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SATURATION OF AN INHOMOGENEOUSLY BROADENED MAGNETIC RESONANCE LINE

G. R. KHUTSISHVILI

Tbilisi State University

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The saturation of an inhomogeneously broadened EPR line is investigated theoretically. The stationary case is considered. The imaginary part of the complex magnetic susceptibility χ'' is calculated. The investigation is carried out first on the basis of the theory of homogeneous saturation developed by Bloembergen, Purcell and Pound,[2] and then on the basis of the theory developed by Provotorov.[5,6] The shape and the width of the hole burnt out when an inhomogeneously broadened line is saturated are calculated.

1. WE consider a sample (a crystal) containing atoms or ions having spin. We suppose that the sample is subjected to a strong constant magnetic field (homogeneous or almost homogeneous). For a spin of a given kind we obtain a system of 2S + 1 levels (S is the effective spin of the atom or the ion). Generally speaking, these levels are not equidistant, owing to the effect of the intracrystalline electric field.

If the sample is subjected to a microwave field (the amplitude of which is considerably smaller than the magnitude of the basic field) at right angles to the basic field, then a maximum in the absorbed microwave power occurs when the frequency of this field coincides with the energy difference between any pair of neighboring levels divided by $\hbar$. For a given type of spin the number of maxima in the absorption curve is equal to 2S. For a free spin (more accurately when only effects due to the intracrystalline field are present) each peak would have the shape of a delta function. But in actual fact effects are present which bring about the broadening of the electron paramagnetic resonance peaks.

We consider a spin system consisting of identical spins (we do not exclude the case when spins of other types are present in the sample; we simply do not include them in the spin system under consideration). Portis[1] was the first one to indicate that there occur two types of broadening of magnetic resonance:

a) Homogeneous broadening—this is broadening due to causes which are internal with respect to the spin system. Examples of causes giving rise to homogeneous broadening: dipole-dipole interaction between identical spins, exchange interaction between spins, spin-lattice interaction.

b) Inhomogeneous broadening—this is broadening due to causes external with respect to the spin system. Examples of causes giving rise to inhomogeneous broadening: dipole-dipole interaction with other (i.e., nonidentical) spins, hyperfine interaction with nuclei, a scatter in the values of the gradient of the intracrystalline field, inhomogeneity of the external magnetic field.

Inhomogeneous broadening always occurs. If inhomogeneous broadening is negligible compared to homogeneous broadening, then it is said that one has a homogeneously broadened line. But if the inhomogeneous broadening considerably exceeds homogeneous broadening, then it is said that the resonance line is broadened inhomogeneously. The intermediate case is also possible when the homogeneous and the inhomogeneous broadening are both of the same order of magnitude.

When the amplitude of the alternating field is sufficiently small the distribution of the spins among the different levels is an equilibrium one. But if the amplitude of the alternating field is sufficiently large the excess of spins in the lower state diminishes, the absorption coefficient decreases accordingly, and we obtain the effect of the so-called saturation of a resonance. The problem of the saturation of a resonance in the case of a homogeneously broadened line was investigated by Bloembergen, Purcell and Pound[2] (we shall from now on refer to this paper as BPP), by Bloch,[3] by Redfield[4] and by Provotorov.[5,6] For an inhomogeneously broadened line the problem of saturation has been discussed by Portis.[1] However, it should be noted that experiments on stationary resonance can be performed in two ways (cf., below), and this is not taken into account in the paper by Portis.[1]

In order not to complicate our investigation we restrict ourselves to the case $S = 1/2$ (for those spins the resonance of which is being investigated). In this case the absorption line will have only a single peak.

2. We introduce a line shape function describing homogeneous broadening $\varphi(\omega - \omega_0)$. The integral of φ is normalized to unity. We introduce the quantity

$$T_2 = \pi\varphi(0). \quad (1)$$

We then introduce the line shape function describing inhomogeneous broadening $h(\omega - \omega_0)$. The integral of h is also normalized to unity. In analogy to T_2 we introduce the quantity T_2^*

$$T_2^* = \pi h(0). \quad (2)$$

The quantity ω_0 represents the central Larmor frequency, i.e.,

$$\omega_0 = \gamma H, \quad (3)$$

where γ is the gyromagnetic ratio, H is the magnitude of the external magnetic field (if the external field is inhomogeneous, H is the average value of the field). We note that from the point of view of an experiment it is more convenient to introduce in place of the distribution function with respect to the frequency the distribution function with respect to the field (however, the transition from the one to the other is trivial). The quantities $1/T_2$ and $1/T_2^*$ represent widths with respect to frequency respectively due to homogeneous and inhomogeneous broadening. Widths with respect to the field are obtained by division of γ.

In the case of a homogeneously broadened line the function $\varphi(\omega - \omega_0)$ is much broader than the function $h(\omega - \omega_0)$ and correspondingly $T_2 \ll T_2^*$. Here one can assume that $h(\omega - \omega_0) = \delta(\omega - \omega_0)$. But in the case of an inhomogeneously broadened line the function $h(\omega - \omega_0)$ is much broader than $\varphi(\omega - \omega_0)$, and correspondingly $T_2^* \ll T_2$.

The function $h(\omega - \omega_0)$ plays the role of the distribution function for the resonance frequencies. If $T_2^* \ll T_2$, one can assume that there exist spin packets of width of the order of $1/T_2$; each packet is described by the function φ, while the function $h(\omega - \omega_0)$ gives the envelope of these packets.

3. An experiment on the stationary saturation can be carried out in two ways.

a) A saturating alternating field is applied whose frequency is varied slowly (experimentally it is more convenient to vary the magnitude of the basic field) and the corresponding signal is measured.

b) A saturating alternating field of a definite frequency is applied. A second nonsaturating field is also applied, its frequency is varied and the corresponding signal is measured.

We denote by Ω and H_1 the frequency and the half-amplitude of the saturating alternating field, and by ω and h_1 the frequency and the half-amplitude of the alternating field, the corresponding signal from which is measured experimentally. In case a) above $\Omega = \omega$, $H_1 = h_1$; in case b) we have $\Omega \neq \omega$, $H_1 \gg h_1$.

In magnetic resonance experiments frequently one measures the imaginary part χ'' of the complex magnetic susceptibility which is proportional to the absorption coefficient. For the power absorbed in the sample we have the general expression

$$P(\omega, \Omega) = 2\omega\chi''(\omega, \Omega)h_1^2. \quad (4)$$

By $\chi''(\omega, \Omega)$ we have denoted χ'' in case b). In case a) it can be easily seen that $\chi''(\omega)$ is given by the formula

$$\chi''(\omega) = \chi''(\omega, \omega). \quad (5)$$

The object of the present paper is to calculate the signals obtained in cases a) and b) (i.e., the functions $\chi''(\omega)$ and $\chi''(\omega, \Omega)$) for both homogeneously and inhomogeneously broadened lines. For a homogeneously broadened line these results are well known, but we quote them here for convenience in presentation.

We note that the function $\chi''(\omega)$ for an inhomogeneously broadened line has been calculated in the papers by Portis[1] and by Castner[7] on the basis of the BPP theory. In the paper by Moran[8] the function $\chi''(\omega, \Omega)$ (for an inhomogeneously broadened line) was in fact calculated on the basis of Bloch's theory[3] but only for weak saturation.

In Secs. 4–7 below we shall be basing our results on the theory of saturation developed by BPP. In Sec. 8 we shall quote results obtained on the basis of the theory of saturation developed by Provotorov.[5,6]

4. We first consider the case of a homogeneously broadened line. We have

$$P(\omega, \Omega) = n(\Omega)\hbar\omega W(\omega), \quad (6)$$

where $n(\Omega)$ is the excess in the population of the lower spin level in the case of saturation by the field Ω, H_1; $W(\omega)$ is the probability of transition (per unit time) of a spin from one state to another one brought about by the alternating field ω, h_1. In accordance with BPP we have

$$n(\Omega) = n_0 / [1 + 2T_1W(\Omega)], \quad (7)$$

where n_0 is the equilibrium excess. T_1 is the spin-lattice relaxation time. Further we have[2]

$$W(\omega) = {}^1/_2\pi(\gamma h_1)^2\varphi(\omega-\omega_0). \quad (8)$$

Utilizing formulas (4)–(8) and taking into account the fact that

$${}^1/_2 n_0\gamma^2\hbar = \gamma\chi_0 H = \chi_0\omega_0$$

(χ_0 is the static susceptibility) we obtain

$$\chi''(\omega, \Omega) = \frac{{}^1/_2\pi\chi_0\omega_0\varphi(\omega-\omega_0)}{1+\pi T_2^{-1}s\varphi(\Omega-\omega_0)}, \quad (9)$$

where s is the saturation parameter for the resonance

$$s = (\gamma H_1)^2 T_1 T_2. \quad (10)$$

According to (5) the signal in case a) is obtained by substituting $\Omega = \omega$ into (9). Thus, in case a) saturation broadening occurs.

If, in particular, $\varphi(\omega-\omega_0)$ has the Lorentz shape

$$\varphi(\omega-\omega_0) = T_2/\pi[1+T_2^2(\omega-\omega_0)^2], \quad (11)$$

we obtain

$$\chi''(\omega) = \frac{{}^1/_2\chi_0\omega_0 T_2}{1+T_2^2(\omega-\omega_0)^2+s}. \quad (12)$$

Thus, for $\chi''(\omega)$ we obtain the Lorentz curve whose width is equal to

$$T_2^{-1}\sqrt{1+s}. \quad (13)$$

On the other hand, (9) yields in case b)

$$\chi''(\omega, \Omega) \propto \varphi(\omega-\omega_0)$$

(as a function of ω). In other words, as H_1 increases the quantity $\chi''(\omega, \Omega)$ diminishes, but the decrease is the same for all ω. Therefore, the shape of the absorption line and its width are not altered by saturation.

This result is easy to understand. Indeed, since the line is broadened homogeneously the energy received by the spin-system from the microwave field is distributed among all the spins and equilibrium is maintained in the spin system. Therefore, in the case of saturation at a fixed frequency the spin system is heated as a whole (in other words, the heating is characterized by a single spin temperature equal to the temperature of the lattice multiplied by $1 + \pi T_2^{-1} s\varphi(\Omega-\omega_0)$).

5. We proceed to the general case when the ratio between homogeneous and inhomogeneous broadening is arbitrary. The quantity $h(\omega'-\omega_0)d\omega'$ gives the probability that the resonance frequency lies in the interval $(\omega', d\omega')$. Generalization of (9) yields

$$\chi''(\omega, \Omega) = \frac{1}{2}\pi\chi_0\omega_0\int\frac{\varphi(\omega-\omega')h(\omega'-\omega_0)d\omega'}{1+\pi T_2^{-1}s\varphi(\Omega-\omega')} \quad (14)$$

(the limits of integration over ω' can be taken to be equal to $-\infty$ and $+\infty$, since the function $\varphi(x)$ falls off rapidly with increasing $|x|$). If $h(\omega-\omega_0) = \delta(\omega-\omega_0)$, then (14) reduces to (9).

We should note the following. In limiting cases (T_2^*/T_2 is sufficiently small or sufficiently large), formula (14) is exact. Doubt as to the validity of (14) can arise in the intermediate case when $T_2^* \sim T_2$. However, in future we shall be interested in the case $T_2^* \ll T_2$.

When the function $\varphi(x)$ is of the Lorentz form we can easily obtain

$$\int\chi''(\omega)d\omega = \pi\chi_0\omega_0/2\sqrt{1+s}. \quad (15)$$

In more general form we have

$$\int\chi''(\omega)d\omega = \frac{1}{2}\pi\chi_0\omega_0\int\frac{\varphi(y)dy}{1+\pi T_2^{-1}s\varphi(y)}. \quad (16)$$

This expression does not contain the function h. Therefore $\int\chi''(\omega)d\omega$ has the same value in the presence of inhomogeneous broadening as in its absence.

6. We consider in greater detail the case of an inhomogeneously broadened line $T_2^* \ll T_2$. Then in the region where $\varphi(\omega-\omega')$ is not small, $h(\omega'-\omega_0)$ hardly varies. Therefore, in the factor $h(\omega'-\omega_0)$ we can replace ω' by ω. We obtain

$$\chi''(\omega, \Omega) = \frac{1}{2}\pi\chi_0\omega_0 h(\omega-\omega_0)\int\frac{\varphi(\omega-\omega')d\omega'}{1+\pi T_2^{-1}s\varphi(\Omega-\omega')}. \quad (17)$$

We note that the quantity s given by formula (10) represents the saturation parameter for an individual spin packet in the case when the resonance condition is satisfied exactly.

The integral in (17) is a function of $\omega-\Omega$. Therefore, in case a) we have

$$\chi''(\omega) \propto h(\omega-\omega_0).$$

Thus, in the case of saturation $\chi''(\omega)$ falls off in the same manner for all ω, i.e., the shape and the width of the line do not change.

In the case that the function φ is of the Lorentz form we obtain

$$\chi''(\omega) = \pi\chi_0\omega_0 h(\omega-\omega_0)/2\sqrt{1+s}. \quad (18)$$

We now analyze expression (17). Let s be sufficiently large. For sufficiently small $|\omega-\Omega|$ the numerator and the denominator in the integrand are simultaneously (i.e., for the same range ω') large and, therefore, $\chi''(\omega, \Omega)$ is diminished at saturation. But if $|\omega-\Omega|$ is sufficiently large, then the second term of the denominator is large only for such values of ω' for which the numerator is small and therefore $\chi''(\omega, \Omega)$ is almost unchanged at saturation.

In other words, we find that burning out of a hole occurs in case b) at saturation of an inhomogeneously broadened line. This result can be easily understood.[1] In the case of saturation of an inhomogeneously broadened line by a microwave field of a definite frequency Ω only those spin packets are saturated for which the saturation parameter $\pi(\gamma H_1)^2 T_1 \varphi(\Omega - \omega')$ is sufficiently large. In this case an essential assumption is that the spin packets are independent of one another, and, therefore, no transfer of saturation occurs.

We note that in the case of independent spin packets case b) is equivalent to the case in which the resonance line is at first saturated at a definite place, and then the value of the microwave field is rapidly diminished and the whole line is traversed by the nonsaturating field during a time which is considerably smaller than the spin-lattice relaxation time.

Formula (17) can be rewritten in the following form:

$$\chi''(\omega, \Omega) = {}^1/_2\pi\chi_0\omega_0 h(\omega - \omega_0) F(\omega - \Omega, s), \qquad (19)$$

where

$$F(x, s) = \int_{-\infty}^{+\infty} \frac{\varphi(x+y)\,dy}{1 + \pi T_2^{-1} s\varphi(y)}. \qquad (20)$$

It can be easily seen that F(x, s) is an even function of x (one should take into account that the function $\varphi(y)$ is even). Further, we have that F(x, 0) = 1.

For weak saturation $s \ll 1$, and we obtain

$$\chi''(\omega, \Omega) = \chi''(\omega) = {}^1/_2\pi\chi_0\omega_0 h(\omega - \omega_0), \qquad (21)$$

i.e., the well known expression for a signal in the absence of saturation.

We note that formula (16) can be written in the following form:

$$\int \chi''(\omega)\,d\omega = {}^1/_2\,\pi\chi_0\omega_0 F(0, s). \qquad (22)$$

7. It is of interest to carry out a more detailed investigation of the hole burnt out when an inhomogeneously broadened line is saturated. We assume that the function φ has the Lorentz shape (11). Evaluation of (20) yields

$$F(x, s) = \frac{\xi^4 + \xi^2(4 + s - s/\sqrt{1+s}) + s^2/\sqrt{1+s}}{\xi^4 + \xi^2(4+2s) + s^2}, \qquad (23)$$

where

$$\xi = T_2 x = T_2|\omega - \Omega|. \qquad (24)$$

Expressions (19) and (23) determine the shape of the hole burnt out. It is of interest to investigate the case $s \gg 1$. We obtain

$$F(x, s) = (\xi^4 + s\xi^2 + s^{3/2}) \,/\, (\xi^2 + s)^2. \qquad (25)$$

The halfwidth of the hole can be determined from the condition F(x, s) = $1/2$. Thus, if $s \gg 1$ we obtain for the halfwidth of the hole the expression

$$\sqrt{s} \,/\, T_2 = \gamma H_1 \sqrt{T_1 / T_2}. \qquad (26)$$

The result obtained above can be described in the following manner. For $s \ll 1$ there is no saturation at all, $\chi''(\omega, \Omega)$ is given by formula (21). For $s \sim 1$ saturation of that packet occurs within which the saturation frequency lies. As s increases further, at first the neighboring and then the more distant spin packets become saturated and the width of the burnt out hole gradually increases.

This picture is valid as long as the width of the hole is considerably smaller than the width of the inhomogeneously broadened line $\gamma\Delta H \sim 1/T_2^*$. But if the width of the hole becomes of the order of $1/T_2^*$ then the whole inhomogeneously broadened line will be saturated. Equating (26) to the magnitude of $1/T_2^*$ we find that this occurs beginning with values of H_1 of the order of $\Delta H\sqrt{T_2/T_1}$.[1)]

8. The whole preceding discussion is based on the BPP theory. However, this theory is approximate, and some of its results are incorrect.

Provotorov has developed a consistent theory of saturation of a homogeneously broadened line which is valid when the conditions $T_2 \ll T_1$ and $H_1 < 1/\gamma T_2$ are satisfied. Using Provotorov's result for the absorbed power[6] one can determine the quantity $\chi''(\omega, \Omega)$

$$\chi''(\omega, \Omega) = \frac{1}{2}\pi\chi_0\omega_0\varphi(\omega - \omega_0) \times \frac{1 - \pi\gamma s T_2(\Omega - \omega_0)(\omega - \Omega)\varphi(\Omega - \omega_0)}{1 + \pi T_2^{-1} s[1 + \gamma T_2^2(\Omega - \omega_0)^2]\varphi(\Omega - \omega_0)}, \qquad (27)$$

where the dimensionless quantity γ is given by the formula

$$\hbar^2 T_1' \,/\, \overline{H^2} T_1 = \gamma T_2^2 \qquad (28)$$

(regarding the determination of the quantities T_1' and $\overline{H^2}$ cf., [6]). For $\gamma = 0$ formula (27) goes over into (9).

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1)This result can also be obtained in the following manner. The value of H_1 at which the whole line becomes saturated is determined by the approximate equality $\pi(\gamma H_1)^2 T_1 \varphi(1/T_2^*) \approx 1$. On the other hand, in accordance with (11), $\pi\varphi(1/T_2^*) \sim (T_2^*)^2/T_2$ (we take into account the fact that $T_2^* \ll T_2$). Substitution leads to $H_1 \sim \Delta H\sqrt{T_2/T_1}$.

In accordance with (5) and (27) we have

$$\chi''(\omega)=\frac{{}^1/_2\,\pi\chi_0\omega_0\varphi(\omega-\omega_0)}{1+\pi T_2^{-1}s[1+\gamma T_2^2(\omega-\omega_0)^2]\varphi(\omega-\omega_0)}. \quad (29)$$

Formula (29) gives that in case a) depending on the value of the quantity γ both broadening and narrowing can occur as a result of saturation. If, in particularly, $\varphi(\omega-\omega_0)$ is of the Lorentz shape (11), then for $\chi''(\omega)$ we obtain a Lorentz curve of width (cf., with (13))

$$\frac{1}{T_2}\sqrt{\frac{1+s}{1+\gamma s}}. \quad (30)$$

According to (27) in case b) the shape of the absorption line is altered in an essential manner at saturation. This question has been analyzed in reference [6] for the case $s \gg 1$.

One can easily further generalize the results obtained in Secs. 5–7. The formula generalizing the result (14) will be obtained if on the right hand side of (27) we replace ω_0 by ω', multiply the whole expression by $h(\omega'-\omega_0)$ and integrate over ω'. In particular, for an inhomogeneously broadened line we obtain in place of (19)

$$\chi''(\omega,\Omega)={}^1/_2\pi\chi_0\omega_0 h(\omega-\omega_0)\Phi(\omega-\Omega,\,s,\,\gamma), \quad (31)$$

where

$$\Phi(x,s,\gamma)=\int_{-\infty}^{+\infty}\frac{[1-\pi\gamma sT_2xy\varphi(y)]\varphi(x+y)}{1+\pi T_2^{-1}s(1+\gamma T_2^2y^2)\varphi(y)}dy. \quad (32)$$

It can be easily seen that $\Phi(x, s, \gamma)$ is an even function of x. Further, we have that $\Phi(x, 0, \gamma) = 1$, $\Phi(x, s, 0) = F(x,s)$.

According to (31) in case a) for an inhomogeneously broadened line we again obtain that $\chi''(\omega) \propto h(\omega-\omega_0)$.

We can easily obtain a generalization of formula (22):

$$\int\chi''(\omega)\,d\omega={}^1/_2\pi\chi_0\omega_0\Phi(0,s,\gamma). \quad (33)$$

Further, if $\varphi(\omega-\omega_0)$ has a Lorentz shape, we obtain (cf., with (18))

$$\chi''(\omega)=\pi\chi_0\omega_0 h(\omega-\omega_0)\,/\,2\sqrt{(1+s)(1+\gamma s)}. \quad (34)$$

For a Lorentz shape of the function φ evaluation of (32) leads to the result

$$\Phi(x,s,\gamma)=\frac{\xi^4+\dfrac{\xi^2}{1+\gamma s}\left[(4+s+\gamma s)-\dfrac{s(1+\gamma+2\gamma s)}{\sqrt{(1+s)(1+\gamma s)}}\right]+\dfrac{s^2(1-\gamma)^2}{\sqrt{1+s}(1+\gamma s)^{5/2}}}{\xi^4+\dfrac{2\xi^2}{1+\gamma s}(2+s+\gamma s)+\dfrac{s^2(1-\gamma)^2}{(1+\gamma s)^2}}. \quad (35)$$

Formulas (31) and (35) determine the shape of the hole burnt out. In the limiting case $s \gg 1$, $\gamma s \gg 1$ we obtain

$$\Phi(x,s,\gamma)=\frac{\xi^4+(1-\gamma^{-1/2})^2\xi^2+(1-\gamma)^2/\gamma^{5/2}s}{\xi^4+2(1+\gamma^{-1})\xi^2+(1-\gamma)^2\gamma^{-2}}. \quad (36)$$

9. The discussion given in the present paper assumes that the fundamental assumption of Portis[1] regarding the independence of the spin packets is satisfied, and, therefore, it was assumed that transfer of saturation between packets does not occur.

Experiments show that cases occur when this assumption is approximately satisfied (cf., for example,[7,9,10]), and also that cases exist when it is completely unjustified and, therefore, an inhomogeneously broadened line experiences homogeneous saturation (cf., for example, [8,11,12]). In this connection it is of interest to generalize the investigation made in the present paper and to take into account the transfer of saturation between spin packets.

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