transverse components of $\mathbf{M}(\omega)$, the z component being of order h_1^2, it proves convenient to deal with the combinations $M_\pm(\omega) = M_x(\omega) \pm iM_y(\omega)$. Making use of the commutation relations for the spin operators, $\mathbf{I}\times\mathbf{I} = i\mathbf{I}$, and the invariance property of the trace under cyclic permutations, we obtain from (2.21) and (2.24b)

$$-i\omega M_\pm(\omega) = \mp i\omega_0 M_\pm(\omega) + n\gamma\,\text{tr}\{I_\pm\mathcal{C}_0(\omega)\sigma_1(\omega)\}$$
$$+ i\omega_1\tfrac{1}{2}(M_z{}^0 \pm M_z{}^0), \quad (3.4)$$

where $M_z{}^0 = n\gamma\,\text{tr}\{I_z\sigma(0)\}$ is the equilibrium value of the z component of the magnetization. From (2.24a) and (3.3) it follows after some rearrangement:

$$\text{tr}\{I_\pm\mathcal{C}_0(\omega)\sigma_1(\omega)\} = \sum_\kappa \text{tr}\{[j_\kappa(\omega + \mathcal{Q}_0)[I_\kappa, I_\pm], I_\kappa]\sigma_1(\omega)\},$$

where $\kappa = x, y, z$. Again making use of the commutation

relations for the spin operators and of the relations $\exp(i\mathcal{Q}_0\tau)I_{\pm}=\exp(\mp i\omega_0\tau)I_{\pm}$, we find

$$\mathrm{tr}\{I_{\pm}\mathcal{C}_0(\omega)\sigma_1(\omega)\}=-[j_z(\omega\mp\omega_0)+j_t(\omega)]\,\mathrm{tr}\{I_{\pm}\sigma_1(\omega)\}\,,$$

and thus (3.4) becomes

$$[-i(\omega\mp\omega_0)+j_z(\omega\mp\omega_0)+j_t(\omega)]M_{\pm}(\omega)$$
$$=i\omega_1\tfrac{1}{2}(M_z{}^0\pm M_z{}^0).\quad(3.5)$$

The imaginary parts of $j_{t,z}$ may be viewed as shifts of the Larmor precession frequency ω_0, due to interaction with the bath, whereas the real parts play the role of the inverse of relaxation times for $M_{\pm}(\omega)$. Both depend on the driving frequency ω. If written in terms of the matrix of the components M_x, M_y, Eqs. (3.5) differ from the phenomenological equations of Bloch,[1] apart from the trivial linearization of the driving term, in that the collisions with the bath are described here by ω-dependent, complex matrices with off-diagonal elements, rather than by ω-independent, real and diagonal matrices. The solution of (3.5) is immediately seen to be

$$M_+(\omega)=i\omega_1 M_z{}^0[i(\omega_0-\omega)+j_z(\omega-\omega_0)+j_t(\omega)]^{-1},\quad(3.6a)$$

$$M_-(\omega)=0.\quad(3.6b)$$

It is clear that the resonance line, when measured as a function of ω, is no longer a simple Lorentzian, but its shape depends on the frequency spectrum of the bath correlation functions.

A classical, macroscopic derivation of Eq. (3.5) is outlined in the Appendix, under the assumption that it is permissible to ignore the statistical correlation between the bath and the spin system at a certain stage of the calculation.

It is of importance to point out that the steady state (3.6) describes the phenomenon of "motional" narrowing. A particularly simple example of this phenomenon is obtained by considering the previous system in the special case where $\mathbf{h}_b(t)$ is a magnetic field in the z direction that jumps randomly between two values $\pm\delta/\gamma$ with a probability per unit time $(2\tau_c)^{-1}$. The correlation functions for the bath are then $c_t(\tau)=0$ and[21]

$$c_z(\tau)=\gamma^2\langle h_b(t+\tau)h_b(t)\rangle=\delta^2 e^{-|\tau|/\tau_c},\quad(3.7)$$

and according to (2.22a)

$$j_z(\omega)=\delta^2(\tau_c{}^{-1}+i\omega)(\tau_c{}^{-2}+\omega^2)^{-1}.\quad(3.8)$$

Now the mean power absorption P is given by the time average of $-\mathbf{M}(t)\cdot d\mathbf{h}_1(t)/dt$. For the steady state we have, according to (3.6a) and (3.8),

$$P(\omega)=\omega h_1\,\mathrm{Im}\{M_+(\omega)\}$$
$$\propto\frac{\delta^2\tau_c{}^{-1}}{(\omega-\omega_0)^4+\delta^4+(\tau_c{}^{-2}-2\delta^2)(\omega-\omega_0)^2},\quad(3.9)$$

where Im means imaginary part. For very slow variation of the field $h_b(t)$, i.e., for $\tau_c\delta\gg1$, $P(\omega)$ has two sharp

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[21] See, for example, C. P. Slichter, Ref. 3, Appendix C.

maxima at $\omega=\omega_0\pm\delta$. For very rapid variations of $h_b(t)$, i.e., for $\tau_c\delta\ll1$, the absorption curve has a sharp peak only at the center frequency $\omega=\omega_0$. This elementary example of "motional" narrowing has been considered before and many authors[22-26] have derived (3.9) on the basis of different theories.

A similar calculation gives for the steady state in the Markoffian approximation for the system in the cylindrically symmetric environment, according to (2.27) and (2.28),

$$M_+{}^{(m)}(\omega)=[i\omega_1 M_z{}^0+E(\omega)]$$
$$\times[i(\omega_0-\omega)+j_z(0)+j_t(\omega_0)]^{-1},\quad(3.10)$$

where in this case

$$E(\omega)=[j_z(\omega-\omega_0)-j_z(0)+j_t(\omega)-j_t(\omega_0)]$$
$$\times(\omega-\omega_0)^{-1}\omega_1 M_z{}^0,\quad(3.10a)$$

with the understanding that for $\omega=\omega_0$, $E(\omega)$ assumes the limiting value of (3.10a) as ω approaches ω_0 smoothly, i.e., it equals $[j_z{}'(0)+j_t{}'(\omega_0)]\omega_1 M_z{}^0$, where $j'(\omega)=dj(\omega)/d\omega$. We may compare (3.10) with (3.6a) directly, in order to see for this simple case under what conditions the memory approximation is precisely valid. An analysis of these two expressions yields the following result: for $|\omega-\omega_0|\gg\tau_r{}^{-1}$, i.e., in the wings of the absorption line, the two expressions are identical and thus the memory approximation is valid; for $|\omega-\omega_0|\lesssim\tau_r{}^{-1}$, i.e., in the central region of the absorption line, the two expressions are *not* the same, but $|M_+{}^{(m)}(\omega)-M_+(\omega)|\ll|M_+(\omega)|$ if $\tau_c/\tau_r\ll1$. This is seen by noting that in this region $j_z(\omega-\omega_0)-j_z(0)\cong(\omega-\omega_0)j_z{}'(0)$ and $j_z{}'(0)\cong\tau_c j_z(0)=O(\tau_c/\tau_r)$, and similarly for $j_t(\omega)$. Thus, in the region of interest the memory approximation is *not* valid for sufficiently long correlation times, i.e., for $\tau_c\gtrsim\tau_r$. Thus, the full description of the phenomenon of "motional" narrowing as exemplified by the previous simple system cannot be given by an equation of motion for the spin system which has been obtained by the use of the memory approximation.

The case of finite temperature is more involved. For the particular case of spin $\tfrac{1}{2}$ or arbitrary spin but high temperatures, however, an equation of motion for the magnetization alone can be given, which also describes the phenomena discussed in this section. We shall not exhibit this here, as we shall discuss this system in Sec. 6 for the case of an arbitrarily strong driving field.

4. GENERAL DISCUSSION OF THE LINEAR RESPONSE. HIGHER APPROXIMATIONS

In Sec. 2 we paid particular attention to the case where the effects of the spin-bath interaction are taken into account to the lowest order, and discussed the

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[24] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **21**, 279 (1953).
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[26] J. H. van Vleck, Ned. Tijdschr. Natuurk. **27**, 1 (1961).

steady state on the basis of the assumed existence of a bath correlation time τ_c. We now consider the general equation for $\sigma_1(t)$, (2.13), valid for arbitrary strength of the spin-bath interaction.

First of all it should be noted that the solution of Eq. (2.13) for $\sigma(t)$ is a Hermitian operator, as it should. This is proved by noting that $\sigma_1^\dagger(t)$, due to the structure of the operators $\mathcal{C}$ and D, satisfies the same equation as $\sigma_1(t)$ and the same initial condition, $\sigma_1^\dagger(0)=0$. Also the property $\mathrm{tr}\sigma_1(t)=0$ is satisfied, since (2.13) gives $d\,\mathrm{tr}\sigma_1(t)/dt=0$, on account of the commutator form of the terms on the right-hand side and $\mathrm{tr}\sigma_1(0)=0$.

A complete solution of (2.13) can be obtained by the method of Fourier transforms. Introducing

$$\bar{\sigma}_1(z)=\int_0^\infty dt\sigma_1(t)e^{izt}, \qquad (4.1)$$

with z in the upper half of the complex z plane, and similarly for $\mathcal{C}_1(z)$ and $D(z)$, we obtain from (2.13) (after the first-order renormalization) and the initial condition $\sigma_1(0)=0$ the following equation for $\bar{\sigma}_1(z)$:

$$-iz\bar{\sigma}_1(z)=-i\mathcal{C}_0\bar{\sigma}_1(z)+\mathcal{C}(z)\bar{\sigma}_1(z)$$
$$-i\mathcal{C}_1(z)\sigma(0)+D(z), \quad (4.2)$$

with $\bar{\sigma}_1(z)$ analytic in the upper half-plane above a line parallel to the real axis, since $\sigma_1(t)=0$ for $t\leq0$. Here, use has been made of the convolution theorem in the evaluation of both $\mathcal{C}(z)$ and $D(z)$. We find

$$\mathcal{C}(z)=i\,\mathrm{tr}_b\mathcal{V}\mathcal{R}(z)\mathcal{V}f(B), \qquad (4.2a)$$

$$D(z)=i\,\mathrm{tr}_b\mathcal{V}\mathcal{R}(z)\mathcal{P}\mathcal{C}_1(z)f(H), \qquad (4.2b)$$

where

$$\mathcal{R}(z)=i\int_0^\infty d\tau S(\tau)e^{iz\tau}=(\mathcal{3C}_0+\mathcal{P}\mathcal{V}-z)^{-1} \qquad (4.3)$$

is analogous to the resolvent operator, corresponding to the operator $\mathcal{3C}_0+\mathcal{P}\mathcal{V}$. The solution of (4.2) can be written formally as

$$\bar{\sigma}_1(z)=\{i(z-\mathcal{C}_0)+\mathcal{C}(z)\}^{-1}\{i\mathcal{C}_1(z)\sigma(0)-D(z)\}, \quad (4.4)$$

for $\mathrm{Im}z\geq\epsilon>0$. Since now

$$\sigma_1(t)=\frac{1}{2\pi}\int_{-\infty+i\epsilon}^{+\infty+i\epsilon} dz\bar{\sigma}_1(z)e^{-izt}, \qquad (4.5)$$

the time evolution of $\sigma_1(t)$ for $t>0$ can be obtained by analytically continuing $\bar{\sigma}_1(z)$ in the appropriately cut z plane and deforming the contour in (4.5) in the lower half-plane, so that the techniques of complex integration may be used. Such a procedure will yield not only the steady state, if it exists, but also the approach to it. It entails, however, the knowledge of all the singularities of $\bar{\sigma}_1(z)$ in the plane below the line $-\infty+i\epsilon$, $+\infty+i\epsilon$. Such a general study is beyond the scope of this paper.

It should be noted that no assumption has been made so far about the nature or the state of the subsystem we have been referring to as bath. In particular, its "size" relative to the spin system can be arbitrary and its state can deviate from that of thermodynamic equilibrium. It is clear that a similar theory can be given that treats the two subsystems, spin and bath, in a symmetrical way, by adopting a splitting of $\rho_1(t)$ different from that given by (2.7).

If the driving interaction is of the form (2.19), i.e.,

$$A_1(t)=\sum_\omega e^{-i\omega t}A_1(\omega),$$

then

$$\mathcal{C}_1(z)=i\sum_\omega \frac{1}{z-\omega}\mathcal{C}_1(\omega). \qquad (4.6)$$

It is then clear from (4.6) and (4.2b) that $\mathcal{C}_1(z)$ and $D(z)$ have poles on the real axis at $z=\omega$. $D(z)$ has additional singularities due to $\mathcal{R}(z)$. The solution $\bar{\sigma}_1(z)$, Eq. (4.4), will in general have simple poles (or pseudo-poles) at $z=\omega$ plus additional singularities arising from $D(z)$ and $[i(z-\mathcal{C}_0)+\mathcal{C}(z)]^{-1}$. If, however, we assume that a steady state of the form $\sigma_1^{(s)}(t)=\sum_\omega \sigma_1(\omega)e^{-i\omega t}$ exists for very long times, it is expected that it should arise in general from the contribution of the poles of $\bar{\sigma}_1(z)$ at $z=\omega$, the contribution of all other singularities going to zero as $t\to\infty$. It is then found that $\sigma_1(\omega)=\lim\bar{\sigma}_1(\omega+i\epsilon)$ for $\epsilon\to0^+$, as given by (4.2). In this limit $\mathcal{R}(z)$ becomes $i\theta(\omega-\mathcal{3C}_0-\mathcal{P}\mathcal{V})$, where $\theta(x)$ is given by (2.23b).

Discussion of the necessary and sufficient conditions for the existence of a steady state for long times is beyond the scope of this paper. One obvious necessary condition is that the bath have a continuous energy spectrum.[27]

In the lowest Born approximation for the spin-bath interaction, which obtains by dropping $\mathcal{P}\mathcal{V}$ in the argument of θ, Eq. (4.2) for the steady-state component $\sigma_1(\omega)$ becomes identical to (2.21) with

$$\mathcal{C}_0(\omega)=-\mathrm{tr}_b\mathcal{V}\theta(\omega-\mathcal{3C}_0)\mathcal{V}f(B), \qquad (4.7a)$$

$$D_0(\omega)=-\mathrm{tr}_b\mathcal{V}\theta(\omega-\mathcal{3C}_0)\mathcal{C}_1(\omega)f^{(1)}. \qquad (4.7b)$$

In order to prove the equivalence of these expressions for $\mathcal{C}_0(\omega)$ and $D_0(\omega)$ to Eqs. (2.21a) and (2.21b) in the case of a V given by (2.15), it suffices to use the integral representation of $\theta(x)$, (2.23b). This approximation amounts to keeping effectively the bath in thermodynamic equilibrium corresponding to its unperturbed Hamiltonian B.

The expressions (4.2a) and (4.2b) for $\mathcal{C}(z)$ and $D(z)$ are valid for arbitrary strength of the spin-bath interaction and provide a convenient basis for other approximations. Clearly, these are determined by the approximations to the resolvent operator $\mathcal{R}(z)$. Such an approximation scheme for small V will yield a quantitative criterion for the validity of the lowest Born

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[27] For a detailed mathematical example see R. Zwanzig, Ref. 18.

approximation of the collision operator, which in general is expected to be different from $\tau_c/\tau_r \ll 1$.

The power series in V for $\mathfrak{R}(z)$ is easily obtained by iteration of the following identity

$$\mathfrak{R}(z) = \mathfrak{R}_0(z) - \mathfrak{R}_0(z)\mathcal{P}\mathcal{V}\mathfrak{R}(z), \qquad (4.8)$$

where $\mathfrak{R}_0(z) = (\mathfrak{K}_0 - z)^{-1}$. This is

$$\mathfrak{R}(z) = \mathfrak{R}_0(z) \sum_{l=0}^{\infty} (-1)^l [\mathcal{P}\mathcal{V}\mathfrak{R}_0(z)]^l. \qquad (4.9)$$

Such an expansion, however, produces in general divergences in the scattering and driving operators (4.2). These divergences can be eliminated for a large class of interactions by a different expansion of the resolvent operator $\mathfrak{R}(z)$, which is a generalization of the technique used by Van Hove[13] in the problem of the derivation of the master equation for approach to equilibrium. We have studied such an expansion for the particular case of spin-phonon interaction and shall report it in another publication. Fano[28] has recently discussed the problem of pressure broadening along similar lines.

5. GENERAL EQUATION OF MOTION FOR THE SPIN SYSTEM

We consider now the case of an arbitrary spin Hamiltonian, thus generalizing the results of the previous sections to include the description of the phenomena of resonance saturation and relaxation towards thermodynamic equilibrium.

The equation of motion for the combined system is again (2.2). If we let $A(t) = A_0 + A_1(t)$ be the total spin Hamiltonian and $H_0(t) = A(t) + B$, we may write $H_T(t) = H_0(t) + V$. As in Sec. 2, we seek to find an equation of motion for the spin density operator $\sigma(t) = \mathrm{tr}_b \rho(t)$, by transforming (2.2) into a system of coupled equations for $\sigma(t)$ and $\eta(t) = \mathcal{P}\rho(t)$, where $\mathcal{P}$ is again given by (2.8). We thus have

$$i(d/dt)\sigma(t) = [\mathfrak{A}(t) + \mathrm{tr}_b\mathcal{V}f(B)]\sigma(t) + \mathrm{tr}_b\mathcal{V}\eta(t), \qquad (5.1)$$

$$i(d/dt)\eta(t) = [\mathfrak{K}_0(t) + \mathcal{P}\mathcal{V}]\eta(t) + \mathcal{P}\mathcal{V}f(B)\sigma(t). \qquad (5.2)$$

The solution of Eq. (5.2) for $\eta(t)$ can be given in terms of the solution of the homogeneous equation, which is now denoted by

$$\mathcal{S}(t,t') = \left(\exp\frac{1}{i}\int_{t'}^{t} d\tau[\mathfrak{K}_0(\tau) + \mathcal{P}\mathcal{V}]\right)_+, \qquad (5.3)$$

$(\ )_+$ designating positive time ordering. We thus find

$$\eta(t) = \mathcal{S}(t,0)\mathcal{P}\rho(0) - i\int_0^t d\tau\mathcal{S}(t,\tau)\mathcal{P}\mathcal{V}f(B)\sigma(\tau). \qquad (5.4)$$

Substitution of this expression for $\eta(t)$ into (5.1) gives the general equation of motion for the spin density

[28] U. Fano, Phys. Rev. **131**, 259 (1963).

operator $\sigma(t)$

$$\frac{d}{dt}\sigma(t) = -i\mathfrak{A}(t)\sigma(t) + \mathcal{C}(t,\{\sigma\}) + F(t), \qquad (5.5)$$

where

$$\mathcal{C}(t,\{\sigma\}) = -\mathrm{tr}_b\mathcal{V}\int_0^t d\tau\mathcal{S}(t,\tau)\mathcal{V}f(B)\sigma(\tau), \qquad (5.5a)$$

$$F(t) = -i\,\mathrm{tr}_b\mathcal{V}\mathcal{S}(t,0)\mathcal{P}\rho(0). \qquad (5.5b)$$

In expression (5.5a) for the generalized collision operator, we have already carried out the first order in V renormalization mentioned earlier. The inhomogeneous term $F(t)$ depends on the initial state of the total system and it vanishes if $\mathcal{P}\rho(0) = 0$. Equation (5.5) is clearly valid for all times and for arbitrary V and $A_1(t)$.

It can be easily proved that the solution of (5.5) is indeed a Hermitian operator, as it should, and that it maintains its normalization in time, i.e., $\mathrm{tr}\sigma(t) = 1$. Also, one can verify that (2.13) for the linear response can be obtained from (5.5) by linearizing it and $\mathcal{S}(t,\tau)$ with respect to A_1. The direct procedure of Sec. 2, however, is simpler.

An alternate expression for $\mathcal{C}$, more convenient for perturbative expansions in powers of V, is obtained by writing

$$\mathcal{S}(t,\tau) = \mathcal{S}_0(t,0)\mathcal{S}'(t,\tau)\mathcal{S}_0^{-1}(\tau,0), \qquad (5.6)$$

where

$$\mathcal{S}_0(t,0) = \mathcal{S}_b(t)\mathcal{S}_s(t,0) = \exp(-i\mathfrak{B}t)$$

$$\times \left(\exp\frac{1}{i}\int_0^t d\tau\mathfrak{A}(\tau)\right)_+, \qquad (5.6a)$$

$$\mathcal{S}'(t,t') = \left(\exp\frac{1}{i}\int_{t'}^{t} d\tau\mathcal{V}'(\tau)\right)_+, \qquad (5.6b)$$

with $\mathcal{V}'(t) = \mathcal{S}_0^{-1}(t,0)\mathcal{V}\mathcal{S}_0(t,0)$ being the operator $\mathcal{V}$ in the interaction representation. We thus have

$$\mathcal{C}(t,\{\sigma\}) = -\mathrm{tr}_b\mathcal{V}(t)\mathcal{S}_s(t)$$

$$\times \int_0^t d\tau\mathcal{S}'(t,\tau)\mathcal{S}_s^{-1}(\tau)\mathcal{V}(\tau)f(B)\sigma(\tau), \qquad (5.7)$$

where $V(t) = \exp(i\mathfrak{B}t)V$ is the interaction operator in the Heisenberg representation for the bath system alone and $\mathcal{S}_s(t) = \mathcal{S}_s(t,0)$. Equation (5.7) is identical to the collision operator of Ref. 14.

In the lowest Born approximation for the interaction with the bath, the collision operator is seen from either (5.5a) or (5.7) to be

$$\mathcal{C}_0(t,\{\sigma\}) = -\mathrm{tr}_b\mathcal{V}(t)\int_0^t d\tau\mathcal{S}_s(t,\tau)\mathcal{V}(\tau)f(B)\sigma(\tau), \qquad (5.8)$$

where $\mathcal{S}_s(t,\tau)$ is given by (5.6a). In terms of the bath

correlation functions (2.17), we may express (5.8) in the form

$$\mathcal{C}_0(t,\{\sigma\}) = -\sum_{\kappa\lambda} \int_0^t d\tau \{c_{\kappa\lambda}(\tau)[v_\kappa, \mathcal{S}_s(t, t-\tau)v_\lambda\sigma(t-\tau)]$$

$$- c_{\lambda\kappa}(-\tau)[v_\kappa, \mathcal{S}_s(t, t-\tau)\sigma(t-\tau)v_\lambda]\}. \quad (5.9)$$

We shall use this equation in the following section. An analogous expression can be given for $F_0(t)$, if we take the initial condition $\rho(0)$ of the total system to be given, as in Sec. 2, by $f(A_0+B+V)$. For $t>\tau_c$, where τ_c is the bath correlation time defined by (2.18), the upper limit in the integral of (5.9) can be replaced by ∞ and the inhomogeneous term $F_0(t)$ vanishes, on account of the property (2.18) of the correlation functions. Thus, in the lowest Born approximation and for $t>\tau_c$, the equation of motion for the spin system is

$$\frac{d}{dt}\sigma(t) = -i\mathcal{C}(t)\sigma(t) + \mathcal{C}_0(t,\{\sigma\}), \quad (5.10)$$

where $\mathcal{C}_0$ is given by (5.9) with the upper limit of the integral taken as ∞. We note that (5.10) shows "memory."

We may approximate the "memory" effects of the collision operator (5.9) and obtain a Markoffian equation of motion for the spin system, valid only for long times, i.e., $t>\tau_c$, and for $\tau_c/\tau_r\ll1$, as in Sec. 2. From (5.10) we note that for $t>\tau_c$

$$\sigma(\tau) = \mathcal{S}_s^{-1}(t,\tau)\sigma(t) + O(\tau_c/\tau_r), \quad (5.11)$$

where τ_r is a measure of the relaxation time and of order V^{-2}. Substituting this into (5.8) or (5.9), we have for $t>\tau_c$ and $\tau_c/\tau_r\ll1$

$$\frac{d}{dt}\sigma^{(m)}(t) = -i\mathcal{C}(t)\sigma^{(m)}(t) + \mathcal{C}_0^{(m)}(t)\sigma^{(m)}(t), \quad (5.12)$$

where

$$\mathcal{C}_0^{(m)}(t)\sigma(t) = -\operatorname{tr}_b \mathcal{U}(t)\int_0^\infty d\tau\{\mathcal{S}_s(t,\tau)\mathcal{U}(\tau)\}f(B)\sigma(t)$$

$$= -\sum_{\kappa\lambda}\int_0^\infty d\tau\{c_{\kappa\lambda}(\tau)[v_\kappa, v_\lambda(t, t-\tau)\sigma(t)]$$

$$- c_{\lambda\kappa}(-\tau)[v_\kappa, \sigma(t)v_\lambda(t, t-\tau)]\}, \quad (5.12a)$$

with $v_\lambda(t, t-\tau) = \mathcal{S}_s(t, t-\tau)v_\lambda$. Equation (5.12) is identical to the most general equation for the spin density operator derived by Bloch[7] and others.[8-11] It has been obtained here as a special case and without any statistical assumptions.

The description of the approach to thermal equilibrium of a spin system is included in the previous equations. For such a case, the spin Hamiltonian A is time-independent and the equation of motion for the

spin is again given in general by (5.5) where now

$$\mathcal{C}(t,\{\sigma\}) = -\operatorname{tr}_b \mathcal{U}\int_0^t d\tau \exp[-i(\mathcal{K}_0+\mathcal{P}\mathcal{U})\tau]$$

$$\times \mathcal{U}f(B)\sigma(t-\tau), \quad (5.13a)$$

$$F(t) = -i\operatorname{tr}_b\mathcal{U}\exp[-i(\mathcal{K}_0+\mathcal{P}\mathcal{U})t]\mathcal{P}\rho(0). \quad (5.13b)$$

It should be noted that the time dependence of the collision operator is of the same form as in the preceding section, and thus the techniques discussed there apply equally well to this case. We shall not discuss this problem here any further. A detailed discussion of this problem has been given recently by Sher and Primakoff[29] from a different point of view.

6. SIMPLE APPLICATION—THE PHENOMENON OF SPIN RESONANCE SATURATION

The very general results of the previous section are now illustrated by applying them to the simple system of a collection of independent spins in a typical spin resonance arrangement as in Sec. 3. The difference here is that we consider the driving field to be of arbitrary strength and the temperature to be finite.

The Hamiltonian for the spin system is $A(t)=A_0+A_1(t)$, where A_0 and $A_1(t)$ are given by (3.1) and (3.2). The interaction with the bath is again taken to be given by (3.3), with the bath constituting, as before a cylindrically symmetric environment, i.e., $c_{\kappa\lambda}(\tau)=c_\kappa(\tau)\delta_{-\kappa\lambda}=c_{-\kappa}(\tau)\delta_{-\kappa\lambda}=\gamma^2\langle h_b^\kappa(\tau)h_b^{-\kappa}\rangle\delta_{-\kappa\lambda}$, where $\kappa,\lambda=-1,0,1,h_b^{\pm1}=(\frac{1}{2})(h_{bx}\pm ih_{by})$ and $h_b^0=h_{bz}$.

In order to find the steady state, it is convenient to work in a frame of reference rotating around the z axis with angular frequency ω, so that its x axis lies along the driving magnetic field $\mathbf{h}_1$, because in this frame the total magnetic field is constant in time. In the rotating frame the spin density operator is

$$\sigma^r(t) = \exp(-i\omega I_z t)\sigma(t)\exp(i\omega I_z t), \quad (6.1)$$

and according to (5.10) its equation of motion for $t>\tau_c$ is found to be, in the lowest Born approximation,

$$\frac{d}{dt}\sigma^r(t) = -i\mathcal{C}^r\sigma^r(t) + \mathcal{C}_0^r\{\sigma^r\}. \quad (6.2)$$

From (6.1), (3.1) and (3.2) it is clear that

$$A^r = -\omega_1 I_x - \Delta I_z = -\mathbf{I}\cdot\boldsymbol{\omega}_e, \quad (6.3)$$

where $\Delta\equiv\omega_0-\omega$ and $\boldsymbol{\omega}_e=(\omega_1,0,\Delta)$ is the effective magnetic field (multiplied by γ) in the rotating frame. $\mathcal{C}_0^r$ is similarly obtained from (5.9) and (5.6a). Since

$$U(t, t-\tau) \equiv \left(\exp\frac{1}{i}\int_{t-\tau}^t d\tau' A(\tau')\right)_+$$

$$= e^{i\omega I_z t}\exp(-iA^r\tau)e^{-i\omega I_z(t-\tau)}, \quad (6.4)$$

[29] A. Sher and H. Primakoff, Phys. Rev. 119, 178 (1960); 130, 1267 (1963).

and $S_s(t,\tau)\sigma = U(t,\tau)\sigma U^{-1}(t,\tau)$, it is found that, because of the cylindrical symmetry of the environment,

$$\mathcal{C}_0^r\{\sigma^r\} = -\sum_\kappa \int_0^\infty d\tau e^{i\kappa\omega\tau}$$

$$\times \{c_\kappa^+(\tau)[I_{-\kappa}, \exp(-i\mathcal{Q}^r\tau)[I_\kappa, \sigma^r(t-\tau)]]$$

$$+c_\kappa^-(\tau)[I_{-\kappa}, \exp(-i\mathcal{Q}^r\tau)[I_\kappa, \sigma^r(t-\tau)]_+]\},$$
(6.5)

where $I_0 = I_z$, $I_{\pm 1} = I_x \pm iI_y$. If we now assume that a steady state exists and that in the rotating frame it takes the form $\sigma^r(t) \to \sigma^r(\omega)$ as $t \to \infty$, (6.2) and (6.5) give for the steady state the equation

$$-i\mathcal{Q}^r\sigma^r(\omega) + \mathcal{C}_0^r(\omega)\sigma^r(\omega) = 0,$$
(6.6)

where, because of the property (2.18) of the bath correlation functions as argued in Sec. 2,

$$\mathcal{C}_0^r(\omega)\sigma^r(\omega) = -\sum_\kappa [I_{-\kappa}, j_\kappa^+(\kappa\omega - \mathcal{Q}^r)[I_\kappa, \sigma^r(\omega)]$$

$$+j_\kappa^-(\kappa\omega - \mathcal{Q}^r)[I_\kappa, \sigma^r(\omega)]_+],$$
(6.7)

where $j^\pm$ are defined by (2.22a).

As in Sec. 3, it is convenient to use (6.6) and (6.7) to construct an equation for the steady-state magnetization in the rotating frame, $\mathbf{M}^r(\omega) = n\gamma \operatorname{tr}\{\mathbf{I}\sigma^r(\omega)\}$, where n is the density of the spins. The first term of (6.6) gives

$$(-i)n\gamma \operatorname{tr}\{\mathbf{I}\mathcal{Q}^r\sigma^r(\omega)\} = \mathbf{M}^r(\omega) \times \boldsymbol{\omega}_e.$$
(6.8)

The second term of (6.6) yields, on account of the invariance property of the trace under cyclic permutations,

$$\operatorname{tr}\{\mathbf{I}\mathcal{C}_0^r(\omega)\sigma^r(\omega)\}$$

$$= \sum_\kappa \operatorname{tr}\{[j_\kappa^+(\kappa\omega + \mathcal{Q}^r)[I_{-\kappa}, \mathbf{I}], I_\kappa]\sigma^r(\omega)$$

$$+[j_\kappa^-(\kappa\omega + \mathcal{Q}^r)[I_{-\kappa}, \mathbf{I}], I_\kappa]_+\sigma^r(\omega)\}.$$
(6.9)

The commutator $[I_{-\kappa}, \mathbf{I}]$ can always be expressed as a linear combination of the spin components themselves, on account of the commutation relations $\mathbf{I} \times \mathbf{I} = i\mathbf{I}$. It can also be proved[30] that $\exp(i\mathcal{Q}^r\tau)I_\mu$ can again be expressed as a linear combination of the spin components, and thus one finds

$$j_\kappa^\pm(\kappa\omega + \mathcal{Q}^r)I_\mu = \sum_{\nu\lambda} \alpha_{\mu\nu}(-\theta)\alpha_{\nu\lambda}(\theta) j_\kappa^\pm(\kappa\omega - \nu\omega_e)I_\lambda,$$

where μ, ν, $\lambda = -1$, 0, 1 and $\alpha_{\mu\nu}(\theta)$ are as follows: $2\alpha_{11} - 1 = 2\alpha_{-1-1} - 1 = 2\alpha_{1-1} + 1 = 2\alpha_{-11} + 1 = \alpha_{00} = \cos\theta = \Delta/\omega_e$ and $2\alpha_{0-1} = 2\alpha_{01} = -\alpha_{-10} = -\alpha_{10} = \sin\theta = \omega_1/\omega_e$, where θ is the angle the effective field $\boldsymbol{\omega}_e$ makes with the z axis. Thus, the first term of (6.9) can be expressed as a linear combination of the components of the magnetization $\mathbf{M}^r(\omega)$, on account of the commutation rules for the spin operators. For the second term, however, this is not

[30] See, for example, Ref. 7, p. 1217.

true, since the anticommutator $[I_\lambda, I_\kappa]_+$ cannot be transformed in the same way. For spin $I = \frac{1}{2}$ the anticommutator is a pure number, and thus the second term of (6.9) becomes for all temperatures an inhomogeneous term in the equation for the steady-state magnetization. For arbitrary spin and high temperatures, i.e., $\beta \times (\text{spin energy}) \ll 1$, again the latter term becomes a constant. Since to the lowest order in β, $j_\kappa^+(\omega) = j_\kappa(\omega)$ and $j_\kappa^-(\omega) = j_\kappa(\omega)(\beta\omega/2)$, where $j_\kappa(\omega)$ is the one-sided Fourier transform of $c_\kappa(\tau)$, we find for this case,[31] to which we shall restrict our attention from now on,

$$n\gamma \operatorname{tr}\{I_\mu\mathcal{C}_0^r(\omega)\sigma^r(\omega)\}$$

$$= \sum_{\kappa\lambda\nu} (-1)^{\mu+\kappa}(\kappa-\mu)\alpha_{\mu+\kappa,\nu}(-\theta)\alpha_{\nu\lambda}(\theta) j_\kappa(-\nu\omega_e - \kappa\omega)$$

$$\times \{(-1)^{\lambda-\kappa}(\lambda+\kappa)M_{\lambda-\kappa}^r(\omega)$$

$$+ (\chi_0/\gamma)(-\nu\omega_e - \kappa\omega)\delta_{\lambda\kappa}\epsilon_\kappa\},$$
(6.10)

where $\epsilon_{-1} = \epsilon_1 = 2\epsilon_0 = 2$ and $\chi_0 = n\gamma^2\beta I(I+1)/3$ is the equilibrium susceptibility of the spin system. Combining (6.8) and (6.10), we find for $\mathbf{M}^r(\omega)$ the system of equations

$$\begin{bmatrix} T_x^{-1} & -(\Delta+N_0) & T_{xz}^{-1} \\ \Delta+N_0 & T_y^{-1} & -(\omega_1+N_1) \\ T_{xz}^{-1} & \omega_1+N_1 & T_z^{-1} \end{bmatrix} \begin{bmatrix} M_x^r \\ M_y^r \\ M_z^r \end{bmatrix}$$

$$= \left(\frac{\chi_0}{\gamma}\right) \begin{bmatrix} T_{xz}^{-1}\omega + D_x\omega_1 \\ -N_1\omega + D_y\omega_1 \\ T_z^{-1}\omega + D_z\omega_e \end{bmatrix},$$
(6.11)

where the four relaxation times are given by

$$T_x^{-1} = j_{z}'(\omega_e) + c^2 j_{t}'(\omega) + \frac{s^2}{2} j_{t}'(\omega-\omega_e)$$

$$+ \frac{s^2}{2} j_{t}'(\omega+\omega_e),$$
(6.11a)

$$T_y^{-1} = T_x^{-1} + s^2[j_z'(0) - j_z'(\omega_e)],$$
(6.11b)

$$T_z^{-1} = s^2 j_{t}'(\omega) + \frac{(c-1)^2}{2} j_{t}'(\omega-\omega_e)$$

$$+ \frac{(c+1)^2}{2} j_{t}'(\omega+\omega_e),$$
(6.11c)

$$T_{xz}^{-1} = s\left[-cj_{t}'(\omega) + \frac{(c-1)}{2} j_{t}'(\omega-\omega_e)\right.$$

$$\left. + \frac{(c+1)}{2} j_{t}'(\omega+\omega_e)\right],$$
(6.11d)

[31] Although these statements are not quite correct for the imaginary parts of $j^\pm$, we shall accept them as approximately valid, in view of the qualitative nature of our considerations.

the two frequency shifts by

$$N_0 = -cj_z''(\omega_e) + c^2 j_t''(\omega) + \frac{s^2}{2} j_t''(\omega-\omega_e)$$

$$+ \frac{s^2}{2} j_t''(\omega+\omega_e), \quad (6.11\text{e})$$

$$N_1 = s\left[cj_t''(\omega) - \frac{(c-1)}{2} j_t''(\omega-\omega_e) \right.$$
$$\left. - \frac{(c+1)}{2} j_t''(\omega+\omega_e) \right], \quad (6.11\text{f})$$

and

$$D_x = j_z'(\omega_e) - \frac{(c-1)}{2} j_t'(\omega-\omega_e)$$
$$+ \frac{(c+1)}{2} j_t'(\omega+\omega_e), \quad (6.11\text{g})$$

$$D_y = -cj_z''(\omega_e) - \frac{(c-1)}{2} j_t''(\omega-\omega_e)$$
$$+ \frac{(c+1)}{2} j_t''(\omega+\omega_e), \quad (6.11\text{h})$$

$$D_z = -\frac{(c-1)^2}{2} j_t'(\omega-\omega_e) + \frac{(c+1)^2}{2} j_t'(\omega+\omega_e). \quad (6.11\text{i})$$

In these expressions $s \equiv \sin\theta = \omega_1/\omega_e$, $c \equiv \cos\theta = \Delta/\omega_e$ and $j'(\omega)$, $j''(\omega)$ are, respectively, the real and imaginary parts of $j(\omega)$. Equations (6.11) represent the generalization of the original phenomenological equations of Bloch for the steady state referred to a coordinate system rotating with the driving field. It should be noted that the relaxation times and the shifts depend on all three frequency parameters of the system ω, ω_1, ω_0. The detailed character of the absorption line is thus determined by the ω dependence of the relaxation times *and* the shifts.

The system under consideration here has been examined by Bloch[7] and Tomita.[10] Our analysis differs from theirs primarily in that we have allowed for memory effects and thus equations (6.11) are not restricted to the case of a rapidly fluctuating bath, i.e., roughly speaking $\tau_c/T_{x,y,z}$ need not be $\ll 1$. In particular, however, (6.11) shows that there are only four independent relaxation times and two energy shifts, in contrast to five and four, respectively, according to the memory approximation.[7,10]

The variety of facts contained in the generalized phenomenological equations (6.11) is indicated briefly below, by consideration of some special cases:

(a) *Static transverse field.* For $\omega=0$ the rotating frame is identical to the fixed frame and the total magnetic field $\omega_e/\gamma = \mathbf{h}_0 + \mathbf{h}_1$ is along a z' axis inclined at an angle θ to the z direction. The solution of (6.11) can then be

verified to be in a $x'y'z'$ coordinate system

$$M_{x'} = M_x \cos\theta - M_z \sin\theta = 0, \quad M_{y'} = M_y = 0,$$
$$M_{z'} = M_x \sin\theta + M_z \cos\theta = \chi_0(\omega_e/\gamma) = \chi_0(h_0^2+h_1^2)^{1/2},$$

i.e., the steady state describes the thermal equilibrium magnetization corresponding to the total magnetic field ω_e/γ, as it should.

(b) *No transverse field.* For $\omega_1=0$ it is clear from (a) that the steady state is just the thermal equilibrium situation corresponding to a magnetic field $\mathbf{h}_0$. This can also be established from (6.11) for arbitrary ω.

(c) *Very small transverse field.* For sufficiently small ω_1 the linear response can be obtained by noting that we may put $s=0$, $c=1$. It is then easily checked that (6.11) gives all the results of Sec. 3 and their generalization to finite temperatures. It also yields the exact conditions for the applicability of the linear description.

(d) *Small transverse field near resonance.* If $\omega_1 \ll \omega_0$, and $\Delta \approx \omega_1 \ll \omega_0$, we have $\omega_e \approx \omega_1 \ll \omega \approx \omega_0$, a situation frequently encountered in practice. The parameters of (6.11) are then considerably simplified, since we can put $j_t(\omega \pm \omega_e) \approx j_t(\omega)$, although $\omega_1^2 T_y T_z$ and $\omega_1 \tau_c$ could be large. It is then found that

$$T_x^{-1} = j_z'(\omega_e) + j_t'(\omega), \quad T_y^{-1} = T_x^{-1} + s^2[j_z'(0) - j_z'(\omega_e)] \quad (6.12\text{a})$$

$$T_z^{-1} = 2j_t'(\omega), \qquad N_0 = -cj_z''(\omega_e) + j_t''(\omega) \quad (6.12\text{b})$$

$$D_y = D_x = T_x^{-1}, N_0, \qquad D_z = cT_z^{-1} \quad (6.12\text{c})$$

and all the others vanish. Equation (6.11) becomes then simply

$$\mathbf{M}^r \times \omega_e + \mathbf{R} \cdot (\mathbf{M}^r - \mathbf{M}') = 0, \quad (6.13)$$

where the collision tensor is given by

$$\mathbf{R} = -\begin{bmatrix} T_x^{-1} & -N_0 & 0 \\ N_0 & T_y^{-1} & 0 \\ 0 & 0 & T_z^{-1} \end{bmatrix}, \quad (6.13\text{a})$$

and $\mathbf{M}' = \chi_0(\mathbf{h}_0+\mathbf{h}_1) = (\chi_0/\gamma)(\omega_1, 0, \omega_0)$ is the thermal equilibrium magnetization corresponding to the *instantaneous total* magnetic field. Thus, the collisions with the bath may be said to tend to restore, in the rotating frame, thermodynamic equilibrium appropriate to the instantaneous value of the total magnetic field. The collision tensor, however, still depends on the strength of the driving field ω_1. The steady-state magnetization is then

$$M_x^r = (\chi_0/\gamma)\omega_1\left[1 + \frac{\omega(\Delta+N_0)T_x T_y}{1+\omega_1^2 T_y T_z + (\Delta+N_0)^2 T_x T_y}\right], \quad (6.14\text{a})$$

$$M_y^r = (\chi_0/\gamma)\frac{\omega\omega_1 T_y}{1+\omega_1^2 T_y T_z + (\Delta+N_0)^2 T_x T_y}, \quad (6.14\text{b})$$

$$M_z{}^r = (\chi_0/\gamma)\left[\omega_0 - \frac{\omega\omega_1{}^2 T_y T_z}{1+\omega_1{}^2 T_y T_z + (\Delta+N_0)^2 T_x T_y}\right].$$
(6.14c)

Thus, the situation is characterized by three relaxation times, all of which depend on ω and ω_1. If, however, $\omega_1\tau_c\ll1$, it is clear that $T_y=T_x$ and all relaxation times become independent of the strength of the driving field. In this case (6.14) become identical to the solution of the modified phenomenological Bloch equations,[2,3] and upon saturation they exhibit the usual saturation broadening of the absorption line. Furthermore, in the case of "extreme narrowing," i.e., for $\omega_0\tau_c\ll1$ all relaxation times become constant, and for an isotropic environment, i.e., $j_t=j_z$, equal to one another. On the other hand, for $\omega_1\tau_c\gtrsim1$ and at resonance, i.e., $\omega=\omega_0$, T_x depends on ω_1, whereas T_y and T_z do not, and in general $T_z{}^{-1}\lesssim T_x{}^{-1}$, $T_y{}^{-1}$; in particular $T_z{}^{-1}\ll T_x{}^{-1}$, $T_y{}^{-1}$ if $\omega_0\tau_c\gg1$. Thus, for sufficiently strong driving field, i.e., for $\omega_1\tau_c\gtrsim1$, the effects of saturation upon the various measurable quantities of the steady state is given not only through the $\omega_1{}^2$ of the denominator of (6.14), but also through the ω_1 dependence of T_x as given by (6.12a). Thus, we note that the behavior of the dispersion signal upon saturation is not the same as that of the absorption signal, as has been observed experimentally. We demonstrate this for the case of exact resonance (we also ignore here the frequency shift N_0). From (6.14) and (6.12) we find for $\Delta=\omega_0-\omega=0$

$$M_y{}^r/(M_y{}^r)_0 = M_z{}^r/(M_z{}^r)_0 = 1/(1+\omega_1{}^2 T_y T_z),$$
(6.15a)

$$\frac{(dM_x{}^r/d\omega_0)/(dM_x{}^r/d\omega_0)_0}{M_y{}^r/(M_y{}^r)_0} = \frac{T_x}{T_{x0}}$$

$$= \frac{j_z{}'(0)+j_t{}'(\omega_0)}{j_z{}'(\omega_1)+j_t{}'(\omega_0)}.$$
(6.15b)

Here $T_{x,y,z}$ are understood to be evaluated at resonance ($\Delta=0$) and T_{x0} denotes the value of T_x for $\omega_1=0$. The symbol ( )$_0$ denotes the value of the quantity before saturation. It is clear from (6.15) that, while the absorption and z component of the magnetization saturate (at resonance) in the way expected from Bloch's phenomenological equations,[1] the dispersion derivative saturates more slowly with strong driving fields (for $\omega_1\tau_c\gtrsim1$). It is also possible to analyze the line width of the absorption line and to demonstrate that it could decrease before it increases upon saturation. Both of these qualitative features have been observed experimentally. Finally, it is easy to see from (6.14) that in the case of extreme saturation, i.e., for $\omega_1{}^2 T_y T_z\gg1$, the steady-state magnetization in the rotating frame is equal to the thermal equilibrium magnetization in the rotating frame corresponding to the *effective* magnetic field, ω_e/γ, and a temperature given through $\beta_e=\beta\omega_0\Delta/(\Delta^2+\omega_1{}^2 T_z T_x{}^{-1})$.

(e) *Slowly rotating transverse field.* If $\omega\tau_c\ll1$ and

$\omega_e\tau_c\ll1$, but ω_1/ω_0 arbitrary, then all relaxation times are constant, and for an isotropic environment equal to $T=[2j_z{}'(0)]^{-1}$. The steady-state magnetization is then as given by the modified phenomenological Bloch equations,[2,3] i.e.,

$$M_x{}^r + iM_y{}^r = (\chi_0/\gamma)\omega_1\left[1+\frac{\omega(\Delta+iT^{-1})}{T^{-2}+\omega_e{}^2}\right], \quad (6.16\text{a})$$

$$M_z{}^r = (\chi_0/\gamma)\left[\omega_0 - \frac{\omega\omega_1{}^2}{T^{-2}+\omega_e{}^2}\right]. \quad (6.16\text{b})$$

These expressions are applicable to the case of a purely rotating field, i.e., $\omega_0=0$, and include the result of Gorter and Kronig.[32]

ACKNOWLEDGMENTS

APPENDIX

The classical equation of motion for the magnetization $\mathbf{M}_T(t)$ of a spin system (with magnetomechanical ratio γ) in a magnetic field $\mathbf{h}_T(t)$ is

$$\frac{d}{dt}\mathbf{M}_T(t) = \gamma\mathbf{M}_T(t)\times\mathbf{h}_T(t). \quad (\text{A1})$$

The magnetic field $\mathbf{h}_T(t)$ is taken to be the sum of the static field $\mathbf{h}_0$, the rotating driving field $\mathbf{h}_1(t)$, and the fluctuating field $\mathbf{h}_b(t)$ of the bath. In a frame of reference rotating with angular velocity $-\boldsymbol{\omega}_0=-\gamma\mathbf{h}_0$, we have

$$\frac{d}{dt}\mathbf{M}_T{}'(t) = \gamma\mathbf{M}_T{}'(t)\times\mathbf{h}'(t), \quad (\text{A2})$$

where $\mathbf{h}(t)=\mathbf{h}_b(t)+\mathbf{h}_1(t)$. The primes indicate that the vectors should be taken as they appear in the rotating coordinate system. In particular, if we take $\mathbf{h}_0$ along the z direction, we have clearly $h_\pm{}'(t)=h_\pm(t)\exp(\pm i\omega_0 t)$, $h_z{}'(t)=h_z(t)$, where $h_\pm=h_x\pm ih_y$ and similarly for $\mathbf{M}_T{}'(t)$. We write now (A2) as an equivalent integral equation

$$\mathbf{M}_T{}'(t) = \mathbf{M}^0 + \gamma\int_0^t d\tau\,\mathbf{M}_T{}'(\tau)\times\mathbf{h}'(\tau). \quad (\text{A3})$$

Here we have put $\mathbf{M}_T{}'(0)=\mathbf{M}_T(0)=\mathbf{M}^0$, which is true if we choose the two coordinate systems to coincide at $t=0$. We now substitute the expression (A3) for $\mathbf{M}_T{}'$ in

[32] C. J. Gorter and R. Kronig, Physica **3**, 1009 (1936); R. Kronig, *ibid.* **5**, 75 (1938).

the right-hand side of Eq. (A2), and obtain

$$\frac{d}{dt}\mathbf{M}_{T}'(t)=\gamma^2\int_0^t d\tau \mathbf{h}'(t)$$
$$\times(\mathbf{h}'(\tau)\times\mathbf{M}_{T}'(\tau))+\gamma\mathbf{M}^0\times\mathbf{h}'(t). \quad (A4)$$

In order to find the magnetization $\mathbf{M}(t)$ proportional to h_1, we write $\mathbf{M}_T(t)=\mathbf{M}_0(t)+\mathbf{M}(t)$ and find from (A4)

$$\frac{d}{dt}\mathbf{M}'(t)=\gamma^2\int_0^t d\tau \mathbf{h}_b(t)\times(\mathbf{h}_b'(\tau)\times\mathbf{M}'(\tau))$$

$$+\gamma^2\int_0^t d\tau\{\mathbf{h}_1'(t)\times(\mathbf{h}_b'(\tau)\times\mathbf{M}_0'(\tau))+\mathbf{h}_b'(t)$$

$$\times(\mathbf{h}_1'(\tau)\times\mathbf{M}_0'(\tau))\}+\gamma\mathbf{M}^0\times\mathbf{h}_1'(t), \quad (A5)$$

and an analogous equation for $\mathbf{M}_0'(t)$. If now we take ensemble averages and *assume* that it is permissible to neglect *at this point* the correlation between the random functions $\mathbf{h}_b'(t)$ and $\mathbf{M}'(t)$ and average them separately, and in addition take for convenience $\langle\mathbf{h}_b'(t)\rangle=0$, we find from (A5)

$$\frac{d}{dt}\mathbf{M}'(t)=\gamma^2\int_0^t d\tau \mathbf{h}_b'(t)$$

$$\times(\mathbf{h}_b'(\tau)\times\mathbf{M}'(\tau))+\gamma\mathbf{M}^0\times\mathbf{h}_1'(t), \quad (A6)$$

where the ensemble averaging for $\langle\mathbf{h}_b'(t)\mathbf{h}_b'(\tau)\rangle$ and $\langle\mathbf{M}'(t)\rangle$ has not been indicated explicitly. In the stationary frame of reference an equation of motion for $\mathbf{M}(t)$ is easily obtained from (A6). For simplicity, we shall state the result only in the case of a cylindrically symmetric environment, i.e., $c_{xx}(\tau)=c_{yy}(\tau)=c_t(\tau)$, $c_{zz}(\tau)=c_z(\tau)$, $c_{xy}(\tau)=c_{yz}(\tau)=c_{zx}(\tau)=0$, where $c_{\kappa\lambda}(\tau)$ $=\gamma^2\langle h_b^\kappa(t)h_b^\lambda(t-\tau)\rangle$ are the correlation functions for the bath. We find for a transverse, circularly polarized driving field $\mathbf{h}_1(t)=h_1(\mathbf{i}\cos\omega t-\mathbf{j}\sin\omega t)$

$$\frac{d}{dt}M_\pm(t)=\mp i\omega_0 M_\pm(t)-\int_0^t d\tau M_\pm(t-\tau)$$

$$\times(c_t(\tau)+c_z(\tau)e^{\mp i\omega_0\tau})\pm i\omega_1 M_z^0 e^{\mp i\omega t}, \quad (A7)$$

where as in the text $\omega_1=\gamma h_1$. Seeking now a steady-state solution of (A7) of the form $\mathbf{M}(t)\to\mathbf{M}(\omega)\exp(-i\omega t)$ $+$c.c. as $t\to\infty$, we find, making as before use of the assumed property (2.18) for the correlation functions,

$$[-i(\omega\mp\omega_0)+j_t(\omega)+j_z(\omega\mp\omega_0)]M_\pm(\omega)$$
$$=i\omega_1\tfrac{1}{2}(M_z^0\pm M_z^0), \quad (A8)$$

which is identical to (3.5).

It is evident that an identical derivation can be given for an equation of motion of the spin density operator, when its interaction with the bath can be described by $V(t)=\sum_\kappa u_\kappa(t)v_\kappa$, where $u_\kappa(t)$ are random functions and v_κ various combinations of spin operators. This equation of motion is identical to (2.14), where $\mathcal{C}_0(t,\{\sigma_1\})$ is given by (2.16a) with $c_{\kappa\lambda}(\tau)=c_{\lambda\kappa}(-\tau)$ and $D_0(t)=0$. For the steady state this leads to Eq. (2.21), where $\mathcal{C}_0(\omega)$ and $D_0(\omega)$ are given by (2.24).

The general response of the system can be obtained in the same way.

This method of derivation is clearly weak, since it rests upon the assumption of statistical independence of the spin and the semiclassical bath. Clearly this assumption is *not* correct to all orders in the interaction. The general method given in the text justifies the use of this assumption, in so far as second order effects are concerned. This method, however, does describe correctly the "memory" effects, which were not obtained by previous theories.

A similar classical derivation of (A8) has been obtained independently by Dr. H. J. Zeiger.