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Modulation-Effect Corrections for Moments of Magnetic Resonance Line Shapes*

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Corrections are derived for the calculation of the second and fourth moments of magnetic resonance lines from experimental data, obtained by using the low-frequency modulation method. The results for 0° phase shift between field modulation and the lock-in reference are

$$\langle\Delta\omega_{\exp}^2\rangle_{\mathrm{Av}}=\langle\Delta\omega^2\rangle_{\mathrm{Av}}+\tfrac{1}{3}\omega_M^2+\tfrac{1}{4}(\gamma H_M)^2,$$
$$\langle\Delta\omega_{\exp}^4\rangle_{\mathrm{Av}}=\langle\Delta\omega^4\rangle_{\mathrm{Av}}+\langle\Delta\omega^2\rangle_{\mathrm{Av}}[2\omega_M^2+\tfrac{3}{2}(\gamma H_M)^2]+\tfrac{1}{5}\omega_M^4+\tfrac{3}{4}\omega_M^2(\gamma H_M)^2+\tfrac{1}{8}(\gamma H_M)^4.$$

Furthermore, it is found that no corrections are necessary for the calculation of intensities despite distortion of the line shape resulting from modulation effects.

The equivalence of field and frequency modulation is proved for signals describable by Bloch's equations and the discussion of the general case strongly supports the general validity of this equivalence.

I. INTRODUCTION

SEVERAL years ago Andrew[1] derived formulas to correct the experimentally-obtained second and fourth moments for finite modulation *amplitude*. This paper deals with this amplitude correction and, furthermore, with corrections needed when the modulation *frequency* is not negligibly small compared to the line width. This analysis should be useful not only in nuclear magnetic resonance experiments, but especially in paramagnetic resonance studies which presently tend to employ higher and higher modulation frequencies to improve the signal-to-noise ratio.

II. CALCULATION OF EXPERIMENTALLY-OBTAINED MOMENTS AND INTENSITIES

Let $\chi(\omega)=\chi-i\chi''$ be the complex susceptibility, where χ'' describes the absorption and χ' the dispersion curve; the frequency scale is assumed to be so displaced that the center of the line is at $\omega=0$. The nth moment of the absorption curve then is defined by

$$\langle\omega^n\rangle_{\mathrm{Av}}''=\mathrm{M}_n''/\mathrm{M}_0''; \quad \mathrm{M}_n''=\int_{-\infty}^{\infty}\chi''(\omega)\omega^n d\omega$$
$$=-\int_{-\infty}^{\infty}\omega^{n+1}\frac{d\chi''(\omega)}{d\omega}d\omega/(n+1). \quad (1)$$

Since the output of the lock-in detector gives, in first approximation, a signal $S(\omega)$ proportional to $d\chi''/d\omega$, the formula usually employed to calculate the experimental moments[2] is

$$\langle\omega_{\exp}{}^n\rangle_{\mathrm{Av}}''=M_n''/M_0'';$$
$$M_n''=-\int_{-\infty}^{\infty}\omega^{n+1}S(\omega)d\omega/(n+1). \quad (2)$$

These moments will differ from the correct ones [Eq. (1)] if modulation effects are present.

If the field modulation is of the form $H_M\cos\omega_M t$, the signal immediately before lock-in detection can be simply obtained from the expression[3]:

$$A(\omega,t)=-\sum_{m=-\infty}^{\infty}\chi(\omega+m\omega_M)\times(K_{m,0}\cos\omega_M t+iK_{m,90}\sin\omega_M t), \quad (3a)$$

$$K_{m,0}=mJ_m^2(2a)/a; \quad K_{m,90}=d[J_m^2(2a)]/d(2a);$$
$$2a=\gamma H_M/\omega_M. \quad (3b)$$

(γ=gyromagnetic ratio, J_m=Bessel functions of first kind.) The imaginary part of Eq. (3a) represents the signal corresponding to an absorption-mode hf (high-frequency) demodulation (i.e., detection of the signal component 90° out of phase with respect to the driving hf field). The real part describes the signal obtained for dispersion mode hf demodulation. It may be noted that, for either absorption or dispersion-mode hf demodulation, both χ' and χ'' contribute to the signal before lock-in detection because of the factor i of the second bracket term of (3a).

The conditions under which Eq. (3) can be applied to the present problem are that (1) the line width, ω_M and γH_M have to be small compared to the resonance frequency, (2) H_1 has to be so small that no saturation effects are present, and (3) it is assumed that frequency and field modulation are equivalent. (This is discussed in the Appendix.)

Assuming an absorption-mode hf demodulation and 0° phase shift between the field modulation and the phase reference of the lock-in detector, the lock-in output is

$$S(\omega)=\sum_{m=-\infty}^{\infty}\chi''(\omega+m\omega_M)K_{m,0},$$

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[1] E. R. Andrew, Phys. Rev. 91, 425 (1953).

[2] G. E. Pake and E. M. Purcell, Phys. Rev. 74, 1184 (1948).

[3] K. Halbach, Helv. Phys. Acta 29, 37 (1956). (A more convenient expression for the discussion of the modulation-distorted line shape is also given in this paper.)

and M_n'' becomes

$$M_n''=-\int_{-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\chi''(\omega+m\omega_M)\omega^{n+1}K_{m,0}d\omega/(n+1),$$

$$M_n''=-\int_{-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\chi''(\omega)(\omega-m\omega_M)^{n+1}K_{m,0}d\omega/(n+1),$$

$$M_n''=-\sum_{p=0}^{n+1}M_{n+1-p}''(-\omega_M)^p\binom{n+1}{p}\times\sum_{m=-\infty}^{\infty}K_{m,0}m^p/(n+1). \quad (4)$$

Using the identities

$$\sum_{m=-\infty}^{\infty}J_mJ_{m+r}\begin{cases}=1 & \text{for } r=0\\ =0 & \text{for } r\neq 0,\end{cases}$$

and

$$mJ_m(2a)=a[J_{m-1}(2a)+J_{m+n}(2a)],$$

the sums

$$a\sum_{m=-\infty}^{\infty}K_{m,0}m^p=\sum_{m=-\infty}^{\infty}J_m^2(2a)m^{p+1}=B_{p+1}$$

are easily calculated:

$$\begin{aligned}B_0&=1,\\ B_2&=2a^2,\\ B_4&=2a^2(3a^2+1),\\ B_6&=2a^2(10a^4+15a^2+1),\\ B_{2p+1}&=0.\end{aligned} \quad (5)$$

Thus, the experimental intensity M_0'', the second moment and the fourth moment are related to the true values by

$$\begin{aligned}M_0''&=\gamma H_M M_0'',\\ \langle\omega_{\text{exp}}^2\rangle_{\text{Av}}''&=\langle\omega^2\rangle_{\text{Av}}''+\tfrac{1}{3}\omega_M^2+\tfrac{1}{4}(\gamma H_M)^2,\\ \langle\omega_{\text{exp}}^4\rangle_{\text{Av}}''&=\langle\omega^4\rangle_{\text{Av}}''+\langle\omega^2\rangle_{\text{Av}}''[2\omega_M^2+\tfrac{3}{2}(\gamma H_M)^2]\\ &\quad+\tfrac{1}{5}\omega_M^4+\tfrac{3}{4}\omega_M^2(\gamma H_M)^2+\tfrac{1}{8}(\gamma H_M)^4.\end{aligned} \quad (6a)$$

For $\omega_M=0$, these results are in agreement with Andrew's. This agreement is not completely obvious because Andrew derived his formula via a Taylor expansion of the shape function χ'' which for arbitrary functions χ'' is not justified for all values of H_M. Since our Eqs. (6a) are valid only for small H_1 and one might be interested in the intensity or moments of the H_1-broadened line, we give a method for rigorously deriving Andrew's result. Let χ_1'' be the H_1-broadened line shape of the absorption line. If ω_M is small enough so that the signal is all the time determined by the instantaneous value of the applied z field, the lock-in output is given by

$$S(\omega)=\int_0^{2\pi}\chi_1''(\omega+\gamma H_M\cos\omega_Mt)\cos\omega_Mt\,d(\omega_Mt),$$

and M_n'' becomes

$$M_n''=-\int_{-\infty}^{\infty}\int_0^{2\pi}\chi_1''(\omega+\gamma H_M\cos y)\omega^{n+1}\times\cos y\,dy\,d\omega/(n+1),$$

$$M_n''=-\int_{-\infty}^{\infty}\int_0^{2\pi}\chi_1''(\omega)(\omega-\gamma H_M\cos y)^{n+1}\times\cos y\,dy\,d\omega/(n+1),$$

which can be verified to confirm Andrew's result.

[4] It can be shown that the relation between the experimental and true intensities and moments has the same structure as (6b) even for arbitrary periodic modulation, as Professor Bloch kindly pointed out to the author. The following is a brief outline of the derivation of the correction formulas for this more general case.

The procedure for obtaining $A(\omega,t)$ is the same as in reference 3. We represent the hf field by $H_1(t)=\text{Re}\exp i[\omega t+\alpha(x)]$. $\alpha(x)=\alpha(\omega_Mt)$ describes the effect of the field modulation and is therefore proportional to $\gamma H_M/\omega_M$, where H_M is a measure of the modulation amplitude and ω_M the fundamental frequency of the modulation. If we represent $e^{i\alpha(x)}$ through

$$e^{i\alpha(x)}=\sum_{m=-\infty}^{\infty}c_me^{imx},$$

we obtain, for the signal $B(\omega)$, after lock-in demodulation (it is assumed that the lock-in detector responds only to the fundamental frequency ω_M, i.e.,

$$B(\omega)\sim\int_0^{2\pi/\omega_M}A(\omega,t)\cos\omega_Mt\,\omega_Mdt):$$

$$B(\omega)=-\sum_{m=-\infty}^{\infty}\chi(\omega+m\omega_M)c_m(c_{m+1}^*+c_{m-1}^*).$$

Using $M_n=-\int_{-\infty}^{\infty}B(\omega)\omega^{n+1}d\omega/(n+1)$ and $\mathrm{M}_n=\int_{-\infty}^{\infty}\chi(\omega)\omega^nd\omega$, we obtain

$$-(n+1)M_n=\sum_{p=0}^{n+1}\mathrm{M}_{n-p+1}(-\omega_M)^p\binom{n+1}{p}D_p,$$

with

$$D_p=\sum_{m=-\infty}^{\infty}c_m(c_{m+1}^*+c_{m-1}^*)m^p$$

It can easily be shown that D_p can be expressed by

$$D_p=\int_0^{2\pi}\cos x\,e^{-i\alpha(x)}\frac{d^p}{dx^p}e^{i\alpha(x)}dx/\pi(i)^p.$$

Since $\alpha(x)$ is proportional to $\gamma H_M/\omega_M=2a$, D_p can be represented by

$$D_p=\sum_{\mu=1}^{p}\delta_\mu\cdot a^\mu,$$

where the coefficients δ_μ are independent of H_M and ω_M. Using this in the last expression for M_n, it is clear that M_n can be represented by

$$M_n=\gamma H_M\sum_{r=0}^{n}\{\mathrm{M}_r'\sum_{\mu=0}^{r}\omega_M^\mu(\gamma H_M)^{n-r-\mu}b_{nr\mu}'+\mathrm{M}_r''\sum_{\mu=0}^{r}\omega_M^\mu(\gamma H_M)^{n-r-\mu}b_{nr\mu}''\}$$

with H_M- and ω_M-independent complex coefficients $b_{nr\mu}'$, $b_{nr\mu}''$. Because $\mathrm{M}_0'=0$, we get, particularly for the intensity M_0: $M_0=\gamma H_Mb_{000}''\mathrm{M}_0''$. Assuming again sinusoidal modulation and 0° phase shift between field modulation and the phase reference of the lock-in detector, the integrals in the expressions for the coefficients D_p are easily calculated and lead, of course, with a $D_p=B_{p+1}$, to a reproduction of Eq. (5).

It may be worthwhile to mention that, except for a trivial proportionality to H_M, the experimentally-obtained intensity M_0'' is completely independent of H_M and ω_M. Hence, the intensity is invariant even though the line shape may be wildly distorted by modulation effects.

The effect of a mixture of absorption and dispersion-mode hf demodulation upon the experimentally-determined moments is sufficiently simple that no discussion is necessary here. The results are more complicated when a phase shift ψ between the field modulation and the lock-in phase reference is present. If we assume absorption-mode hf demodulation, the experimentally-obtained nth moment is

$$\langle \omega_{\psi,\exp}{}^n \rangle_{\text{Av}}'' = \frac{M_n'' \cos\psi + M_{n,90}'' \sin\psi}{M_0'' \cos\psi + M_{0,90}'' \sin\psi},$$

where M_n'' is given by Eq. (4) and $M''_{n,90}$ is determined by

$$M_{n,90}'' = \sum_{p=0}^{n+1} \mathrm{M}_{n+1-p}'(-\omega_M)^p \binom{n+1}{p} \sum_{m=-\infty}^{\infty} K_{m,90} m^p/(n+1).$$

Evaluating these expressions, using (3b) and (5), we finally get [with $\mathrm{M}_n' = \int_{-\infty}^{\infty} \chi'(\omega)\omega^n d\omega$]:

$$M_{0,90}''=0,$$
$$\langle \omega_{\psi,\exp}{}^2 \rangle_{\text{Av}}'' = \langle \omega_{\exp}{}^2 \rangle'' + (\omega_M \mathrm{M}_1'/\mathrm{M}_0'') \tan\psi,$$
$$\langle \omega_{\psi,\exp}{}^4 \rangle_{\text{Av}}'' = \langle \omega_{\exp}{}^4 \rangle_{\text{Av}}'' + \{2\omega_M \mathrm{M}_3' + \omega_M \mathrm{M}_1' [\omega_M{}^2 + \tfrac{3}{2}(\gamma H_M)^2]\} \tan\psi/\mathrm{M}_0''. \quad (6b)$$

Since $\mathrm{M}_1'/\mathrm{M}_0''$ can be expected to be of the order of magnitude of $(\mathrm{M}_2''/\mathrm{M}_0'')^{\frac{1}{2}}$, the phase of the reference signal has to be correct whenever ω_M is large enough to produce significant modulation effects. The phase setting is, however, unimportant for intensity comparisons (as long as the phase setting remains constant) because $M_{0,90}''=0$.[4]

III. APPENDIX. EQUIVALENCE OF FIELD AND FREQUENCY MODULATION

Equation (3) was originally derived for frequency modulation.[3] Since it is the author's experience that the equivalence of field and frequency modulation is often questioned or not clearly understood, it may be useful to make a few remarks on this subject.

The condition under which (3) is correct for field modulation is that the signal components with a phase shift of 0° and 90° with respect to the driving hf field are the same for either field or frequency modulation. Another way of expressing this equivalence of the two modulation methods is to say that the signal, in that rotating coordinate system in which the applied rotating hf field is at rest, is the same whether field or frequency modulation has been used.

The equivalence of field and frequency modulation can be proved very easily for signals which can be described by Bloch's equation.[5] If one applies a hf field of the form $H_x = H_1 \cos\varphi$; $H_y = -H_1 \sin\varphi$, the Bloch equations in the coordinate system in which this field is at rest contain the z component of the original magnetic field minus $\dot{\varphi}/\gamma$. These equations are therefore identical, whether one applies a modulated z field,[6] $H_0 = H_{00} - H_M \cos\omega_M t$ and a hf field with constant frequency $\dot{\varphi} = \omega_0$ or a constant z field $H_0 = H_{00}$ and a frequency-modulated hf field with $\dot{\varphi} = \omega_0 + \gamma H_M \cos\omega_M t$.[7] To the extent $H_M/H_0 \ll 1$, field and frequency modulation are therefore completely equivalent for signals describable by Bloch's equations, contrary to a statement of Primas.[8]

Next, we consider the general case. Let

$$\hbar\mathcal{H} = -\hbar\gamma I_0 H_0 - \hbar\gamma H_1(I_x \cos\varphi - I_y \sin\varphi) + \hbar\mathcal{H}_0,$$

represent the Hamiltonian of the total system under the influence of a magnetic field H_0 in the z direction and a hf field rotating in the x-y plane. $\hbar I_x$, $\hbar I_y$, $\hbar I_0$ are the operators of the x, y, and z components of the total spin angular momentum for the species under observation. $\hbar\mathcal{H}_0$ is the sum of the lattice, spin-lattice, and spin-spin Hamiltonians, which are assumed to be independent of the amplitude of the amplitude H_1 of the hf field. If ρ is the density matrix of the total system, the equation of motion is

$$i\dot{\rho} = [\mathcal{H}, \rho],$$

and the signal can be simply obtained from

$$\langle I_\pm \rangle = \mathrm{Tr}(\rho I_\pm),$$

where

$$I_\pm = I_x \pm i I_y.$$

Introducing a new density matrix $r = S^{-1}\rho S$ through the transformation matrix $S = \exp[i(I_0 + L_0)\varphi]$, where $\hbar L_0$ is the operator of the z component of the total lattice angular momentum, we finally get

$$i\dot{r} = [\mathcal{H}_T, r],$$
$$\mathcal{H}_T = -\gamma I_0(H_0 - \dot{\varphi}/\gamma) - \gamma H_1 I_x + \dot{\varphi} L_0 + \mathcal{H}_0.$$

Use has been made of the relations $S^{-1} I_\pm S = I_\pm e^{\mp i\varphi}$ and $[\mathcal{H}_0, I_0 + L_0] = 0$; the latter holds because of the conservation of the z component of the total angular momentum in the absence of the hf field.

If we introduce r into the expression for $\langle I_\pm \rangle$, we see

[5] F. Bloch, Phys. Rev. **70**, 460 (1946).

[6] Although there is no difficulty in dealing with an arbitrary time dependence of the modulation field, we use the cosine form for simplicity.

[7] The inhomogeneous term in the equation for the z component, describing the equilibrium polarization in the z direction [Eq. (42c) of reference 5] has, in principle, a small time-dependent contribution for field modulation, whereas this term is constant for frequency modulation. This effect is at most of the order H_M/H_{00} and has therefore been neglected in all calculations known to the author.

[8] H. Primas, Helv. Phys. Acta **31**, 17 (1958).

that the amplitude of the signal and its phase shift with respect to the hf field are determined by $\mathrm{Tr}(rI_\pm)$:

$$\langle I_\pm \rangle = e^{\mp i\varphi}\mathrm{Tr}(r\cdot I_\pm),$$

or, since

$$\mathrm{Tr}(rI_\pm) = |\mathrm{Tr}(rI_\pm)|e^{\pm i\alpha}:$$
$$I_x = |\mathrm{Tr}(rI_\pm)| \cos(\varphi-\alpha);$$
$$I_y = -|\mathrm{Tr}(rI_\pm)| \sin(\varphi-\alpha).$$

The two modulation methods can therefore give different results only if $\mathcal{H}_T$ is not the same in each case. Introducing again $H_0 = H_{00} - H_M \cos\omega_M t$ and $\dot{\varphi} = \omega_0$ for field modulation and $H_0 = H_{00}$ and $\dot{\varphi} = \omega_0 + \gamma H_M \cos\omega_M t$ for frequency modulation, we see that all contributions to $\mathcal{H}_T$ remain the same, except $L_0\dot{\varphi}$, which becomes $L_0\omega_0$ for the first, $L_0(\omega_0 + \gamma H_M \cos\omega_M t)$ for the second case. Since these terms concern only the lattice and since γH_M is assumed to be very small compared to ω_0, with no chance of compensating $L_0\omega_0$ considerably by parts of $\mathcal{H}_0$, it seems justified to neglect $L_0\gamma H_M \times \cos\omega_M t$. Although a more detailed and complicated calculation appears to be necessary to prove fully the equivalence of field and frequency modulation for this general case, we believe our discussion supports this equivalence strongly when $\gamma H_M \ll \omega_0$.

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Cross Relaxation in Ruby

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A pulsed microwave method has been used to study paramagnetic relaxation in synthetic ruby at Cr/Al concentrations from 0.02% to 0.3%, and over a wide range of fields and angles with respect to the crystal axis. The experimental frequency was 7.17 kMc/sec. At settings for which one interval between energy levels was twice as large as another, decay traces with two characteristic periods were observed. The more rapid decay was independent of temperature, and is attributed to a cross-relaxation process involving three spins. Similar behavior became apparent at all concentrations whenever two intervals approached the same value. At 0.3%, two period decay traces were observed for any arbitrary field and angle setting, indicating at this concentration, a general cross relaxation between the Zeeman levels in times of 0.3 millisecond and less.

INTRODUCTION

THE classical treatment of paramagnetic relaxation by Casimir and duPre[1,2] assumes two systems, spins and lattice oscillators, physically interspersed but weakly coupled with each other. The coupling within each system is assumed to be strong, so that each is in a state of internal thermodynamic equilibrium characterized by a temperature, and relaxation is depicted as a kind of heat conduction whereby energy given initially to the spin system becomes transferred to the crystal lattice. A number of experiments have turned on the question of temperature equilibrium in the interacting systems, in particular on equilibrium within the spin system which, until the recent extension of acoustic techniques into the kilomegacycle range[3] was the only one open to direct observation. De Vrijer and Gorter[4] modified the spin equilibrium concept to account for a "third" or "intermediate" relaxation effect which appeared in their experiments on the chromium alums. This effect was too slow to be due to simple spin-spin interaction and yet considerably faster than lattice relaxation. It was independent of temperature in the hydrogen to helium range, could be seen only in those salts where the spins were clearly separated into two classes due to the presence of two different magnetic complexes, and was explained in terms of transfers between subgroups within the spin system. Similar effects were later observed by Verstelle, Drewes, and Gorter[5] in magnetically dilute materials.

These experiments were made by the nonresonant method. Magnetic resonance has made it possible to study the behavior of spin groups in more detail, and to observe different types of "intermediate" or "cross relaxation" between them. In the simplest case, where two spin groups have the same resonance frequency, energy transfer will take place in the spin-spin time, and for most purposes the spins will behave as a single group. If groups have a small frequency separation, as in the

[1] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., Amsterdam, 1947).
[2] C. J. Gorter, *Progress in Low-Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.
[3] H. Bommel and K. Dransfeld, Phys. Rev. Letters 1, 234 (1958).
[4] F. W. de Vrijer and C. J. Gorter, Physica 18, 549 (1952).
[5] J. C. Verstelle, G. W. J. Drewes, and C. J. Gorter, Physica 24, 632 (1958).