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MAGNETIC RESONANCE SATURATION IN CRYSTALS

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A kinetic equation for magnetic resonance in solids is deduced from the quantum equation for the density matrix. With the aid of this equation, equations describing the variation of the absorption and dispersion signals with increasing high-frequency field amplitude H_1 are derived. According to these equations, the absorption and dispersion lines become narrower, and $\chi''(\omega, H_1)$ decreases at a faster rate than $\chi'(\omega, H_1)$ with increasing H_1, in agreement with previous experimental observations.[2]

THE fundamental equation of the theory of magnetic resonance in solids is given by Bloembergen, Purcell, and Pound[1]:

$$dn(t)/dt = -\gamma^2 H_1^2 \pi g(\Delta) n(t) + (n_0 - n(t))/T_1. \quad (1)$$

Here $n(t)$ is the difference in the populations of the two levels between which the high-frequency field induces transitions, n_0 is the equilibrium population difference of the two levels, $\Delta = \omega - \omega_0$, $\gamma = \mu/\hbar$, ω and H_1 are the frequency and amplitude of the high-frequency field, $\omega_0 = \mu H_0/\hbar$, $s\mu$ is is the magnetic moment of the particle, H_0 is the dc magnetic field, and T_1 is the spin-lattice relaxation time.

This equation was deduced from qualitative considerations. While in principle it provides a correct description of the phenomena observed in the region of weak saturation, this equation disagrees strongly with experiment in the region of strong saturation.[2,3] For example, as H_1 is increased the absorption line first broadens but with further increase in H_1, it becomes narrow again and acquires a Lorentz shape. Such narrowing cannot be deduced from Eq. (1). According to Eq. (1) the absorption line shape has the form

$$P(\Delta, H_1) = \frac{\hbar\omega}{2}\frac{\varepsilon(\Delta) n_0}{1 + \varepsilon(\Delta) T_1}, \quad \varepsilon(\Delta) = \gamma^2 H_1^2 \pi g(\Delta). \quad (2)$$

It can be immediately seen from this expression that the absorption line should widen with increasing H_1 for all values of H_1.

Our problem is to obtain a kinetic equation from the rigorous equation for the density matrix and to derive the magnetic resonance equations from this kinetic equation. The equation for the density matrix has in our case the form

$$\frac{\partial\rho(t)}{\partial t} = -\frac{i}{\hbar}\Big[-\hbar\omega_0 \hat{I}_z + \frac{\mu H_1}{2}(\hat{I}^1 e^{i\omega t} + \hat{I}^{-1} e^{-i\omega t}) + \hat{H}_{dip}, \rho(t)\Big],$$

$$\hat{H}_{dip} = g^2\hbar^2 \sum_{i>k}\left(\frac{\hat{\mathbf{s}}_i\hat{\mathbf{s}}_k}{r_{ik}^3} - 3\frac{(\hat{\mathbf{s}}_i\mathbf{r}_{ik})(\hat{\mathbf{s}}_k\mathbf{r}_{ik})}{r_{ik}^5}\right). \quad (3)$$

Here $\hat{I}_x$, $\hat{I}_y$, $\hat{I}_z$ are the projection operators of the total spin on the coordinates axes, $\hat{I}^{\pm 1} = \hat{I}_x \pm i\hat{I}_y$, $\mathbf{s}_i$ is the spin operator situated on the i-th crystal lattice site, and $\mathbf{r}_{ik}$ is a vector connecting the i-th and k-th crystal lattice sites. For simplicity we have neglected here all interactions other than the magnetic dipole-dipole interaction.

To make clear the nature of the physical processes occurring in the spin system under the action of the high-frequency field, it is convenient to transform to a rotating coordinate system. As is well known, this is done with the aid of the transformation[2,4]

$$\rho(t) = \exp(i\omega\hat{I}_z t)\, \rho'(t) \exp(-i\omega\hat{I}_z t), \quad (4)$$

where $\rho'(t)$ is the density matrix in the rotating coordinate system. Substituting (4) into (3), we obtain

$$\frac{\partial\rho'(t)}{\partial t} = -\frac{i}{\hbar}\Big[\hbar\Delta\hat{I}_z + \frac{\mu H_1}{2}(\hat{I}^1 + \hat{I}^{-1}) + \sum_{m=-2}^{+2} \hat{H}^m e^{i\omega m t}, \rho'(t)\Big]. \quad (5)$$

Here $\hat{H}^0$ is the secular part of the dipole-dipole interaction, which commutes with $\hat{I}_z$. Rapidly oscillating terms of the type $\hat{H}^m e^{im\omega t}$ can be neglected, since they can give a significant contribution only in the satellites.[2,4]

The initial conditions in the rotating coordinate system will have the form

$$\rho_0' = \frac{\exp\{(\hbar\omega_0\hat{I}_z - \hat{H}^0)/kT_0\}}{\operatorname{Sp}\exp\{(\hbar\omega_0\hat{I}_z - \hat{H}^0)/kT_0\}}. \tag{6}$$

(In the usual system of coordinates we assume statistical equilibrium at the initial moment of time.)

From Eq. (5) it is easy to see that

$$\operatorname{Sp}\rho'(t)\,(\hat{H} + \tfrac{1}{2}\mu H_1(\hat{I}^1 + \hat{I}^{-1})) = \text{const};$$
$$\hat{H} = \hbar\Delta\hat{I}_z + \hat{H}^0. \tag{7}$$

Below, we shall find this relation necessary for the selection of the correct solution of Eq. (5).

Going over in Eq. (5) to the interaction representation

$$\rho'(t) = e^{-i\hat{H}t/\hbar}\rho''(t)\,e^{i\hat{H}t/\hbar}, \tag{8}$$

we obtain for $\rho''(t)$

$$\partial\rho''(t)/\partial t = -i\hbar^{-1}[V(t), \rho''(t)], \tag{9}$$

$$V(t) = \tfrac{1}{2}\mu H_1 e^{i\hat{H}t/\hbar}(\hat{I}^1 + \hat{I}^{-1})\,e^{-i\hat{H}t/\hbar}. \tag{10}$$

To derive the kinetic equation we use Zwanzig's method,[5] the gist of which is the application of the projection operator $\hat{P}$. Let us divide the density matrix $\rho''(t)$ into two parts:

$$\rho''(t) = \rho_1(t) + \rho_2(t), \quad \rho_1(t) = \hat{P}\rho''(t),$$
$$\rho_2(t) = (1 - \hat{P})\,\rho''(t).$$

where $\hat{P}$ is the projection operator which extracts from the density matrix $\rho''(t)$ the part that is diagonal in the representation in which $\hat{I}_z$ and $\hat{H}^0$ are simultaneously diagonal. (In what follows we shall always be using this representation.) Multiplying Eq. (9) from the left by $\hat{P}$ and $1 - \hat{P}$, we obtain respectively

$$\partial\rho_1(t)/\partial t = -i\hbar^{-1}\hat{P}L(t)\,\rho_2(t), \tag{11}$$

$$\partial\rho_2(t)/\partial t = -i\hbar^{-1}\hat{L}(t)\,\rho_1(t) - i\hbar^{-1}(1 - \hat{P})\,\hat{L}(t)\,\rho_2(t), \tag{12}$$

where the operator $\hat{L}(t)$ is defined by the relation

$$\hat{L}(t) = [V(t), \rho(t)].$$

In Eq. (11) we have omitted the term $\hat{P}\hat{L}(t)\rho_1(t)$, which is equal to zero because the diagonal matrix elements of the operator $[V(t), \rho_1(t)]$ are equal to zero [see the definition (10)]. For the same reason the factor $1-\hat{P}$ is omitted from the first term of the right member of Eq. (12).

Multiplying Eq. (12) on the left by an operator $\hat{A}(t)$ satisfying the operator equation

$$\partial\hat{A}(t)/\partial t = i\hbar^{-1}\hat{A}(t)\,(1 - \hat{P})\,\hat{L}(t), \tag{13}$$

we obtain

$$\rho_2(t) = \hat{A}^{-1}(t)\left(\rho_2(0) - i\hbar^{-1}\int_0^t dt'\,\hat{A}(t')\,\hat{L}(t')\,\rho_1(t')\right). \tag{14}$$

Here the operator $\hat{A}^{-1}(t)$ is defined by the relation $\hat{A}^{-1}(t)\,\hat{A}(t) = 1$. In virtue of the relations (6) and (8), we can write $\rho_2(0) = 0$. Substituting Eq. (14) in Eq. (11), we find

$$\rho_1(t) = -\frac{1}{\hbar^2}\int_0^t dt''\int_0^{t''} dt'\,\hat{P}\hat{L}(t'')\,\hat{A}^{-1}(t'')\,\hat{A}(t')\,\hat{L}(t')\,\rho_1(t') + \rho_1(0). \tag{15}$$

If we now expand the operators $\hat{A}^{-1}(t)$ and $\hat{A}(t)$ in this equation in a series in the small quantity $\hat{L}(t)$ and discard all terms except those quadratic in $\hat{L}(t)$, then we arrive at the equation for the diagonal part of the density matrix

$$\rho_1(t) = -\frac{1}{\hbar^2}\int_0^t dt''\int_0^{t''} dt'\,\hat{P}\hat{L}(t'')\,\hat{L}(t')\,\rho_1(t') + \rho_1(0). \tag{16}$$

With the aid of this equation we shall now calculate the difference $\rho_1(t + \tau) - \rho_1(t)$ for $\hbar/H_{\text{loc}} \ll \tau \ll \hbar/\mu H_1$, where $H_{\text{loc}} = \mu/d^3$, and d is the separation between neighboring magnetic moments in the crystal lattice:

$$\rho_1(t + \tau) - \rho_1(t) = -\frac{1}{\hbar^2}\int_t^{t+\tau} dt''\int_0^{t''} dt'\,\hat{P}\,[V(t'')\,[V(t'), \rho_1(t')]]. \tag{17}$$

Expressing the operators occurring in V(t) as Fourier integrals,[6]

$$\hat{I}^{\pm 1}(t) = \exp\left(\frac{i}{\hbar}\hat{H}^0 t\right)\hat{I}^{\pm 1}\exp\left(-\frac{i}{\hbar}\hat{H}^0 t\right) = \int_{-\infty}^{+\infty} d\omega\,\hat{I}_\omega^{\pm 1}e^{i\omega t},$$

$$\hat{I}_\omega^{\pm 1} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\,e^{-i\omega t}\exp\left(\frac{i}{\hbar}\hat{H}^0 t\right)\hat{I}^{\pm 1}\exp\left(-\frac{i}{\hbar}\hat{H}^0 t\right), \tag{18}$$

we obtain, upon taking

$$\exp(i\Delta\hat{I}_z t)\,\hat{I}^{\pm 1}\exp(-i\Delta\hat{I}_z t) = \hat{I}^{\pm 1}\exp(\pm i\Delta t),$$

into account

$$\rho_1(t + \tau) - \rho_1(t) = -\left(\frac{\mu H_1}{2\hbar}\right)^2\int_t^{t+\tau} dt''\int_0^{t''} dt'\int_{-\infty}^{+\infty} d\omega''\int_{-\infty}^{+\infty} d\omega'\exp(i\omega''t'' + i\omega't')$$
$$\times\{\hat{P}\,[\hat{I}_{\omega''}^{1}\,[\hat{I}_{\omega'}^{-1}, \rho_1(t')]]\exp(i\Delta(t'' - t'))$$
$$+ \hat{P}\,[\hat{I}_{\omega''}^{-1}\,[\hat{I}_{\omega'}^{1}, \rho_1(t')]]\exp(-i\Delta(t'' - t'))\}.$$

In the right member of this equality we have omitted the vanishing terms

$$\hat{P}\,[\hat{I}^1(t'')\,[\hat{I}^1(t'), \rho_1(t')]].$$

If it is now recalled that $\rho_1(t')$ is a diagonal operator, and the operator $\hat{I}_\omega^{\pm 1}$ has, by virtue of Eq. (18), nonvanishing matrix elements only for transitions with an energy change $\hbar\omega$, then it is easy to see that

$$\hat{P}\,[\hat{I}_{-\omega''}^{1}[\hat{I}_{\omega'}^{-1}, \rho_1(t')]]$$
$$= \delta(\omega'' + \omega')\,\hat{P}'\,[\hat{I}_{-\omega''}^{1}\,[\hat{I}_{\omega''}^{-1}, \rho_1(t')]]. \tag{19}$$

[The operator $\hat{P}'$, besides separating out the diagonal parts of the operators that follow, also eliminates the singular functions $\delta(0)$ contained in the diagonal matrix elements of the operators $\hat{I}^1_\omega \hat{I}^{-1}_{-\omega}$ and $\hat{I}^{-1}_\omega \hat{I}^1_{-\omega}$ by definition (18).] Consequently,

$$\rho_1(t+\tau) - \rho_1(t) = -\left(\frac{\mu H_1}{2\hbar}\right)^2 \int\limits_t^{t+\tau} dt'' \int\limits_0^{t''} dt' \int\limits_{-\infty}^{+\infty} d\omega'' \{\hat{P}' [\hat{I}^1_{-\omega''} [\hat{I}^{-1}_{\omega''}, \rho_1(t')]] \times \exp[i(\omega'' + \Delta)(t'' - t')] + \hat{P}' [\hat{I}^{-1}_{\omega''} [\hat{I}^1_{-\omega''}, \rho_1(t')]] \times \exp[-i(-\omega'' + \Delta)(t'' - t')]\}.$$

Changing now the variable of integration in the second component in the curly brackets of this equation from ω'' to $-\omega''$ and using the easily verified relation

$$\hat{P}' [\hat{I}^1_{\omega''} [\hat{I}^{-1}_{-\omega''}, \rho_1(t')]] = \hat{P}' [\hat{I}^{-1}_{-\omega''} [\hat{I}^1_{\omega''}, \rho_1(t')]],$$

we obtain, after integrating over t′,

$$\rho_1(t+\tau) - \rho_1(t) = -\frac{1}{2}\left(\frac{\mu H_1}{\hbar}\right)^2 \int\limits_t^{t+\tau} dt'' \int\limits_{-\infty}^{+\infty} d\omega'' \frac{\sin[(\omega'' + \Delta)t'']}{\omega'' + \Delta} \hat{P}' \times [\hat{I}^1_{\omega''} [\hat{I}^{-1}_{-\omega''}, \rho_1(t)]].$$

We have replaced here $\rho_1(t')$ by $\rho_1(t)$ in the integration over t′. This change is completely justified in our case, for when $H_1 \ll H_{loc}$, $\rho_1(t)$ changes markedly in the time interval $\hbar/\mu H_1$, whereas

$$\int\limits_{-\infty}^{+\infty} d\omega'' \cos[(\omega'' + \Delta)(t'' - t')] \hat{P}' [\hat{I}^1_{\omega''} [\hat{I}^{-1}_{-\omega''}, \rho_1(t')]]$$

is a rapidly changing function of $t'' - t'$, which differs from zero only in the region $|t'' - t'| \lesssim \hbar/\mu H_{loc}$, since the spectral width of the operators $\hat{I}^{\pm 1}_\omega$ is $\sim \mu H_{loc}/\hbar$. For the same reason we can replace $\rho_1(t+\tau) - \rho_1(t)$ by $\tau d\rho_1(t)/dt$ when $\tau \ll \hbar/\mu H_1$.

The integration over ω'' in Eq. (21) is easily accomplished, for when $\hbar/\mu H_{loc} \ll t''$ the function $\sin[(\omega'' + \Delta)t'']/(\omega'' + \Delta)$ can be replaced by $\pi\delta(\omega'' + \Delta)$. This comes about because the function $\hat{P}'[\hat{I}^1_{\omega''}[\hat{I}^{-1}_{\omega''}, \rho_1(t')]]$ changes with frequency much more slowly than $\sin[(\omega'' + \Delta)t'']/(\omega'' + \Delta)$ when $t'' \gg \hbar/\mu H_{loc}$. With this in mind, we find

$$\frac{d\rho_1(t)}{dt} = -\frac{\pi}{2}\left(\frac{\mu H_1}{\hbar}\right)^2 \hat{P}' [\hat{I}^1_{-\Delta} [\hat{I}^{-1}_{\Delta}, \rho_1(t)]]. \tag{22}$$

We shall now show that this equation corresponds to the conservation law

$$\frac{d}{dt} \mathrm{Sp} \{\rho_1(t) \hat{H}\} = 0. \tag{23}$$

(This relation derives from Eq. (7) under the condition $H_1 \ll H_{loc}$.) In fact, after making use of Eq. (22), we obtain

$$\frac{d}{dt} \mathrm{Sp} \{\rho_1(t) \hat{H}\} = -\frac{\pi}{2}\left(\frac{\mu H_1}{\hbar}\right)^2 \mathrm{Sp} \{\hat{P}' [\hat{H}, \hat{I}^1_{-\Delta}] [\hat{I}^{-1}_{\Delta}, \rho_1(t)]\}.$$

We note further that the commutator $[\hat{H}, \hat{I}^1_{-\Delta}]$ vanishes, since it is easy to obtain from definition (18) the relations

$$[\hat{H}^0, \hat{I}^1_{-\Delta}] = -\hbar\Delta \hat{I}^1_{-\Delta}, \qquad [\hat{I}_z, \hat{I}^1_{-\Delta}] = \hat{I}^1_{-\Delta}. \tag{24}$$

From this we obtain the desired Eq. (23).

Because of Eq. (24), any function of the operator $\hat{H}$ will commute with the operator $\hat{I}^1_{-\Delta}$. Hence the stationary solution of Eq. (22) will be an arbitrary function $\rho_{st} = f(\hat{H})$. In order to find the actual solution it is necessary to require that the solution $\rho_{st} = f(\hat{H})$ possess, by virtue of the homogeneity of our macroscopic system, the property of quasi-independence of the separate parts of the system $f(\hat{H}) = f(\hat{H}_1) f(\hat{H}_2)$. Here $\hat{H}_1$ and $\hat{H}_2$ refer to any two arbitrarily chosen parts of the system for which $\hat{H}_1 + \hat{H}_2 \approx \hat{H}$. The only normalized solution of this type would be

$$\rho_{st} = \exp(-\hat{H}/kT^*)/\mathrm{Sp}\exp(-\hat{H}/kT^*). \tag{25}$$

The quantity T^* can be defined by making use of Eq. (23):

$$T^* = T_0 \frac{\Delta^2 + \mathrm{Sp}(\hat{H}^0)^2/\mathrm{Sp}\,\hat{I}_z^2}{\omega_0\Delta + \mathrm{Sp}(\hat{H}^0)^2/\mathrm{Sp}\,\hat{I}_z^2}. \tag{26}$$

(In deriving this relation it has been assumed that $\hbar\omega_0/kT_0$ and $\hbar\Delta/kT^*$ are small in magnitude.)

As a consequence of the definitions (4) and (8) it is possible to substitute $\rho''(t)$ in place of $\rho(t)$ in the calculation of the mean values of $\hat{H}^0(t) = \mathrm{Sp}[\hat{H}^0 \rho(t)]$ and $\hat{I}_z(t) = \mathrm{Sp}[\hat{I}_z \rho(t)]$. Taking ρ_{st} from Eq. (27) and ρ_0 from Eq. (6), we obtain when $\Delta = 0$

$$\mathrm{Sp}(\hat{H}^0 \rho_0) = \mathrm{Sp}(\hat{H}^0 \rho_{st}), \qquad \mathrm{Sp}(\hat{I}_z \rho_{st}) = 0,$$

because $\hbar\omega_0/kT_0$ and $\hbar\Delta/kT^*$ are small and because $\mathrm{Sp}(\hat{I}_z \hat{H}_0) = 0$, as can be verified by direct calculation. This means that the average value of the energy of the dipole-dipole interaction in the case $\Delta = 0$ is not changed after the high-frequency field is turned on, and the average value of the projection of the total spin $I_z(t)$ tends to zero in accordance with Eq. (1).

A completely different situation arises in the case $\Delta \neq 0$. In this case the absorption of each quantum of the high frequency field is accompanied by a change of $\hbar\Delta$ in the dipole-dipole energy. This process leads to a limitation of the absorbing capability of the spin system. As a consequence $I_z(t)$ no longer approaches zero, but

$$I_{z\,st} = \frac{\hbar\omega_0}{kT_0} \frac{\Delta^2}{\Delta^2 + \mathrm{Sp}(\hat{H}^0)^2/\mathrm{Sp}\,\hat{I}_z^2}. \tag{27}$$

Here $\mathrm{Sp}\,(\hat{H}^0)^2/\mathrm{Sp}\,\hat{I}_z^2 \sim \langle\omega^2\rangle$, where $\langle\omega^2\rangle$ is the second moment of the absorption line. Hence, for resonant frequencies within the absorption line, $I_{z\,\mathrm{st}}$ can attain values $\sim I_{z0}/2$, whereas Eq. (1) gives zero for $I_{z\,\mathrm{st}}$ under these conditions. This contradiction is not accidental, because Eq. (1) does not take into account changes in the energy of the dipole-dipole interaction in the saturation process, which leads to a cessation of absorption of high-frequency quanta at values of I_z that are different from zero.

A comparison of the stationary solution, Eq. (25), with the initial value of the density matrix, Eq. (6), shows that the application of a sufficiently weak high-frequency field leads only to a change in the exponents of the coefficients for the operators $\hat{I}_z$ and $\hat{H}^0$. This change in $\rho_1(t)$ is due to the strong disordering influence of the dipole-dipole interaction. Before the application of the high-frequency field the magnetic dipoles of the spin system precess incoherently about the constant magnetic field. Consequently the components of transverse magnetization equal zero.

The influence of the high-frequency field is manifest in the emergence of coherent precession of the magnetic moments, i.e., in the appearance of transverse components of magnetization M_x and M_y. The dipole-dipole interaction, on the other hand, tends to bring the spin system to a state of equilibrium with $M_x = M_y = 0$. Lowe and Norberg[7] measured directly the decay time of the transverse magnetization. It turned out to be equal to $\sim\hbar/\mu H_{\mathrm{loc}}$. Therefore in the case of sufficiently weak high frequency fields we can consider, with an accuracy of $\sim H_1/H_{\mathrm{loc}}$, that the spin system will be characterized at every instant of time by an equilibrium partition function. The most general form of the equilibrium partition function is[8]

$$\rho_1(t) = \exp(\alpha(t)\hat{I}_z + \beta(t)\hat{H}^0)/\mathrm{Sp}\exp(\alpha(t)\hat{I}_z + \beta(t)\hat{H}^0). \tag{28}$$

All of the foregoing has pertained to the case in which there is no contact between the spin system and the lattice. However it is obvious that all the above reasoning is appropriate also for the case $\hbar/\mu H_{\mathrm{loc}} \ll T_1$ (T_1 is the spin-lattice relaxation time). Since this condition is fulfilled almost always in solids, we shall consider Eq. (28) as valid in solids even when spin-lattice interaction is present.

It is easily seen that the form of the solution (28) incorporates solutions corresponding to the BPP equation as a special case. In fact, in the two-level BPP model it is assumed that the levels corresponding to the same projections I_z have the same populations in the saturation process. Such a population distribution is obtained if $\beta(t)$ is set equal to zero in Eq. (28). Then, from the equations introduced below [see (36) and (37)], it is seen that for a value of $I_z(t)$ proportional to the population difference of the levels, an equation of the BPP type is obtained.

It is interesting to note that a density matrix of the form

$$\rho_1(t) = C\exp(\alpha(t)\hat{I}_z) \tag{29}$$

cannot, generally speaking, be a solution of Eq. (22) because the exact conservation law (23) is not obeyed when $\rho_1(t)$ is in the form (29). In fact, noting that the normalization condition $\mathrm{Sp}\,\rho_1(t) = 1$ gives $C = (2s+1)^{-N}$, where s is the spin of an individual particle and N is the total number of particles in the sample [$\alpha(t)$ and $\beta(t)$ can be considered small if the initial temperatures are not too low], we obtain

$$\frac{\partial}{\partial t}\mathrm{Sp}\,(\rho_1(t)\hat{H}) = \alpha'(t)\hbar\Delta\,(2s+1)^{-N}\,\mathrm{Sp}\,\hat{I}_z^2. \tag{30}$$

From the equality obtained it is obvious that the rigorous conservation law (23) is compatible with the form of the solution (29) and with the BPP equation corresponding to it only if $\Delta = 0$. Consequently the BPP equation can be considered correct only when $\Delta = 0$. This explains why the spin-lattice relaxation times measured by Redfield in the course of using the BPP equation for the analysis of his experiment were found to be correct, in spite of the fact that the absorption line observed under strong saturation failed to coincide with the theoretical curve. The point is that the saturation curve was taken by Redfield precisely at $\Delta = 0$, where the BPP equation can be considered correct. But measuring the shape of the absorption line, associated with a transition in the region $\Delta \neq 0$ in the strong saturation case, led Redfield perfectly naturally to results that were incompatible with the BPP equation.

In order to determine $\alpha(t)$ and $\beta(t)$ we shall calculate with the aid of Eq. (22) the derivative

$$\frac{d}{dt}\mathrm{Sp}\,\rho_1(t)\,\hat{I}_z = -\frac{\pi}{2}\left(\frac{\mu H_1}{\hbar}\right)^2(2s+1)^{-N} \times \mathrm{Sp}\,\{\hat{P}'\hat{I}_z\,[\hat{I}_{-\Delta}^{1}\,[\hat{I}_{\Delta}^{-1}, \exp(\alpha(t)\hat{I}_z + \beta(t)\,\hat{H}^0)]]\}. \tag{31}$$

Using the equalities

$$[\hat{H}^0, \hat{I}_{\Delta}^{-1}] = \hbar\Delta\hat{I}_{\Delta}^{-1}, \qquad [\hat{I}_z, \hat{I}_{\Delta}^{-1}] = -\hat{I}_{\Delta}^{-1},$$

it is easy to verify the relation

$$[\exp(\alpha(t)\hat{I}_z + \beta(t)\hat{H}^0), \hat{I}_{\Delta}^{-1}] = \exp(\alpha(t)\hat{I}_z + \beta(t)\hat{H}^0)\,\hat{I}_{\Delta}^{-1}\,(1 - \exp(-\alpha(t) + \hbar\Delta\beta(t))).$$

Considering the easily verified equality

$$\mathrm{Sp}\,(\hat{P}'\hat{I}_z\,[\hat{I}^{1}_{-\Delta}, \hat{A}\,]) = -\,\mathrm{Sp}\,(\hat{P}'\,[\hat{I}^{1}_{-\Delta}, \hat{I}_z]\,\hat{A}), \qquad (32)$$

we further find

$$\frac{dI_z(t)}{dt} = -\frac{\pi}{2}\left(\frac{\mu H_1}{\hbar}\right)^2 (2s+1)^{-N}\,(\alpha(t) - \hbar\Delta\beta(t)) \times \mathrm{Sp}\,\{\hat{P}'\hat{I}^{1}_{-\Delta}\hat{I}^{-1}_{\Delta}\exp(\alpha(t)\,\hat{I}_z + \beta(t)\,\hat{H}^0)\}. \qquad (33)$$

We note that in the right-hand member of this equation it is now possible to replace the exponential by unity, because of the smallness of $\alpha(t)$ and $\beta(t)H^0$. For the same reason we obtain for the average values of $I_z(t)$ and $H^0(t)$

$$I_z(t) = \alpha(t)\,(2s+1)^{-N}\mathrm{Sp}\,\hat{I}_z^2 = \tfrac{1}{3}\alpha(t)\,Ns\,(s+1),$$

$$H_0(t) = \beta(t)\,(2s+1)^{-N}\,\mathrm{Sp}\,(\hat{H}^0)^2. \qquad (34)$$

Substitution of $\alpha(t)$ and $\beta(t)$ from these expressions into Eq. (33) yields

$$dI_z(t)/dt = -(\mu H_1/\hbar)^2\,\pi g(\Delta)\,(I_z(t) - y(t)),$$

$$y(t) = \hbar\Delta\frac{H_0(t)}{\overline{H}_0^2}, \qquad \overline{H}_0^2 = \frac{\mathrm{Sp}\,(\hat{H}^0)^2}{\mathrm{Sp}\,\hat{I}_z^2},$$

$$g(\Delta) = \frac{\mathrm{Sp}\,(\hat{P}'\hat{I}^{1}_{-\Delta}\hat{I}^{-1}_{\Delta})}{2Ns\,(s+1)\,(2s+1)^N/3}. \qquad (35)$$

The expression for dy/dt is easily obtained, using the conservation law, Eq. (23):

$$dH_0(t)/dt = -\hbar\Delta\, dI_z(t)/dt,$$

$$dy(t)/dt = (\hbar^2\Delta^2/\overline{H}_0^2)\,\pi g(\Delta)\,(I_z(t) - y(t)).$$

If we now take into account the spin-lattice relaxation in the manner of Bloembergen, Purcell, and Pound,[1] we arrive at the following system of equations:

$$dI_z(t)/dt = -(\mu H_1/\hbar)^2\,\pi g(\Delta)\,(I_z(t) - y(t)) + (I_{0z} - I_z(t))/T_1, \qquad (36)$$

$$dy(t)/dt = (\hbar^2\Delta^2/\overline{H}_0^2)\,(\mu H_1/\hbar)^2\,\pi g(\Delta)\,(I_z(t) - y(t)) + (y_0 - y(t))/T_1'. \qquad (37)$$

Here I_{0z} and y_0 are the initial values of $I_z(t)$ and $y(t)$, while T_1 and T_1' are the times for the spin-lattice relaxation of $I_z(t)$ and $H_0(t)$.

For the energy absorbed per unit time in steady state we find, with the aid of these equations (in our case $y_0 \ll I_{0z}$),

$$P(\Delta, H_1) = \varepsilon(\Delta)\,\hbar\omega\,(I_{z\,\mathrm{st}} - y_{\mathrm{st}}) = \frac{\hbar\omega\varepsilon(\Delta)\,I_{0z}}{1 + \varepsilon(\Delta)\,T_1\,(1 + \hbar^2\Delta^2 T_1'/\overline{H}_0^2 T_1)}. \qquad (38)$$

In the case of strong saturation, when $\varepsilon(\Delta)T_1 \gg 1$, we can neglect the ones in the denominator of Eq. (38), after which we obtain a relatively narrow Lorentz absorption line

$$P(\Delta, H_1) = \frac{\hbar\omega}{T_1'}\,\frac{\overline{H}_0^2}{\hbar^2\Delta^2 + \overline{H}_0^2 T_1/T_1'}. \qquad (39)$$

In order of magnitude $\overline{H}_0^2$ equals $(\mu H_{\mathrm{loc}})^2$.

Redfield[2] has investigated nuclear magnetic resonance absorption in metals. Even with $H_1 = 0.4$ oe he was able to observe the appearance of the narrow Lorentz absorption line. If, following[2], we take for aluminum $T_1 = 4 \times 10^{-3}$ sec and $2\pi g(0) = 10^{-4}$ sec, then we find for the saturation parameter $\varepsilon(\Delta)T_1 \sim 10$. In other words, the field value $H_1 = 0.4$ oe corresponds to the region of strong saturation and consequently the absorption line shape in correspondence to our Eq. (39) should be Lorentzian, just as Redfield observed.

In order to investigate the behavior of the dispersion signal it is necessary to determine the non-diagonal part of the density matrix $\rho_2(t)$. In order to determine $\rho_2(t)$ we make use of Eq. (14). Although this equation was obtained for the case in which there is no contact between the spin system and the lattice, it can be used also for the case $\hbar/\mu H_{\mathrm{loc}} \ll T_1$. The point is that the inclusion of such a weak spin-lattice interaction cannot have a significant influence on the rate of change of the off-diagonal matrix elements $(\rho_2(t))_{nm}$, equal to $\sim \mu H_{\mathrm{loc}}/\hbar$. [The rate of change with time of the diagonal matrix elements $(\rho_1(t))_{nn}$ for $H_1 \ll H_{\mathrm{loc}}$ is very small, $\sim \mu H_1^2/\hbar H_{\mathrm{loc}}$, as can be seen from Eq. (22), hence it is impossible to neglect the spin-lattice interaction in the determination of the change with time of the function $\rho_1(t)$.]

If we carry out in Eq. (14) a power series expansion in the small quantity $\hat{L}(t)$, as has already been done in the derivation of Eq. (22), and keep only the terms of lowest order in $\hat{L}_1(t)$, then we arrive at the equation

$$\rho_2(t) = -\frac{i}{\hbar}\int_0^t dt'\,[V(t'), \rho_1(t')]. \qquad (40)$$

The function $\rho_1(t)$ is determined by Eqs. (36), (37), (34), and (28). Hence Eq. (40) gives the desired non-diagonal part of the density matrix. To calculate the average values of $I_{x,y}(t)$ in the rotating coordinate system it is now necessary to determine the non-diagonal part of the density matrix $\rho_2'(t)$ in the same system of coordinates. Using the rule for transforming to rotating coordinates, Eq. (8), and the fact that $\rho_1(t)$ is diagonal, we obtain

$$\rho_2'(t) = -\frac{i}{\hbar}\int_0^t dt'\,[V(t-t'), \rho_1(t')]. \qquad (41)$$

Using further the expansions (18), we find

$$I_{x,y}(t) = \frac{\mu H_1}{4\hbar}\,i^{1/2\pm 1/2}\int_{-\infty}^{+\infty} d\omega \int_0^t dt'\,\mathrm{Sp}\,\{\hat{P}'\hat{I}^{1}_{-\omega}\,[\hat{I}^{-1}_{\omega}, \rho_1(t')]\} \times \{\exp[i(\omega - \Delta)(t - t')] \mp \exp[i - (\omega - \Delta)(t - t')]\}. \qquad (42)$$

In the derivation of this relation use was made of the easily verified relations

$$\mathrm{Sp}\,\{\hat{P}'\hat{I}^{1}_{-\omega}[\hat{I}^{-1}_{\omega},\rho_1(t')]\} = -\mathrm{Sp}\,\{\hat{P}'\hat{I}^{-1}_{\omega}[\hat{I}^{1}_{-\omega},\rho_1(t')]\}.$$

Note that the function $\rho_1(t)$ changes significantly only in the time interval $\hbar H_{loc}/\mu H_1^2$, and the function

$$\int_{-\infty}^{+\infty} d\omega\,\mathrm{Sp}\,\{\hat{P}'\hat{I}^{1}_{-\omega}[\hat{I}^{-1}_{\omega},\rho_1(t')]\}\exp[i(\omega-\Delta)(t-t')]$$

differs from zero only in the region $|t-t'| \lesssim \hbar/\mu H_{loc}$ [cf. derivation of Eq. (21)]. Hence in the integration over the time in the right member of Eq. (42) $\rho_1(t')$ can be considered a constant, equal to $\rho_1(t)$, and the integration over t' extended to $+\infty$. Changing further the variable of integration t' to $t-t'$ and using the well known relation[9]

$$\int_{0}^{\infty} d\tau e^{i\omega\tau} = \pi\delta(\omega) + P\frac{i}{\omega} \tag{43}$$

(the symbol P means that the integrals over ω are to be taken in the sense of the principal value), we obtain

$$I_{x,y}(t) = \frac{\mu H_1}{4\hbar}\int_{-\infty}^{+\infty} d\omega\,\mathrm{Sp}\,\{\hat{P}'\hat{I}^{1}_{-\omega}[\hat{I}^{-1}_{\omega},\rho_1(t)]\}$$

$$\times\, i^{1/2\pm 1/2}\Big\{\Big(\pi\delta(\omega-\Delta) + P\frac{i}{\omega-\Delta}\Big)$$

$$\mp\Big(\pi\delta(\omega-\Delta) - P\frac{i}{\omega-\Delta}\Big)\Big\}. \tag{44}$$

Substitution of $\rho_1(t)$ from Eqs. (36), (37), (34), and (28) leads to

$$I_x(t) = -(\mu H_1/\hbar)\, I_z(t)\, J_1(\Delta) + \Big(\frac{\mu H_1 y(t)}{\hbar\Delta}\Big) J_2(\Delta), \tag{45}$$

$$I_y(t) = (\mu H_1/\hbar)\,\pi g(\Delta)\,(I_z(t) - y(t));$$

$$J_1(\Delta) = P\int_{-\infty}^{+\infty}\frac{d\omega g(\omega)}{\omega-\Delta}, \qquad J_2(\Delta) = 1 + \Delta J_1(\Delta) \tag{46}$$

[the derivation of these equations is completely analogous to the derivation of Eq. (35).]

Determining $I_{z\,st}$ and y_{st} from (36) and (37) we obtain for χ'_{st} and χ''_{st} the expressions

$$\chi'_{st} = \frac{\mu I_{x\,st}}{2H_1} = -\frac{\mu^2 I_{0z}}{2\hbar}\left\{\frac{(1+\varepsilon(\Delta)T'_1\hbar^2\Delta^2/\overline{H}_0^2)J_1(\Delta)}{1+\varepsilon(\Delta)T_1(1+\hbar^2\Delta^2T'_1/\overline{H}_0^2T_1)}\right.$$

$$\left.-\frac{\varepsilon(\Delta)T'_1(\hbar^2\Delta/\overline{H}_0^2)J_2(\Delta)}{1+\varepsilon(\Delta)T_1(1+\hbar^2\Delta^2T'_1/\overline{H}_0^2T_1)}\right\}, \tag{47}$$

$$\chi''_{st} = \frac{\mu I_{y\,st}}{2H_1} = \frac{\mu^2 I_{0z}}{2\hbar}\,\frac{\pi g(\Delta)}{1+T_1\varepsilon(\Delta)(1+\hbar^2\Delta^2T'_1/\overline{H}_0^2T_1)}. \tag{48}$$

As expected, Eq. (48) agrees with the expression for energy absorbed per unit time calculated earlier [see (38)]. In strong saturation at small values of Δ the greatest term in the right member of Eq. (47) is the second. Because of the presence of the additional factor $(1+\hbar^2\Delta^2T'_1/\overline{H}_0^2T_1)^{-1}$ this term will lead to a more narrow dispersion line relative to the dispersion line in the absence of saturation. Such a narrowing of the dispersion line was actually observed by Redfield.[2]

It is to be noted that for $\varepsilon(\Delta)T_1 \ll 1$ Eq. (47) goes over into the well known formula

$$\chi'_{st}(\Delta) = -\mu^2 I_{0z}J_1(\Delta)/2\hbar. \tag{49}$$

For a comparison with the experimental data and theory of Redfield[2] we calculate $(d'_{st}/d)_{=0}$. Differentiating Eq. (47), we obtain for $\varepsilon(\Delta)T_1 \gg 1$

$$\left.\frac{d\chi'_{st}}{d\Delta}\right|_{\Delta=0} = \frac{\mu^2 I_{0z}}{4}\,\frac{\hbar}{\overline{H}_0^2}, \tag{50}$$

in view of the equality $dJ_2(\Delta)/d\Delta = 0$. Comparison of this formula with Eq. (41) of Redfield's paper[2] shows that our Eq. (50) transforms into Redfield's formula, which agrees well with experiment, when $H_1^2 \ll \overline{H}_0^2 = \delta H^2$, if, in correspondence with Redfield, it is assumed that the quantity $y(t)$, quadratic in spin, relaxes under the influence of the lattice twice as fast as $I_z(t)$. (Redfield's theory is valid only in cases of very strong saturation.)

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