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Electron Paramagnetic Resonance in Inhomogeneously Broadened Systems: A Spin Temperature Approach

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The EPR responses of inhomogeneously broadened electron spin systems are considered in detail under the assumption that a spin temperature situation in the rotating reference frame obtains in the constituent spin packets. Expressions are derived for the rapid passage and slow passage responses of such systems, including situations where magnetic field modulation and subsequent phase sensitive first harmonic detection is employed. It is shown that for rapid passage situations in which $\omega_m T_1 \gg 1$ (where ω_m is the angular frequency of the magnetic field modulation) a dispersive response π out of phase with the modulation is obtained, whereas when $\omega_m T_1 \ll 1$ a response is obtained in quadrature with the modulation, both of which are in close agreement with experiment. Further, in very inhomogeneously broadened systems the first harmonic dispersive response has an absorption type shape given by $G(\Delta)$, where $G(\Delta)$ describes the inhomogeneous distribution of local fields, which is of the same form as the absorption response obtained under slow passage. In the slow passage regime it is shown that the saturation behavior of the system is strongly dependent on the relative values of the Zeeman spin–lattice relaxation time T_1 and the spin–spin reservoir relaxation time T_{ss}. For situations in which $T_1 = T_{ss}$, the saturation behavior of Bloembergen *et al.* is predicted, whereas when $T_{ss} \ll T_1$ the saturation behavior observed by Castner is obtained. Finally, techniques that allow measures of the spin packet width, T_{ss} and T_1 are discussed.

INTRODUCTION

Electron spin systems whose constituent spins have a distribution of resonant frequencies are commonly encountered in electron paramagnetic resonance (EPR) studies (*1–3*). Such "inhomogeneously broadened" systems arise when the paramagnetic spins are relatively dilute and localized to particular regions of the sample. The spins may therefore experience local magnetic fields due to contact interactions with nearby nuclei, inhomogeneities in the applied magnetic field, or anisotropy of the g-tensor.

The slow passage response of very inhomogeneously broadened systems is well described by the "spin-packet" approach suggested by Portis (*4*) and subsequently extended by Castner (*5*). In these formulations each spin packet is characterized as a (homogeneously broadened) spin or group of spins with the same resonant frequency. The net inhomogeneously broadened response is then obtained as a convolution of the individual packet responses with a function describing the inhomogeneous distribution of the packet resonant frequencies due to the local fields. Castner (*5*) assumes the spin packet width (written here as $1/T_3$) to be a variable parameter, and the fact that $1/T_3$ is observed to increase as the paramagnetic spin concentration is raised suggests

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that the spin packet width reflects the strength of the spin–spin interactions present in the sample. Under these assumptions a functional form of the saturation behavior in inhomogeneous systems may be obtained for various values of an inhomogeneity parameter $a = 1/T_3 \Delta\omega_G$ (where $\Delta\omega_G$ is the width of the inhomogeneous distribution function), which gives good agreement with experiment.

In the rapid passage regime the situation is somewhat more confused. Portis (*6*) has given a description of rapid passage in very inhomogeneously broadened systems ($a = 0$) arriving at results that agree, at least qualitatively, with experiment. This theory however, provides no parameter corresponding to the spin packet width that reflects the strength of spin–spin interactions. The situation is further complicated by the usual experimental device of increasing sensitivity by using magnetic field modulation and subsequent first harmonic detection. As described by Portis (*6*), the contributions of the individual spins to the first harmonic signal become a rather complicated expansion of the individual spin susceptibilities, which do not converge for many experimental situations. A detailed analysis of the many special rapid passage conditions and corresponding EPR responses that may be obtained has been presented by Weger (*7*).

In the present work the slow and rapid passage responses of inhomogeneously broadened systems are analysed in a manner analogous to that of Castner (*5*), except that a spin temperature situation in the rotating reference frame (*8*) is assumed for the spin packets. The response of the individual spin packets is obtained using the spin temperature formalism to include situations where sinusoidal magnetic field modulation and subsequent first harmonic detection is employed. The net response of the entire inhomogeneous system is then given by the convolution of a function describing the distribution of local fields with these individual packet responses.

The suggestion that a rotating frame spin temperature situation exists in inhomogeneously broadened electron spin systems has been well discussed by Atsarkin and Rodak (*9*), and offers good agreement with experiment. These authors, however, were primarily concerned with the response of the system to irradiation at a particular frequency, rather than the more usual situation where the resonance is swept by variation of the magnetic field, which is the case explicitly considered here.

In the following section the spin packet concept is discussed, and the operational definition employed in this work is explained. Subsequently, in the section Spin Temperature Theory the relevant spin temperature formulation is outlined, and a theoretical form of the rapid and slow passage responses of inhomogeneously broadened electron spin systems is obtained. Finally, in the section Comparison with Experiment, the excellent agreement between theory and experiment is demonstrated.

THE SPIN PACKET

The spin packet concept proposed by Portis (*4*) applies rigorously to a system of noninteracting spins. In the case of EPR each spin packet then consists of a single electron spin, the response of which is lifetime broadened by the spin–lattice relaxation rate $1/T_1$. The inhomogeneously broadened nature of the resonance is produced by local magnetic fields (usually contact interactions with nearby nuclear spins) which provide a distribution of possible resonant frequencies. Thus the homogeneously broadened response of each spin (or spin packet) has the "spin packet width" $1/T_1$ and a characteristic resonant frequency.

The Castner (*5*) extension of the Portis theory assumes that more than one spin may be in a given spin packet, and the spin packet width is then a variable parameter. This proposal provides good agreement with experiment but has produced some confusion about the nature of the spin packet entity, as it implies that while intrapacket spin–spin interactions are strong enough to result in a homogeneously broadened resonance the interpacket spin–spin interactions are negligible. The criteria for a spin to be a member of a spin packet are therefore somewhat arbitrary, and interpacket spectral spin diffusion processes are not explicitly considered.

In this work an alternative model of the spin packet is proposed which applies particularly to electron spins which are a minority species randomly distributed in a host lattice and where the dominant electron spin–spin interactions are exchange processes. There is good evidence (*11*) to suggest that as the concentration of such "impurity" spins is increased, local clusters of two or more strongly interacting spins are formed until, at high enough concentrations, the cluster may be thought to include all the spins in the sample. As has been well discussed by Anderson (*12*), if the exchange rates between spins in a particular cluster are much faster than the resonant frequency differences between them (produced by the local environments of each spin), a single homogeneously broadened "exchange narrowed" resonance is observed at a frequency corresponding to the mean resonant frequency of the constituent spins. On the other hand, if the exchange rate is slower than the resonant frequency separations, the resonances become "exchange broadened" and maintain their spectral separation. We may therefore picture a spin packet as a cluster of highly coupled spins (which therefore have a single exchange narrowed resonant frequency) where the dominant contribution to the spin packet linewidth arises from the relatively weak interactions that the spins "inside" the packet experience with other spins that have resonant frequencies which are distinct from the packet resonant frequency. This model includes such processes as spectral diffusion in a natural manner. It should be noted, however, that this statistical description will be less correct at low impurity concentrations were the spin packet may be more correctly analyzed as, for example, a two or three spin system (*13*).

The spin Hamiltonian of an inhomogeneously broadened spin system may be written as

$$\mathscr{H} = \sum_i \omega_i S_{iz} + \tfrac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \mathscr{H}_{ij}^{ss} \qquad [1]$$

where ω_i is the resonant frequency of the ith spin and $\mathscr{H}_{ij}{}^{ss}$ represents the spin–spin interactions (exchange and dipolar) between the ith and jth spins. This Hamiltonian may be separated into parts corresponding to each of the highly coupled clusters or spin packets according to

$$\mathscr{H} = \sum_k \mathscr{H}_k; \qquad \mathscr{H}_k = \sum_{i=1}^{n_k} \omega_i S_{iz} + \mathscr{H}_k^{ss} \qquad [2]$$

where n_k is the number of spins in the kth spin packet, and

$$\mathscr{H}_k^{ss} = \tfrac{1}{2} \sum_{i=1}^{n_k} \sum_j \mathscr{H}_{ij}^{ss}.$$

The fast intracluster exchange processes that have been used to define the spin packet will result in the distribution of ω_i over the cluster making a negligible contribution to the packet linewidth. The resonant frequency of this exchange narrowed packet resonance is therefore

$$\omega_k = \frac{1}{n_k} \sum_{i=1}^{n_k} \omega_i$$

and the packet Hamiltonian is, to a very good approximation, given by

$$\mathscr{H}_k = \omega_k \sum_{i=1}^{n_k} S_{iz} + \mathscr{H}_k^{ss}. \quad [3]$$

SPIN TEMPERATURE THEORY

In this section the slow and rapid passage resonant responses of an inhomogeneously broadened electron spin system are derived under the assumption that a rotating frame spin temperature situation exists in each of the constituent spin packets. The net response of the system is then characterized as the convolution of the packet response with a function describing the distribution of resonant frequencies that the packets may exhibit. We initially, therefore, obtain the homogeneously broadened packet response using the spin temperature formulation.

In the presence of the irradiating microwave field, the packet Hamiltonian obtained in the previous section may be written

$$\mathscr{H} = \omega_k \sum_j S_{jz} + \gamma H_1 \cos(\omega t) \sum_j S_{jx} + \mathscr{H}_{ss} \quad [4]$$

where H_1 is the amplitude of the applied microwave field and where the subscripts k have been suppressed. It is also understood that the summations are over the n_k spins in the packet. Moving into the frame rotating at ω via the transformation $U_1 = e^{i\omega t} \sum_j S_{jz}$ we obtain

$$\tilde{\mathscr{H}} = \Delta \sum_j S_{jz} + \gamma H_1 \sum_j S_{jx} + \mathscr{H}'_{ss} \quad [5]$$

where the superscript ~ indicates the rotating frame, $\Delta = \omega_k - \omega$ and where only the secular part $\mathscr{H}'_{ss}$ of the spin–spin Hamiltonian has been included, which is a good first-order approximation. Subsequently, following Clough (*14*) and Clough and Scott (*15*), we move into the tilted rotating frame such that the z axis is aligned along the effective magnetic field via the transformation $U_2 = e^{i\phi} \sum_j S_{jy}$ where $\phi = \tan^{-1}(\gamma H_1/\Delta)$. We obtain

$$U_2 \tilde{\mathscr{H}} U_2^{-1} = \omega_e \sum_j S_{jz} + U_2 \mathscr{H}'_{ss} U_2^{-1} \quad [6]$$

where $\omega_e = (\Delta^2 + \gamma^2 H_1^2)^{1/2}$. The approximation now made is that ϕ is small, thus allowing the identification $U_2 \approx 1 - i\phi \sum_j S_{jy}$. This approximation indicates that our equations will not be strictly correct for those spins very near resonance. However, as the condition $\phi \ll 1$ will be obeyed by the vast majority of spins in an inhomogeneously broadened system (especially by those spins "outside" the spin packet we are considering) we may consider that most of the observed response arises from such spins and that the approximation is therefore valid. We obtain

$$U_2 \tilde{\mathscr{H}} U_2^{-1} = \omega_e \sum_j S_{jz} + \mathscr{H}'_{ss} + i\phi \sum_j [\mathscr{H}'_{ss}, S_{jy}] \quad [7]$$

to first order in ϕ. We identify $U_2\tilde{\mathscr{H}}U^{-1} \equiv \mathscr{H}_0 + V$ where $\mathscr{H}_0 = \omega_e \sum_j S_{jz} + \mathscr{H}'_{ss}$ and the perturbation $V = i\phi \sum_j [\mathscr{H}'_{ss}, S_{jy}]$ It is important to note the role played by V. As both the Zeeman and spin–spin terms in $\mathscr{H}_0$ commute with each other, but do not commute with V, the perturbation couples the Zeeman and spin–spin reservoirs which would otherwise be independent. This perturbation therefore allows the transfer of Zeeman energy to the spin–spin reservoir, which is necessary for spectral diffusion (and subsequent broadening of the spin packet) to occur. As $V = 0$ when $H_1 = 0$, we may expect to observe larger spin-packet widths when the microwave irradiation is on than when it is off. Such effects have recently been observed by Taylor *et al.* (*16*) in a study of the spin–echo response of an inhomogeneously broadened phosphorus-doped silicon sample to a two pulse microwave stimulation. This result serves to give added confidence in both the spin-temperature approach and the spin-packet model of the previous Section. It may also be noted that this larger spin-packet width in the presence of H_1 corresponds to the "instantaneous diffusion" effect of Klauder and Anderson (*17*).

Returning to Eq. [7] we move into the interaction representation via the transformation $U_3 = {}^{i\mathscr{H}_0 t}$, where it is easily shown that

$$d\rho^*/dt = (i/\hbar)[\rho^*, \overset{*}{V}(t)] \quad [8]$$

where ρ^* is the density matrix of the system in the interaction representation and $V^*(t) = U_3(t)VU_3^{-1}(t)$. Solving this equation by the normal method of successive iterations, we obtain

$$\rho^*(t) = \rho^*(0) + \frac{i}{\hbar}\int_0^t [\rho^*(0), V^*(t')]\,dt' + \left(\frac{i}{\hbar}\right)^2 \int_0^t [[\rho^*(0), V^*(t'')], V^*(t')]\,dt''\,dt' \quad [9]$$

to second order in ϕ, or, equivalently, V. Upon moving back into the simply rotating frame via the inverse transformation $\tilde{\rho}(t) = U_2^{-1}U_3^{-1}(t)\rho^*(t)U_3(t)U_2$ (where $\tilde{\rho}(t)$ is the density matrix in the rotating frame) it is straightforward to show that

$$\tilde{\rho}(t) = \tilde{\rho}(0) + i\phi \sum_j [\tilde{\rho}(0), S_{jy}] + \frac{i}{\hbar}\int_0^t [\tilde{\rho}(0), V(t'-t)]\,dt'$$
$$+ \left(\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t'} [[\tilde{\rho}(0), V(t''-t)], V(t'-t)\,dt''\,dt' \quad [10]$$

to second order in ϕ. Thus we obtain

$$\frac{d\tilde{\rho}(t)}{dt} = \frac{i}{\hbar}[\tilde{\rho}(0), V(0)] + \left(\frac{i}{\hbar}\right)^2 \int_0^\infty [[\tilde{\rho}(0), V(-\tau)], V(0)]\,d\tau \quad [11]$$

where the limits of the integral have been extended, as the commutator in the integral is very small except at very short times. At $t = 0$ (i.e. before the microwave irradiation is switched on) we obtain from Eq. [5] that

$$\tilde{\rho}(0) = Ce^{-(\alpha Z + \beta \mathscr{H}'_{ss})} \quad [12]$$

where $Z = -\Delta \sum_j S_{jz}$; C is a normalizing constant such that $\mathrm{Tr}\rho(0) = 1$ and α and β are the initial "inverse" Zeeman and spin–spin temperatures, respectively. We now proceed to calculate the equation of motion of the z component of the magnetization in the rotating frame, assuming it is isolated from the lattice, via the relation

$$\frac{dM_z}{dt} = \gamma\hbar \,\mathrm{Tr}\left(\frac{d\tilde{\rho}(t)}{dt} \sum_j S_{jz}\right). \qquad [13]$$

The calculation of the trace in the above expression has been performed by Goldman (*8*). He obtains, for the particular form of the perturbation V we employ, that

$$\mathrm{Tr}\left(\frac{d\tilde{\rho}(t)}{dt} \sum_j S_{jz}\right) = -\pi\omega_1^2 g(\omega_e)\left(\frac{M_z}{\gamma\hbar} - \beta\Delta\right) \qquad [14]$$

where $\omega_1{}^2 = \gamma^2 H_1{}^2$ and where

$$g(\omega_e) = \frac{1}{\pi \,\mathrm{Tr}\left(\sum_j S_{jx}^2\right)} \int_0^\infty \mathrm{Tr}(S_{jx} S_{jx}(\tau)) \cos(\omega_e \tau)\, d\tau. \qquad [15]$$

We note that $g(\omega_e)$ is the shape of the absorption signal from the packet at low microwave level.

We examine the form of the correlation function

$$G(\tau) = \mathrm{Tr}\left(\sum_j S_{jx} S_{jx}(\tau)\right) \Big/ \left[\mathrm{Tr} \sum_j S_{jx}^2\right] \qquad [16]$$

in Eq. [15]. In this work we assume that

$$G(\tau) = e^{-\tau/T_3} \qquad [17]$$

where T_3 is the effective "T_2" of the spin packet and corresponds to the time necessary for a spin temperature situation to obtain in the spin packet after the microwave irradiation is applied. The assumption expressed by Eq. [17] is similar to that made by Clough and Scott (*15*). In Clough and Scott's work, however, $1/T_3$ refers to the rate at which equilibrium is established between all the spins experiencing different local fields, whereas in this work $1/T_3$ refers only to the rate at which equilibrium is established for spins in the same packet which therefore experience effectively the same magnetic field. It is also important to note that the exponential form of $G(\tau)$ corresponds to a Lorentzian profile in the frequency domain. As it is suggested in this work that the spin packet approach is valid when spectral diffusion occurs, Eq. [17] implies that the "diffusion envelope" obtained by exciting an inhomogeneously broadened system at a particular frequency ω, and monitoring the amount of excitation that spins at different resonant frequencies experience, should be a Lorentzian profile about ω. The analysis by Klauder and Anderson (*17*) of the data due to Mims *et al.* (*18*) shows that the diffusion envelope is indeed Lorentzian and, furthermore, that such Lorentzian diffusion may be expected in all inhomogeneously broadened paramagnetic spin systems. These results give some justification for the assumed exponential form of $G(\tau)$.

Upon substituting the relation [17] into Eq. [15] we have that

$$g(\omega_e) = T_3/\pi(1 + (\Delta^2 + \omega_1^2)T_3^2). \qquad [18]$$

Similarly, the sine Fourier transform of $G(\tau)$ may be written

$$g'(\omega_e) = \Delta T_3^2/\pi(1 + (\Delta^2 + \omega_1^2) T_3^2. \quad [19]$$

Upon substituting relation [14] back into Eq. [13], we obtain the equation of motion of the z component of the magnetization as

$$dM_z/dt = \pi\omega_1^2 g(\omega_e) [M_z - \beta\Delta\gamma\hbar] \quad [20]$$

excluding the effects of spin–lattice relaxation.

Similarly, it can be shown that the inverse spin–spin temperature β obeys the relation

$$\frac{d\beta}{dt} = \frac{\pi\omega_1^2 g(\omega_e)\,\Delta}{\gamma\hbar D^2}[M_z - \beta\Delta\gamma\hbar] \quad [21]$$

$D^2 = \mathrm{Tr}\mathscr{H}'^2_{ss}/\mathrm{Tr}\sum_j S_{jz}^2$.where D gives a measure of the width of the frequency distribution of the packet, and we may therefore write $T_3 = 1/D$, by making reference to Eq. [18] when ω_1 is small. Equations [20] and [21] are the Provotorov (*19*) equations in the absence of spin–lattice relaxation.

The dispersive and absorptive responses of the packet may be calculated from the density matrix in the rotating frame given by Eq. [11], according to the relations

$$v(\Delta) = \left\langle \sum_j S_{jy} \right\rangle = \mathrm{Tr}\left(\tilde{\rho}(t) \sum_j S_{jy}\right) \quad [22]$$

$$u(\Delta) = \left\langle \sum_j S_{jx} \right\rangle = \mathrm{Tr}\left(\tilde{\rho}(t) \sum_j S_{jx}\right) \quad [23]$$

where $v(\Delta)$ and $u(\Delta)$ are the absorptive and dispersive responses respectively. As shown by Goldman (*8*), upon calculation of the traces one obtains

$$v(\Delta) = \pi\omega_1[M_z - \beta\Delta\gamma\hbar]\, g(\omega_e) \quad [24]$$

and

$$u(\Delta) = \omega_1\gamma\hbar\beta + \pi\omega_1 g'(\omega_e) [M_z - \beta\Delta\gamma\hbar]. \quad [25]$$

The derivation of the resonant responses of the spin packet therefore necessitates calculation of β and $M_z - \beta\gamma\hbar$ from Eqs. [20] and [21] when the effects of spin relaxation are included. The resulting expressions may then be introduced into Eqs. [24] and [25], thus obtaining the observed absorption and dispersion.

Expressions are now derived for the absorption and dispersion of the spin-packet under conditions of rapid passage (the packet response is traversed in a time much shorter than the spin–lattice relaxation times of the system) and under the opposite condition of slow passage. The usual experimental situation in which sinusoidal magnetic field modulation and subsequent phase sensitive first harmonic detection is employed is considered specifically. It is interesting to note that the experimental situation is substantially simpler for the electron spins under discussion than for the lower frequency nuclear spins. This is primarily due to the fact that complicating effects (*8*) due to "rotary saturation" (power is absorbed from the modulating field) and non-adiabatic responses which may occur when the modulation frequency $\omega_m \geqslant \gamma H_1$ occur only at rather high modulation frequencies for reasonable H_1's, due to the larger electronic gyromagnetic ratio γ. Such experimental situations can usually be easily avoided.

Rapid Passage

The rapid passage spin-packet response is obtained under the condition that the time Δt taken to sweep through the packet obeys the inequality $T_3 \ll \Delta t \ll T_1, T_{ss}$. Thus, after a time T_3 the system has established a spin temperature and, as the Zeeman and spin–spin terms are coupled by the irradiation applied, this temperature is the same for both reservoirs. The density matrix of the system in the rotating frame is therefore

$$\tilde{\rho} = c e^{-\beta(Z+X+\mathscr{H}'_s)} \qquad [26]$$

where $X = \omega_1 \sum_j S_{jx}$. The effects of spin relaxation may be included as

$$\begin{aligned} \frac{d\langle Z\rangle}{dt} &= \mathrm{Tr}\left(Z\frac{d\tilde{\rho}}{dt}\right) - \frac{\langle Z\rangle - \langle Z\rangle_L}{T_1} \\ \frac{d\langle X\rangle}{dt} &= \mathrm{Tr}\left(X\frac{d\tilde{\rho}}{dt}\right) - \frac{\langle X\rangle}{T_{1x}} \\ \frac{d\langle \mathscr{H}'_{ss}\rangle}{dt} &= \mathrm{Tr}\left(\mathscr{H}'_{ss}\frac{d\tilde{\rho}}{dt}\right) - \frac{\langle \mathscr{H}_{ss}\rangle}{T_{ss}} \end{aligned} \qquad [27]$$

where T_1, T_{1x}, and T_{ss} are the spin lattice relaxation times of the Zeeman, microwave, and spin–spin reservoirs respectively. Summing the system of equations [27], it is straightforward to show that

$$\frac{d\beta}{dt} = -\frac{\beta\left[\dfrac{\Delta^2}{T_1} + \dfrac{\omega_1^2}{T_{1x}} + \dfrac{D^2}{T_{ss}}\right]}{\Delta^2 + \omega_1^2 + D^2} + \frac{\beta_L \omega_0 \Delta}{T_1(\Delta^2 + \omega_1^2 + D^2)}. \qquad [28]$$

In this work it is assumed that $T_{1x} = T_{ss}$ as the microwave irradiation and the spin–spin terms are in good contact. Equation [28] may then be rewritten as

$$\frac{d\beta}{dt} = -\frac{\beta}{T_1} - \frac{\beta(\omega_1^2 + D^2)}{T_{1s}(\Delta^2 + \omega_1^2 + D^2)} + \frac{\beta_L \omega_0 \Delta}{T_1(\Delta^2 + \omega_1^2 + D^2)} \qquad [29]$$

where $T_{1s}^{-1} = (T_1 - T_{ss})/T_1 T_{ss}$. Equation [29] describes the effects of spin relaxation in the rotating frame when the rapid passage conditions are observed.

From Eq. [21] it is noted that in order to completely characterize the time dependence of β it is necessary to know the time dependent evolution of $x = M_z - \beta\Delta\gamma\hbar$. We follow Goldman (*8*) and note that, employing Eqs. [20] and [21][1]

$$\begin{aligned} dx/dt &= -\pi\omega_1^2 g(\omega_e)x - (\omega_e^2/D^2)\pi\omega_1^2 g(\omega_e)x - \dot{\Delta}\beta\gamma\hbar \\ &= -(x/\tau) - \dot{\Delta}\beta \end{aligned} \qquad [30]$$

where

$$1/\tau = \pi\omega_1^2 g(\omega_e)\left[1 + (\Delta^2 + \omega_1^2)/D^2\right].$$

Using the relation [18], and identifying $1/T_3 = D$ we have that

$$1/\tau = \omega_1^2 T_3 \qquad [31]$$

[1] It should be recognized that the variable Δ in Eqs. [20] and [21] is really $\omega_e = (\Delta^2 + \omega_1^2)^{\frac{1}{2}} \approx \Delta(1 + (\phi^2/2))$ which is equal to Δ to first order in ϕ. However, when factors of $O(\Delta^2)$ are considered the explicit form ω_e should be used in order to include the ω_1^2 dependence.

We make the "adiabatic" passage condition that Δ and β do not vary appreciably during the time τ. Formal integration of Eq. [30] then results in the relation

$$x = -\dot{\Delta}\beta\gamma\hbar/\omega_1^2 T_3. \qquad [32]$$

It is important to realize that the adiabatic passage condition gives a strict upper limit to the modulation frequency ω_m. Given that the frequency width of the packet response is $1/T_3$ the condition states that this width must be swept in a time much longer than τ. In the case where magnetic field modulation is employed, we write $\Delta(t) = \Delta + \gamma H_m \sin\omega_m t$. Thus the maximum rate $d\Delta/dt$ at which the field is swept is $\gamma H_m \omega_m$, and we may write the adiabatic rapid passage condition as

$$H_m \omega_m \ll \gamma H_1^2. \qquad [33]$$

Upon substituting the relation [32] into Eq. [21] and including the effects of spin–lattice relaxation as given by Eq. [29], we obtain an equation describing the time dependent evolution of β as

$$\frac{d\beta}{dt} = -\frac{\beta\Delta(t)\dot{\Delta}(t)}{\Delta(t)^2 + \omega_1^2 + D^2} - \frac{\beta(\omega_1^2 + D^2)}{T_{1s}(\Delta(t)^2 + \omega_1^2 + D^2)} + \frac{\beta_L \omega_0 \Delta(t)}{T_1(\Delta(t)^2 + \omega_1^2 + D^2)}. \qquad [34]$$

The $\Delta(t)$ are written explicitly as functions of time in order to emphasize that they are sinusoidally varying with time. Equation [34] is solved to a second-order approximation in the Appendix for the two extremes $\omega_m T_1 \gg 1$ and $\omega_m T_1 \ll 1$. In the case when $\omega_m T_1 \gg 1$ we obtain the first harmonic response as

$$\beta_1(t) = \frac{\beta_L \omega_0 \Delta^2 \gamma H_m}{\sigma_1 \sigma}\left[1 - \frac{5\gamma^2 H_m^2}{8\sigma}\right]\sin(\omega_m t - \pi) + \frac{D^2 \beta_L \omega_0 \Delta^2 \gamma H_m}{\omega_m T_{1s} \sigma_1 \sigma^2}\sin\left(\omega_m t + \frac{\pi}{2}\right) \qquad [35]$$

where $\sigma = \Delta^2 + \omega_1^2 + D^2 + \gamma^2 H_m^2/2$ and $\sigma_1 = \Delta^2 + \omega_1^2 + D^2$. For $\omega_m T_1 \ll 1$ the first harmonic response may be written

$$\begin{aligned}\beta_1(t) = {} & \frac{\beta_L \omega_0 \omega_m T_1 \gamma H_m}{\sigma^2}\left[\frac{\gamma^2 H_m^2}{4} + \Delta^2 + \frac{\Delta^2 \gamma^2 H_m^2}{\sigma}\right]\sin\left(\omega_m t - \frac{\pi}{2}\right) \\ & + \frac{D^2 \beta_L \omega_0 T_1 \gamma H_m}{T_{1s}\sigma^2}\left[1 + \frac{2}{\sigma}\left(\Delta^2 - \frac{\gamma^2 H_m^2}{4}\right)\right]\sin(\omega_m t - \pi) \\ & + \frac{\beta_L \omega_0 \gamma H_m}{\sigma}\left[1 + \frac{1}{\sigma}\left(2\Delta^2 - \frac{\gamma^2 H_m^2}{4}\right)\right]\sin(\omega_m t).\end{aligned} \qquad [36]$$

By employing relations [32], [35], and [36] we are now in a position to calculate the absorptive and dispersive packet responses. The dispersion is given by

$$u(\Delta) = \omega_1 \beta\left[1 - \frac{H_m \omega_m}{\gamma H_1^2}\left(\frac{\Delta T_3 \cos(\omega_m t)}{1 + (\Delta^2 + \omega_1^2)T_3^2}\right)\right]\gamma\hbar. \qquad [37]$$

As we obey the adiabatic condition $H_m \omega_m \ll \gamma H_1^2$ we obtain to a very good approximation that

$$u(\Delta) = \omega_1 \beta\gamma\hbar. \qquad [38]$$

A similar analysis for the absorption reveals that it is smaller than the dispersion by the factor $\varepsilon = H_m \omega_m/\gamma H_1^2$ and is therefore effectively zero. Thus we obtain the result that only the dispersive component, which is directly proportional to the spin temperature β, is observable.

The net rapid passage first harmonic response $U_1(\Delta)$ from the inhomogeneously broadened system is then obtained as a convolution of the packet responses with a normalized function $G(\Delta)$ describing the distribution of local fields. We obtain

$$U_1(\Delta) = \omega_1 \gamma \hbar \int_{-\infty}^{\infty} G(\Delta')\beta_1(\Delta - \Delta')\, d\Delta'. \quad [39]$$

A full discussion of the response $U_1(\Delta)$ in the limits $\omega_m T_1 \gg 1$ and $\omega_m T_1 \ll 1$ is presented in the next Section.

Slow Passage

The basic slow passage criterion employed here is that the time Δt taken to sweep through the packet response obeys the inequality $\Delta t \gg T_3, T_1, T_{ss}$. As T_1 is the longest of these characteristic times, this slow passage condition implies the inequality

$$\omega_m T_1 \ll 1/\gamma T_3 H_m. \quad [40]$$

The situation becomes somewhat simpler if it can be assumed that the "mixing time" W^{-1}, where

$$W = \pi\omega_1^2 g(\omega_e) \quad [41]$$

that is characteristic of Eqs. [20] and [21], is much less than the time taken to sweep through resonance. This may be written as the inequality

$$\omega_m H_m \ll \gamma H_1^2/1 + T_3^2(\Delta^2 + \omega_1^2). \quad [42]$$

Obviously, this condition will not be obeyed far from resonance. As most of the packet response will arise near $\Delta \sim 0$, however, it is a good approximation to say that W^{-1} is less than the time taken to sweep through resonance if $\omega_m H_m \ll \gamma H_1^2$, which is of course, the adiabatic condition, It is important to note that this condition is far more easily obeyed for electron spins than for nuclear spins, and thus that many of the complications due to nonadiabaticity discussed by Goldman (*8*) may be avoided.

If both the slow passage and adiabatic passage conditions are obeyed, the Zeeman and spin–spin reservoirs will be in equilibrium with the sinusoidally varying magnetic field. The equations of motion of the z component of the magnetization and the spin–spin temperature β including the effects of relaxation may then be written from Eqs. [20] and [21] as

$$dM_z/dt = -\pi\omega_1^2 g(\omega_e)\,[M_z - \beta\Delta\gamma\hbar] + (M_0 - M_z)/T_1 \quad [43]$$

where $M_0 = \gamma\hbar\beta_L\omega_0$ and

$$\frac{d\beta}{dt} = \frac{\pi\omega_1^2 g(\omega_e)\,\Delta}{D^2}[M_z - \beta\Delta\gamma\hbar] - \frac{\beta}{T_{ss}}. \quad [44]$$

As Δ is slowly varying compared to W, $1/T_1$, and $1/T_{ss}$, we may therefore solve for the equilibrium values of β and $M_z - \beta\Delta\gamma\hbar$, obtain the dispersion and absorption using Eqs. [24] and [25], and subsequently obtain the first harmonic response from a Fourier analysis of these expressions.

A solution of Eqs. [43] and [44] under the equilibrium conditions $dM_z/dt = d\beta/dt = 0$ is easily obtained as

$$\gamma\hbar\beta = \frac{M_0\omega_1^2 g(\omega_e)\,\Delta T_{ss}}{D^2\left(1 + \pi\omega_1^2 g(\omega_e)\left[T_1 + \frac{\Delta^2 T_{ss}}{D^2}\right]\right)} \qquad [45]$$

$$M_z - \beta\Delta\gamma\hbar = \frac{M_0}{1 + \pi\omega_1^2 g(\omega_e)\left[T_1 + \frac{\Delta^2 T_{ss}}{D^2}\right]}. \qquad [46]$$

These expressions may be introduced into Eqs. [24] and [25] to obtain the slow passage absorptive and dispersive spin packet responses

$$v(\Delta) = \frac{\pi\omega_1 M_0 g(\omega_e)}{1 + \pi\omega_1^2 g(\omega_e)\left[T_1 + \frac{T_{ss}\Delta^2}{D^2}\right]} \qquad [47]$$

$$u(\Delta) = \frac{\omega_1 M_0[\omega_1^2 g(\omega_e)\,\Delta T_{ss}/D^2 + \pi g'(\omega_e)]}{1 + \pi\omega_1^2 g(\omega_e)\,[T_1 + T_{ss}\,\Delta^2/D^2]}. \qquad [48]$$

The net slow passage absorption and dispersion responses of the inhomogeneously broadened system may now be examined in detail.

Slow Passage Absorption

As previously stated, the net inhomogeneously broadened response is a convolution of the packet responses with a normalized distribution function $G(\Delta)$. Thus the slow passage absorption may be written

$$V(\Delta) = \int_{-\infty}^{\infty} G(\Delta')\,v(\Delta - \Delta')\,d\Delta' \qquad [49]$$

where $v(\Delta)$ is given by Eq. (47). It is noted (*3*) that most sources of inhomogeneous broadening elicit a Gaussian distribution function, and it is this form of distribution function that will be considered explicitly. Equation (49) may then be written as

$$V(\Delta) = \frac{\omega_1 M_0 T_3}{(2\pi)^{1/2}\,\Delta\omega_G}\int_{-\infty}^{\infty} \frac{e^{-\left(\frac{\Delta'}{\sqrt{2}\,\Delta\omega_G}\right)^2}}{\left[1 + \frac{\omega_1^2 T_3(T_1 + T_{ss}(\Delta - \Delta')^2/D^2)}{1 + T_3^2[(\Delta - \Delta')^2 + \omega_1^2]}\right][1 + T_3^2((\Delta - \Delta')^2 + \omega_1^2)]}. \qquad [50]$$

Changing variables according to $y = \Delta/\Delta\omega_G'$, where $\Delta\omega_G' = \sqrt{2}\Delta\omega_G$, assuming the identity $T_3 = 1/D$ and rearranging terms we have that

$$V(v) = \frac{\omega_1 M_0 T_3}{\pi^{1/2}}\int_{-\infty}^{\infty} \frac{e^{-y^2}\,dy}{1 + \omega_1^2 T_3^2 + (v - y)^2\,\Delta\omega_G'^2 T_3^2 + \omega_1^2 T_1 T_3 + (v - y)^2\,\Delta\omega_G'^2 T_{ss} T_3} \qquad [51$$

where $v = \Delta/\Delta\omega_G'$.

We now introduce the inhomogeneity parameter $a = 1/T_3 \Delta\omega'_G$ which relates the packet width to the width of the inhomogeneous distribution of local fields. The absorption may then be written

$$V(v) = \frac{\omega_1 M_0 T_3}{\pi^{1/2}(1 + \omega_1^2 T_3 T_{ss})} \int \frac{e^{-y^2}\, dy}{\dfrac{1 + \omega_1^2 T_{ss} T_1}{1 + \omega_1^2 T_{ss} T_3} + \dfrac{(v - y)^2}{a^2}} \qquad [52]$$

where terms of the form $\omega_1^2 T_3^2$ have been neglected with respect to terms $\omega_1^2 T_1 T_3$ as $T_1 \gg T_3$. We let

$$s^2 = \frac{1 + \omega_1^2 T_1 T_3}{1 + \omega_1^2 T_3 T_{ss}} \qquad [53]$$

and obtain

$$V(v) = \frac{\omega_1 M_0}{(2\pi)^{1/2} \Delta\omega_G[(1 + \omega_1^2 T_3 T_{ss})(1 + \omega_1^2 T_1 T_3)]^{1/2}} \left\{ as \int \frac{e^{-y^2}\, dy}{a^2 s^2 + (v - y)^2} \right\}. \qquad [54]$$

The function in curly brackets in Eq. [54] is known as a Voigt profile (*20*), and has been well documented (*21*). The saturation dependence and the line shape predicted by Eq. [54] are some of the principal results of the theory, as is discussed in the next Section.

Slow Passage Dispersion

The complete saturation behavior of the slow passage dispersion response may be calculated in an analogous manner to the absorption. In this section the expected lineshapes in the limits of low microwave saturation and very high saturation are briefly indicated. For low saturation Eq. [48] may be written as

$$u(\Delta) = \omega_1 M_0 \Delta T_3^2/(1 + \Delta^2 T_3^2). \qquad [55]$$

The net inhomogeneously broadened response is therefore

$$U(\Delta) = \frac{\omega_1 M_0}{(2\pi)^{1/2} \Delta\omega_G} \int_{-\infty}^{\infty} \frac{e^{-y^2}(v - y)\, dy}{a^2 + (v - y)^2} \qquad [56]$$

where the Gaussian distribution function of the previous section has been assumed. At very high saturation it is easily shown that

$$U(\Delta) = \frac{\omega_1 M_0}{(2\pi)^{1/2} \Delta\omega_G} \int_{-\infty}^{\infty} \frac{e^{-y^2}(v - y)\, dy}{a'^2 + (v - y)^2} \qquad [57]$$

where $a' = (T_1/T'_{ss})^{1/2} a$. Thus the dispersion does not saturate, and the dispersion described by Eq. [57] corresponds to Redfields (*22*) strong saturation limit in inhomogeneously broadened systems.

COMPARISON WITH EXPERIMENT

There is already present in the literature a wealth of data on the resonant properties of inhomogeneously broadened paramagnetic spin systems. No further experiments have been performed in this work as it is believed that the available data can be used to give quantitative verification of the spin temperature theory as applied to such paramagnetic systems. Furthermore it would appear that a deeper understanding of the relaxation processes occurring in inhomogeneously broadened systems may be achieved in terms of the spin temperature theory. These conclusions are amplified for the rapid passage dispersion responses and the slow passage absorption response obtained in the previous section.

Rapid Passage

We first discuss the inhomogeneously broadened rapid passage first harmonic response in the limit $\omega_m T_1 \gg 1$. From Eqs. [35] and [39] we have that

$$U_1(\Delta) = M_0 \omega_1 \gamma H_m \int_{-\infty}^{\infty} \frac{G(\Delta')(\Delta-\Delta')^2 \left\{1 - \dfrac{5\gamma^2 H_m^2}{8\left[(\Delta-\Delta')^2+\omega_1^2+D^2+\dfrac{\gamma^2 H_m^2}{2}\right]}\right\} d\Delta'}{\left[(\Delta-\Delta')^2+\omega_1^2+D^2+\dfrac{\gamma^2 H_m^2}{2}\right][(\Delta-\Delta')^2+\omega_1^2+D^2]} \sin(\omega_m t - \pi)$$

$$+ \frac{M_0 D^2 \gamma H_m}{\omega_m T_{1s}} \int_{-\infty}^{\infty} \frac{G(\Delta')(\Delta-\Delta')^2 \, d\Delta'}{[(\Delta-\Delta')^2+\omega_1^2+D^2][(\Delta-\Delta')^2+\omega_1^2+D^2+\gamma^2 H_m^2/2]^2}$$

$$\times \sin\left(\omega_m t + \frac{\pi}{2}\right). \qquad [58]$$

It is easy to show that in the case where ω_1 and γH_m are less than D, and $D \ll \Delta\omega_G$ where $\Delta\omega_G$ is the width of the distribution function that

$$U_1(\Delta) = \frac{\pi\omega \, M_0 \gamma H_m \, G(\Delta)}{2D} \sin(\omega_m t - \pi) + \frac{\pi\omega_1 M_0 \gamma H_m G(\Delta)}{4\omega_m T_{1s} D} \sin\left(\omega_m t + \frac{\pi}{2}\right) \qquad [59]$$

The existence of a first harmonic rapid passage response π out of phase with the modulation with a shape corresponding to $G(\Delta)$ has been well documented (*23*) for situations in which $\omega_m T_1 \gg 1$. These experimental observations correspond very well with the first term of Eq. [59]. The fact that a signal corresponding to the second term has not, as yet, been observed could be due to the fact that either $T_1 = T_{ss}$, thus making $1/T_{1s} = 0$, or $\omega_m T_{ss} \gg 1$ if $T_{ss} \ll T_1$.

The π out of phase term of Eq. [58] is considered in greater detail. Figure 1 shows the computed lineshapes of this first harmonic dispersion signal as H_1 is increased, assuming a Gaussian distribution function $G(\Delta)$. It may be noted that a characteristic distortion of this signal occurs when $\gamma H_1 \geqslant \Delta\omega_G$. Such effects have been observed experimentally (*24*). The expected variation of the signal amplitude as H_1 is increased is given in Fig. 2. Similar effects are also predicted by Eq. [58] as H_m is increased. Such "pseudo-saturation" effects have been observed by Hyde (*24*) in an EPR study of F centers in Li:F. The important aspect of these H_1 and H_m dependencies of the signal amplitude is that they allow a measure of the spin packet width, as it is in the region $\gamma H_1 \sim D$, $\gamma H_m/\sqrt{2} \sim D$ that the saturation effects become noticeable. It should be noted that care must be taken to ensure that the adiabatic condition $\omega_m H_m \ll \gamma H_1^2$ is obeyed as H_m is increased, however.

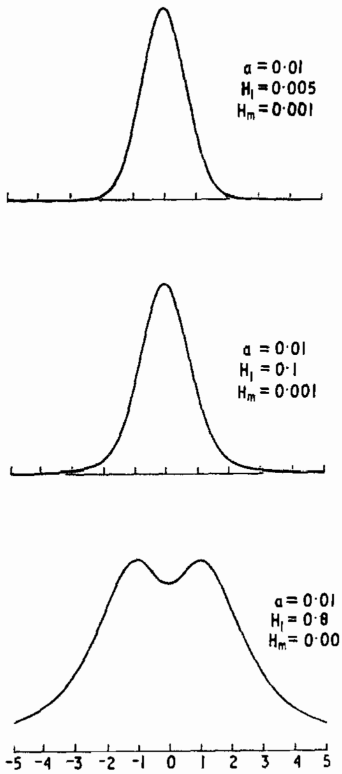

FIG. 1. Theoretical π out of phase first harmonic EPR rapid passage spectra of inhomogeneously broadened systems for various microwave field amplitudes. All parameters are expressed in terms of $\sqrt{2}\Delta\omega_G$, where $\Delta\omega_G$ is the width of the Gaussian distribution function (see text).

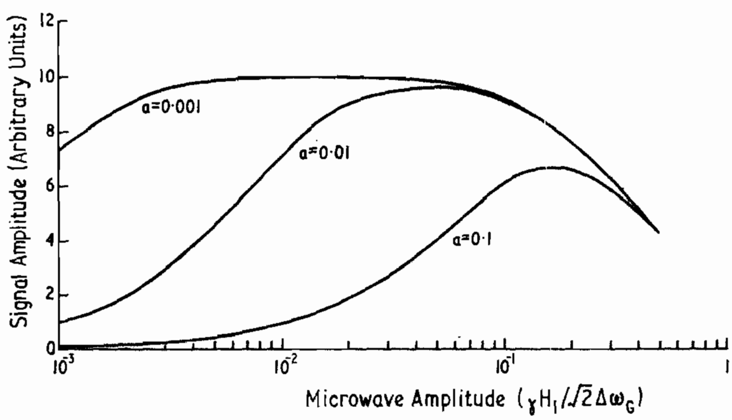

FIG. 2. Theoretical pseudo-saturation behaviour of the π out of phase first harmonic EPR rapid passage responses.

In the situation where $\omega_m T_1 \ll 1$ the expected first harmonic dispersion signal may be obtained from Eqs. [39] and [36] as

$$U_1(\Delta) = \omega_1 M_0 \gamma H_m \omega_m T_1 \times \int_{-\infty}^{\infty} \frac{G(\Delta')\left[\frac{\gamma^2 H_m^2}{4} + (\Delta' - \Delta)^2 \left\{1 + \frac{\gamma^2 H_m^2}{(\Delta - \Delta')^2 + \omega_1^2 + D^2 + \frac{\gamma^2 H_m^2}{2}}\right\}\right]}{\left[(\Delta - \Delta')^2 + \omega_1^2 + D^2 + \frac{\gamma^2 H_m^2}{2}\right]^2} \sin\left(\omega_m t - \frac{\pi}{2}\right)$$

$$+ \omega_1 M_0 \gamma H_m \times \int_{-\infty}^{\infty} \frac{G(\Delta')\left[1 + \frac{2(\Delta - \Delta')^2 - \frac{\gamma^2 H_m^2}{4}}{(\Delta - \Delta')^2 + \omega_1^2 + D^2 + \frac{\gamma^2 H_m^2}{2}} - \frac{D^2 T_1}{T_{1s}}\left\{1 + \frac{2(\Delta - \Delta')^2 - \frac{\gamma^2 H_m^2}{2}}{(\Delta - \Delta')^2 + \omega_1^2 + D^2 + \frac{\gamma^2 H_m^2}{2}}\right\}\right]}{(\Delta - \Delta')^2 + \omega_1^2 + D^2 + \frac{\gamma^2 H_m^2}{2}} \times \sin(\omega_m t) \qquad [60]$$

We do not consider the term in phase with the modulation as it has rather complicated behavior from which it would be difficult to extract useful information. An added complication is that when $\omega_m T_1 \ll 1$ a term arising from the slow passage dispersion may be expected, whose first harmonic signal is always in phase with the modulation.

The interesting term of Eq. [60] is therefore the response in quadrature with the modulation. In the situation where γH_m and ω_1 are less than D and $D \ll \Delta\omega_G$, it is straightforward to show that

$$U_1(\Delta)_{quad} = \pi M_0 \omega_1 \gamma H_m \omega_m T_1 G(\Delta) \sin\left(\omega_m t - \frac{\pi}{2}\right). \qquad [61]$$

This response corresponds very well with the in quadrature response that has been observed (*25*, *26*) in inhomogeneously broadened systems when $\omega_m T_1 \ll 1$. It may be shown that these spectra are somewhat narrower (for similar values of H_m) than was the case with the $\omega_m T_1 \gg 1$ response (Fig. 2), which effect has been observed experimentally (*27*).

The characteristics of the important inhomogeneously broadened first harmonic rapid passage dispersion responses and the relevant passage conditions are summarized in Table 1, for situations in which H_m and H_1 are small. We may close this section by noting that the application of the spin-temperature theory to inhomogeneously broadened paramagnetic spin systems would appear to give excellent agreement with experiment in the rapid passage regime.

Slow Passage

The slow passage response of inhomogeneous spin-systems in the previous section can be shown to give quantitative agreement with experiment in various limits. We first

TABLE 1

PASSAGE CONDITIONS AND CORRESPONDING FIRST HARMONIC SIGNALS IN INHOMOGENEOUSLY BROADENED SYSTEMS[a]

Adiabatic Passage Conditions: $\omega_m H_m \ll \gamma H_1^2$
Inhomogeneity conditions: ω_1 and $\gamma H_m < 1/T_3 \ll \Delta\omega_G$

Spectrometer mode	Passage conditions	First harmonic signal	Phase (relative to modulation)
Dispersion	$\omega_m T_1 \gg 1$ $\omega_m T_1 > \frac{1}{\gamma T_3 H_m}$	$\frac{\pi M_0 \omega_1 \gamma H_m G(\Delta)}{2D}$	π
Dispersion	$\omega_m T_1 \ll 1$	$\frac{\pi M_0 \omega_1 \gamma H_m \omega_m T_1 G(\Delta)}{2D}$	$\frac{\pi}{2}$
Dispersion	$\omega_m T_1 \ll 1$ $\omega_m T_1 < \frac{1}{\gamma T_3 H_m}$	Dispersion derivative	0
Absorption	$\omega_m T_1 \ll 1$ $\omega_m T_1 < 1/\gamma T_3 H_m$ $\gamma^2 H_1^2 T_1 < 1$	$\pi M_0 \omega_1 \gamma H_m dG(\Delta)/d\Delta$	0

[a] It should be noted that if the inhomogeneity condition ω_m, $\gamma H_1 < 1/T_3$ is not obeyed, significant distortions to the signal do not result until ω_1 or $\gamma H_m \geq \Delta\omega_G$.

consider the response under nonsaturating conditions when $1/T_3 \ll \Delta W_G$ (or $a \ll 1$). From Eqs. [47] and [49] we then have that

$$V(\Delta) = \omega_1 M_0 T_3 G(\Delta) \qquad [62]$$

It is easy to show, using the method of the Appendix, that the first harmonic response observed when magnetic field modulation is employed ($\gamma H_m < 1/T_3$) is the derivative of the absorption. Therefore the integrated first harmonic slow passage absorption response reveals the distribution function $G(\Delta)$, which is directly comparable to the first harmonic rapid passage responses previously discussed. This is an important result, as it provides a basic continuity between the spectra obtained from samples in which the concentrations of paramagnetic spins is increased, which often necessitates experimental observation under first rapid conditions and then slow passage conditions as the T_1 of the sample decreases (*11*). This prediction that the integrated first harmonic slow passage response and the first harmonic rapid passage response have the same form in inhomogeneously broadened systems affords excellent agreement with experiment (*11*).

The general form of the absorptive response or "absorption envelope" is given by Eq. [54] when the distribution of local fields is Gaussian. Perhaps the most interesting characteristics of this response concern the saturation behavior. It may be noted from Eq. [53] that if $T_1 = T_{ss}$, then $s = 1$ and the response may be written as

$$V(v) = \frac{\omega_1 M_0}{(2\pi)^{1/2}(1+\omega_1^2 T_1 T_3)} \left\{ a \int_{-\infty}^{\infty} \frac{e^{-y^2}\, dy}{a^2 + (v-y)^2} \right\}. \qquad [63]$$

The resonance therefore saturates in the usual manner discussed by Bloembergen *et al.* (*27*). It may be noted that this is the behavior that might be expected in the limit of very rapid spectral diffusion ($a \gg 1$) for which it may be shown that Eq. [63] reduces to

$$V(\Delta) = \frac{M_0 \omega_1}{1 + \omega_1^2 T_1 T_3} \left(\frac{T_3}{1 + \Delta^2 T_3^2} \right) \qquad [64]$$

which is the BPP (*27*) result, where T_3 corresponds to the T_2 of the system. If the assumption is made that $T_{ss} \ll T_1$ however, the absorption envelope becomes

$$V(v) = \frac{\omega_1 M_0}{(2\pi)^{1/2} \Delta\omega_G s} \left\{ as \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a^2 s^2 + (v - y)^2} \right\}. \qquad [65]$$

At the center of the inhomogeneously broadened resonance (i.e. $v = 0$) it is easily shown that

$$V(0) = \frac{\sqrt{2}\omega_1 M_0 e^{a^2 s^2}}{\Delta\omega_G s} [1 - \mathrm{erf}(as)] \qquad [66]$$

where $s = (1 + \omega_1^2 T_1 T_3)^{1/2}$.

This is the Castner (*5*) saturation curve result for inhomogeneously broadened systems. Castner has assembled abundant evidence to show that inhomogeneously broadened systems saturate in this manner. In the spin-temperature context, therefore, it may be concluded that if $T_{ss} \ll T_1$ in such systems, the spin temperature approach gives quantitative agreement with experiment.

The condition $T_{ss} \ll T_1$ deserves further discussion. The spin–lattice relaxation mechanisms of paramagnetic spins in a dilute random lattice are a subject of some interest. Experimental evidence indicates that a spectral diffusion–cross relaxation (*29*) mechanism is often dominant (*11*, *17*, *30*), whereby "isolated" spins experience spectral diffusion through the lattice until they encounter a fast relaxing center (FRC) with which they can cross-relax. The FRC is conjectured (*20*) to be a group of highly coupled spins that are in more direct contact with the lattice. The suggestion that $T_{ss} \ll T_1$ in such systems, therefore, is very reasonable as the spin–spin reservoir may be expected to be in much closer contact with the fast relaxing species than the more isolated Zeeman reservoir, due to the (secular) dipolar and exchange interactions.

The spin temperature approach indicates that the most general form of the saturation behavior of inhomogeneously broadened systems is given by

$$V(0) = \frac{\sqrt{2}\omega_1 M_0 e^{a^2 s^2}[1 - \mathrm{erf}(as)]}{\Delta\omega_G[(1 + \omega_1^2 T_1 T_3)(1 + \omega_1^2 T_1 T_{ss})]^{1/2}} \qquad [67]$$

where $s = [(1 + \omega_1^2 T_1 T_3)/(1 + \omega_1^2 T_{ss} T_3)]^{1/2}$. It is therefore important to realize that the observed saturation behavior may, in general, be expected to be an intermediary response between the "normal" saturation behavior of BPP and the $T_{ss} \ll T_1$ result. This observation indicates that some caution should be used in obtaining the spin packet width by the method employed by Castner (*5*). A more direct approach for obtaining this parameter, assuming magnetic field modulation is employed, is to increase the modulation amplitude (when $\omega_1 < 1/T_3$), and observe a pseudo-saturation of the first harmonic signal as H_m is increased through $\gamma H_m \approx 1/T_3$. This method is completely analogous to the method of obtaining the spin-packet width in the rapid passage regime.

A comparison of the value of a that may thus be determined with that obtained via the Castner (*5*) technique will then give an estimate of the relative values of T_1 and T_{ss} and detailed examination of the shape of the saturation curve should allow a determination of their absolute values.

Another primary result expressed by Eq. [54] is that the resonance spectra obtained under slow passage always have a Voigt lineshape, assuming that the distribution of local fields is Gaussian. This type of lineshape is observed experimentally (*11*), which is another verification of the theory.

Finally, the validity of the spin temperature approach in situations where spectral diffusion is very rapid ($a \gg 1$) can be demonstrated from the results of Clough and Scott (*15*). Briefly, in such situations the absorption may be written as

$$V(\Delta) = \frac{\omega_1 M_0 T_3}{1 + \omega_1^2 T_3^2 + \omega_1^2 T_1 T_3 + (v^2/a^2)(1 + \omega_1^2 T_3 T_{ss})}. \qquad [68]$$

In situations when the system is highly saturated, therefore,

$$V(0)/V(\Delta) = \Delta^2 T_3^2 T_{ss}/T_1 \qquad [69]$$

which dependence was experimentally observed (*15*).

In summary, therefore, these results conclusively demonstrate the validity of the spin temperature and spin packet assumptions as applied to inhomogeneously broadened electron spin systems in both rapid and slow passage situations. Furthermore, it is envisaged that a substantial clarification of the spin–relaxation mechanisms of the paramagnetic spin species may be achieved within the terms of this model.

APPENDIX

The first harmonic variation of the spin temperature β is required. The differential equation governing its time dependent evolution (Eq. [34]) may be written

$$\frac{d\beta}{dt} + \frac{\beta}{T_1} = \frac{\beta_L \omega_0 \Delta(t)}{T_1(\Delta(t)^2 + \omega_1^2 + D^2)} - \frac{\beta(\omega_1^2 + D^2)}{T_1(\Delta(t)^2 + \omega_1^2 + D^2)} - \frac{\beta \Delta(t)\dot{\Delta}(t)}{\Delta(t)^2 + \omega_1^2 + D^2} \qquad [70]$$

where $\Delta(t) = \Delta + \gamma H_m \sin \omega_m t$, $T_{1s} = T_1 T_{ss}/(T_1 - T_{ss})$, $\omega_1 = \gamma H_1$, T_1 is the Zeeman spin–lattice relaxation time and T_{ss} is the relaxation time of the spin–spin reservoir. The terms in $\Delta(t)$ are expanded in a Fourier series according to

$$\frac{\Delta(t)}{\Delta(t)^2 + \omega_1^2 + D^2} = \sum_p a_p e^{pi\omega_m t} \qquad [71]$$

$$\frac{1}{\Delta(t)^2 + \omega_1^2 + D^2} = \sum_q b_q e^{qi\omega_m t} \qquad [72]$$

$$\frac{\Delta(t)\dot{\Delta}(t)}{\Delta(t)^2 + \omega_1^2 + D^2} = \sum_l c_l e^{li\omega_m t}. \qquad [73]$$

The primary problem is to evaluate the coefficients b_q in Eq. [72], after which it is a relatively simple exercise to obtain the a_p and c_l coefficients of expressions [71] and [73]. Equation [72] may be rewritten as

$$\frac{1}{\Delta(t)^2 + \omega_1^2 + D^2} = \frac{1}{\Delta^2 + \omega_1^2 + D^2 + (\gamma^2 H_m^2/2) + i\gamma H_m \Delta(e^{i\theta} - e^{-i\theta}) - \gamma^2 H_m^2/4(e^{2i\theta} - e^{-2i\theta})} \qquad [74]$$

where $\theta = \omega_m t$. We let $\alpha = \Delta$, $\beta = D$ and $\gamma = \gamma H_m/2$ and obtain

$$\frac{1}{\Delta(t)^2 + \omega_1^2 + D^2} = \frac{1}{\sigma}\left(1 - \frac{x}{\sigma}\right)^{-1} \qquad [75]$$

where $\sigma = \alpha^2 + \beta^2 + \gamma^2$ and $x = 2i\alpha(e^{i\theta} - e^{-i\theta}) + \gamma^2(e^{2i\theta} + e^{-2i\theta})$.

The expression on the right-hand side of Eq. [75] is expanded in a Taylor series according to

$$\frac{1}{\sigma}\left(1 - \frac{x}{\sigma}\right)^{-1} = \frac{1}{\sigma}\sum_{n=0}^{\infty}\left(\frac{x}{\sigma}\right)^n. \qquad [76]$$

Noting that $x^n = (y+z)^n$ where $y = 2i\alpha(e^{i\theta} - e^{-i\theta})$ and $z = \gamma^2(e^{2i\theta} + e^{-2i\theta})$, the Binomial theorem may be employed to give

$$x^n = (y+z)^n = \sum_{m=0}^{n}\binom{n}{m} y^m z^{n-m}. \qquad [77]$$

Similarly

$$y^m = (2i\alpha\gamma)^m (e^{-i\theta} - e^{i\theta})^m = (2i\alpha)^m \sum_{p=0}^{m}\binom{m}{p}(-1)^{m-p} e^{-(m-p)i\theta} \qquad [78]$$

and

$$z^{n-m} = \gamma^{2(n-m)}(e^{2i\theta} + e^{-2i\theta})^{n-m} = \gamma^{2(n-m)} \sum_{q=0}^{n-m}\binom{n-m}{q} e^{(4q-2n-2m)i\theta}. \qquad [79]$$

Upon introducing [79] and [78] into [77], and subsequently into [76], we have that

$$\frac{1}{\sigma}\left(1 - \frac{x}{\sigma}\right)^{-1} = \sum_{n=0}^{\infty}\sum_{m=0}^{n}\sum_{p=0}^{m}\sum_{q=0}^{n-m} C_{nmpq}\, e^{(4q+2p+m-2n)i\theta} \qquad [80]$$

where

$$C_{mnpq} = \frac{n!\,(-1)^{m-p}(2i\alpha\gamma)^m \gamma^{2(n-m)}}{p!\,q!\,(m-p)!\,(n-m-q)!\,\sigma^{n+1}}.$$

We consider terms in the expansion [80] to $n = 1$, or to order $1/\sigma^2$. It is then fairly straightforward to show that

$$b_0 = 1/\sigma; \qquad b_1 = b_{-1} = -2i\alpha\gamma/\sigma; \qquad b_2 = b_{-2} = \gamma^2/\sigma^2 \qquad [81]$$

and that all higher frequency coefficients are equal to zero to second order in $1/\sigma$. Using the results expressed by Eq. [81] it may be shown for Eq. [73] that

$$\begin{aligned} c_0 &= 0 \\ c_1 = c_{-1} &= \frac{\alpha\gamma\omega_m}{\sigma}\left[1 - \frac{\gamma^2}{\sigma}\right] \\ c_2 = -c_2 &= \frac{-i\gamma^2\omega_m}{\sigma}\left[1 - \frac{2\alpha^2}{\sigma}\right] \\ c_3 = c_{-3} &= \frac{3\alpha\gamma^3\omega_m}{\sigma^2} \end{aligned} \qquad [82]$$

whereas, in Eq. [71]

$$\begin{aligned} a_0 &= \frac{\alpha}{\sigma}\left(1 + \frac{4\gamma^2}{\sigma}\right) \\ a_1 &= -a_{-1} = -\frac{i\gamma}{\sigma}\left(1 + \frac{1}{\sigma}(2\alpha^2 - \gamma^2)\right) \\ a_2 &= a_{-2} = -\frac{\alpha\gamma^2}{\sigma^2} \\ a_3 &= -a_{-3} = -\frac{i\gamma^3}{\sigma^2}. \end{aligned} \quad [83]$$

We now return to Eq. [70] which may be rewritten as

$$\frac{d\beta}{dt} + \frac{\beta}{T_1} = -\beta \sum_l (c_l + Ab_l)_e e^{il\omega_m t} + B \sum_p a_p e^{pi\omega_m t} \quad [84]$$

where $A = (D^2 + \omega_1^2)/T_{1s}$ and $B = \beta_L \omega_0/T_1$. Using the integrating factor e^{t/T_1} we have that

$$\frac{d\beta e^{t/T_1}}{dt} = -\beta(t)\, e^{t/T_1} \sum_l (c_l + Ab_l)\, e^{il\omega_m t} + B \sum_p a_p e^{(pi\omega_m + 1/T_1)t}. \quad [85]$$

We solve Eq. [85] to first order by the method of successive iterations, obtaining

$$\begin{aligned} \beta(t) &= e^{-t/T_1}\beta(0) - e^{-t/T_1}\int_0^t \beta(0) \sum_l (c_l + Ab_l)\, e^{li\omega_m t'}\, dt' \\ &+ B e^{-t/T_1} \int_0^t \sum_p a_p e^{(pi\omega_m + 1/T_1)t'}\, dt' \\ &+ B e^{-t/T_1} \int_0^t dt' \int_0^{t'} \sum_p a_p e^{(pi\omega_m + 1/T_1)t''} \sum_l (c_l + Ab_l)\, e^{li\omega_m t'}\, dt'' \\ &+ \beta(0)\, e^{-t/T_1} \int_0^t dt' \int_0^{t'} \sum_l (c_l + Ab_l)\, e^{li\omega_m t} \sum_n (c_n + Ab_n)\, e^{ni\omega_m t'}\, dt''. \end{aligned} \quad [86]$$

The first harmonic response in the limits $\omega_m T_1 \gg 1$ and $\omega_m T_1 \ll 1$ of each of the expressions on the right-hand side of Eq. [86] are now considered in order from term 1 to term 5.

Obviously there is no first harmonic response from term 1. Term 2 may be written, on performing the integration, as

$$② = -e^{-t/T_1}\beta(0) \sum_l \frac{(c_l + Ab_l)(e^{li\omega_m t} - 1)}{li\omega_m} \quad [87]$$

and the first harmonic response is therefore

$$②_1 = -\frac{e^{-t/T_1}\beta(0)\, 2c_1 \sin(\omega_m t)}{\omega_m} - \frac{e^{-t/T_1}\beta(0)\, A2b_1 \cos(\omega_m t)}{i\omega_m}. \quad [88]$$

As the resonance condition is observed for a time $t \leqslant 1/\omega_m$ this response is only large when $\omega_m T_1 \gg 1$.

Term 3, when integrated, becomes

$$③ = BT_1 \sum_p \alpha_p \cos(\phi_p)\, [e^{i(p\omega_m t - \phi_p)} - e^{-(t/T_1 + i\phi_p)}] \qquad [89]$$

where $\phi_p = \tan^{-1}(p\omega_m T_1)$. The first harmonic response is therefore

$$③_1 = BT_1\, a_q \cos\phi_1\, 2i \sin(\omega_m t - \phi_1). \qquad [90]$$

When $\omega_m T_1 \gg 1$, $\cos\phi_1$ approaches zero. Thus the response expressed by [90] is large only for $\omega_m T_1 < 1$.

The integration of term 4 yields

$$④ = -BT_1^2 \sum_p \sum_l a_p(c_l + Ab_l)\cos(\phi_p)\cos(\phi_{l+p})\, e^{i(\phi_p + \phi_{l+p})} \cdot [e^{i(l+p)\omega_m t} - e^{-t/T_1}]$$
$$+ e^{-t/T_1} BT_1 \sum_p \sum_l a_p(c_l + Ab_l)\cos\phi_p\, e^{i\phi_p}\left[\frac{e^{li\omega_m t} - 1}{li\omega_m}\right] \qquad [91]$$

and the first harmonic response is therefore

$$④_1 = -BT_1^2 \cos\phi_1 \left\{ \sum_{l+p=1} a_p(c_l + Ab_l)\cos\phi_p\, e^{-(\phi_p + \phi_1)}\, e^{i\omega_m t} \right.$$
$$\left. + \sum_{l+p=-1} a_p(c_l + Ab_l)\cos\phi_p\, e^{i(\phi_p - \phi_1)}\, e^{-i\omega_m t} \right\}$$
$$+ e^{-t/T_1} \frac{BT_1}{i\omega_m} \left\{ \sum_p a_p(c_1 + Ab_1)\cos\phi_p\, e^{-i\phi_p}\, e^{i\omega_m t} \right.$$
$$\left. - \sum_p a_p(c_{-1} + Ab_{-1})\cos\phi_p\, e^{-i\phi_p}\, e^{-i\omega_m t} \right\}. \qquad [92]$$

When $\omega_m T_1 \gg 1$, $\cos\phi_p \approx 1/p\omega_m T_1$ and the only terms in expression [92] that are large are those for which $p = 0$. Under these conditions $\phi_1 = \pi/2$ and it is then straightforward to show that the two terms of expression [92] cancel. On the other hand, when $\omega_m T_1 \ll 1$, the second term of [92] disappears and we obtain from the first term that

$$④_1 = -BT_1^2(a_0 c_1 + a_2 c_1 - a_1 c_2 - a_1 c_2)\, 2\cos\omega_m t - ABT_1^2(a_0 b_1 + a_1 b_0)\, 2i \sin\omega_m t \qquad [93]$$

where we have kept terms to order $1/\sigma^2$.

It can be shown, by exactly similar methods to those previously used, that the first harmonic response from term 5 is zero for $\omega_m T_1 \ll 1$, whereas when $\omega_m T_1 \gg 1$

$$⑤_1 = -\frac{\beta_0}{\omega_m^2}[2Ac_1 b_0 \cos\omega_m t - 6ic_1 c_2 \sin\omega_m t]. \qquad [94]$$

Upon collecting terms, noting that $\beta(0) = \beta_L \omega_0/\sigma_1$ where $\sigma_1 = \Delta^2 + \omega_1{}^2 + D^2$ and employing the relations [81], [82], and [83] together with those used in Eq. [74], we obtain that when $\omega_m T_1 \gg 1$

$$\beta_1(t) = \frac{\beta_L \omega_0 \Delta^2 \gamma H_m}{\sigma_1 \sigma}\left[1 - \frac{5\gamma^2 H_m^2}{8\sigma^2}\right]\sin(\omega_m t - \pi) + \frac{\beta_L \omega_0 D^2 \Delta^2 \gamma H_m}{\omega_m T_{1s} \sigma_1 \sigma^2}\sin\left(\omega_m t + \frac{\pi}{2}\right), \qquad [95]$$

whereas when $\omega_m T_1 \ll 1$

$$\beta_1(t) = \frac{\beta_L \omega_0 \omega_m T_1 \gamma H_m}{\sigma^2}\left[\frac{\gamma^2 H_m^2}{4} + \Delta^2 + \frac{\Delta^2 \gamma^2 H_m^2}{2\sigma}\right]\sin\left(\omega_m t - \frac{\pi}{2}\right)$$
$$+ \frac{\beta_L \omega_0 D^2 T_1 \gamma H_m}{\sigma^2 T_{1s}}\left[1 + \frac{2}{\sigma}\left(\Delta^2 - \frac{\gamma^2 H_m^2}{4}\right)\right]\sin(\omega_m t - \pi)$$
$$+ \frac{\beta_L \omega_0 \gamma H_m}{\sigma}\left[1 + \frac{1}{\sigma}\left(2\Delta^2 - \frac{\gamma^2 H_m^2}{4}\right)\right]\sin(\omega_m t). \quad [96]$$

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REFERENCES

1. Ludwig and Woodbury, "Solid State Physics," Vol. 13, Academic Press, New York, 1963.
2. G. F. Lancaster, "Electron Spin Resonance in Semiconductors," Hilger and Watts, London, 1966.
3. A. M. Stoneham, *Rev. Mod. Phys.* **41,** 82 (1969).
4. A. M. Portis, *Phys. Rev.* **91,** 1071 (1953).
5. T. G. Castner, *Phys. Rev.* **115,** 1506 (1959).
6. A. M. Portis, Technical Note No. 1, Sarah Mellon Scaife Radiation Laboratory, University of Pittsburgh 1955 (unpublished).
7. M. Weger, Bell Telephone Technical Publications, Monograph 3663 (1960).
8. M. Goldman, "Spin Temperature and Nuclear Magnetic Resonance in Solids," Oxford University Press, London, 1970.
9. V. A. Atsarkin and M. I. Rodak, *Sov. Phys. Uspekchi* **15,** 251 (1972).
10. D. F. Holcomb and J. J. Rehr, *Phys. Rev.* **183,** 773 (1969).
11. P. R. Cullis and J. R. Marko, *Phys. Rev.* B **11,** 4184 (1975).
12. P. W. Anderson, *J. Phys. Soc. Japan* **9,** 316 (1954).
13. P. R. Cullis and J. R. Marko, *Phys. Rev.* **B1,** 632 (1970).
14. S. Clough, *Phys. Rev.* **153,** 355 (1967).
15. S. Clough and C. A. Scott, *J. Phys. Ch.* (*Proc. Phys. Soc.*) **1,** 919 (1968).
16. D. R. Taylor, J. R. Marko, and I. G. Bartlett, *Sol. State Comm.* **14,** 295 (1974).
17. J. R. Klauder and P. W. Anderson, *Phys. Rev.* **125,** 912 (1962).
18. W. B. Mims, K. Nassau, and J. D. McGee, *Phys. Rev.* **123,** 2059 (1961).
19. B. N. Provotorov, *Soviet Phys. JETP* **14,** 1126 (1961).
20. W. Voigt and S. B. Bayer, *Akad. Wiss.* **1912,** 603 (1912).
21. D. W. Posener, *Aust. J. Phys.* **12,** 184 (1959).
22. A. G. Redfield, *Phys. Rev.* **98,** 1787 (1955).
23. G. Feher, *Phys. Rev.* **114,** 1219 (1959).
24. P. R. Cullis, unpublished data.
25. J. S. Hyde, *Phys. Rev.* **119,** 1483 (1960).
26. A. M. Portis, *Phys. Rev.* **100,** 1219 (1955).
27. P. R. Cullis, Ph.D. thesis, University of British Columbia, 1972.
28. N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73,** 679 (1948).
29. N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *Phys. Rev.* **114,** 445 (1959).
30. G. Yang and A. Honig, *Phys. Rev.* **168,** 271 (1968).