Frequency-dependent asymptotic behavior of magnetic-resonance spectra

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The frequency-dependent asymptotic behavior of the spectra of several correlation functions observed in magnetic-resonance experiments has been calculated on the basis of a statistical line-shape theory. The frequency-dependent asymptotic behavior is described by the relation $\exp(-\alpha\omega)$.

In 1967, McArthur *et al.*[1] have observed experimentally for the first time an exponential dependence of the cross-relaxation rate on the frequency shift.[1] This result was viewed with great surprise because of the current belief that the absolute majority of the temporal correlation functions observed by the magnetic-resonance methods

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have spectra similar to the Gaussian or Lorentzian spectra. The results obtained by McArthur *et al.*[1] have subsequently been confirmed experimentally many times using various objects (see, e.g., Ref. 2) and various techniques.[3,4]

The reported observations have so far not been explained, because the meaning of the phenomenological approximations in Ref. 6 for the description of the results of Ref. 1 are, as was pointed out in Ref. 5, not clear, which, incidentally, was also pointed out in Ref. 6. The exponential frequency-dependent asymptotic behavior of the spectra of the temporal correlation functions remain, as Waugh put it, "the most puzzling observation in the physics of the magnetic resonance."[7,8]

In the present letter we study the effect of multispin processes on the asymptotic behavior, in terms of the frequency ($\omega \gg \omega_{\rm loc}$; $\omega_{\rm loc} = \gamma H_{\rm loc}$; $H_{\rm loc}$ is the local magnetic field), of the magnetic-resonance absorption spectra, of the dipole fluctuations,[1] and of the dipole-Zeeman cross relaxation due to spin locking. We show that the spectra mentioned above have an exponential behavior. Although we will carry out specific calculations for the problem involving the absorption spectrum, the absolute majority of the results can easily be used in the calculations of the spectra of the rest of the temporal correlation functions, since the asymptotic behavior is contingent upon, as we will show below, the simultaneous flip of a large number of spins.

We know[9,10] that the model for random local fields proposed by Anderson[11] gives a correct qualitative description of many characteristic features of the magnetic-resonance spectra, despite the fact that it is not sufficiently rigorous. We will accordingly examine the asymptotic behavior of the spectrum on the basis of this popular model.

A temporal correlation function proportional to the free-precession signal, which is a Fourier transform of the line shape, is described by the expression[11]

$$\Gamma(t) = \langle \exp(i \int_0^t \omega(t')dt') \rangle . \tag{1}$$

The symbol $\langle \cdots \rangle$ denotes averaging over the occurrences of the random local field $\omega(t)$. The time evolution of the local fields very frequently (and virtually always in the case of NMR) occurs as a result of flip-flop processes stemming from the term H_{ff} in the secular part of the dipole-dipole interaction which is responsible for the line broadening[9]:

$$H_d = H_{zz} + H_{ff} = \frac{1}{2} \sum_{i \neq j} b_{ij} \left\{ S_{z_i} S_{z_j} - \frac{1}{4} (S_i^+ S_j^- + S_i^- S_j^+) \right\}. \tag{2}$$

Zobov and Provotorov[12] showed that in a spin pair with markedly different frequencies a flip-flop process actually consists of two processes: rapid spin nutations around an "average" direction and a considerably slower change in this direction. As a result, the local field on a certain spin with the index "0" consists of a constant component (we will ignore its slow variations in this case) and a modulation component:

$$\omega_0(t) = \omega_0 + \sum_k a_{0k} \cos(\Omega_k t + \varphi_k) . \tag{3}$$

In the spirit of Anderson's theory, we will assume that the frequencies ω_0 and $\{\Omega_k\}$, the phases $\{\varphi_k\}$, and the amplitudes $\{a_{0k}\}$ (for large values of Ω_k we have in order of magnitude $\alpha_{0k} \sim (b_{kk'}^2 b_{0k}/\Omega_k^2)$ are random values which are characterized by a certain multidimensional distribution function:

$$P(\omega_0; \{\Omega_k\}; \{\varphi_k\}; \{a_{0k}\}) . \tag{4}$$

Substituting (3) into (1), we find

$$\Gamma(t) = \langle e^{i\omega_0 t} \prod_k \exp\{i a_{0k} \int_0^t \cos(\Omega_k t' + \varphi_k) dt'\} \rangle . \tag{5}$$

We easily see that the right side of relation (5) is a sum of the terms which oscillate with each frequency. By combining with the oscillation frequency, which is attributable to the quasistatic component of the local field, the modulation frequencies lead to the appearance in the spectrum of arbitrarily large frequencies, even when the static local fields have a finite spectrum. In exactly the same manner, these processes define the line wing, even when the static-field spectrum falls off faster than the fluctuation spectrum. This case is in fact seen in a solid: The quasistatic local fields, which stem from the H_{zz} interaction of Hamiltonian (2), have a Gaussian spectrum,[13] whereas fluctuations, as will be shown below, account for the exponential wing of the spectrum. We assume below that each spin has many equivalent neighbors, $Z \gg 1$. We can then assume that the fluctuating fields produced by the different neighbors are independent of each other.[14] Consequently,

$$\Gamma(t) = \langle \cos\omega_0 t \rangle \langle a_{0k} \int_0^t \cos(\Omega_k t' + \varphi_k) dt' \rangle^Z . \tag{6}$$

Since we are concerned with the frequency-related asymptotic behavior, the frequencies $\Omega_k \gtrsim \omega_{\rm loc}$ play the dominant role in Eq. (6). The corresponding amplitudes a_{0k} are too small for these frequencies, and the second cosine in (6) can be expanded in a series. We restrict the discussion to the first term

$$\Gamma(t) = \Gamma_0(t)[1 - R(t)]^Z \approx \Gamma_0(t) e^{-ZR(t)} . \tag{7}$$

Here

$$\Gamma_0(t) = \langle \cos\omega_0 t \rangle , \tag{8}$$

$$R(t) = \frac{1}{2} \langle a_{0k}^2 (\int_0^t \cos(\Omega_k t' + \varphi_k) dt')^2 \rangle . \tag{9}$$

Although a_{0k} and Ω_k generally are not statistically independent, we will substitute, for simplicity, $\langle a_{0k}^2 \rangle$ for a_{0k}^2 in our estimates below. Assuming that all values of the phase are equally probable, after some straightforward intermediate transformations, we find

$$ZR(t) = A \int_0^t d\tau (t - \tau) G(\tau) = A \int_0^t dt' \int_0^{t'} dt'' G(t''), \tag{10}$$

with

$$A = \frac{1}{2} Z \langle a_{0k}^2 \rangle ; \qquad G(t) = \langle \cos\Omega_k t \rangle . \tag{11}$$

To calculate the functions $\Gamma_0(t)$ and $G(t)$, we must specify the distribution function for the local static fields $P_\omega(\omega)$ and for the modulation frequencies $P_\Omega(\Omega)$. We consider a Gaussian distribution

$$P_\omega(\omega_0) = \frac{1}{\sqrt{2\pi M_2}} \exp\left\{-\frac{\omega^2}{M^2}\right\}. \qquad (12)$$

The modulation frequency Ω_k is determined principally by the difference in the local static fields on the spins that participate in the flip-flop processes: For this reason, the function P_Ω is a convolution of the distribution functions in (12). Consequently,

$$\Gamma_0(t) = \exp\left(-\frac{M_2 t^2}{2}\right); \quad G(t) = \exp(-M_2 t^2). \qquad (13)$$

The absorption line shape is determined by the integral

$$g(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\,\Gamma_0(t)\exp\{-A\int_0^t\int_0^{t'} dt'dt''G(t'')\}\,dt. \qquad (14)$$

In the limit $\omega \to \infty$, the asymptotic behavior of the integral can be analyzed by the method of steepest descent.[15] We thus find

$$g(\omega) \approx \frac{1}{\sqrt{2\pi f''(x_0)}} \exp\{-f(x_0)\}. \qquad (15)$$

The equation for the saddle point, $ix_0 = t_0$ is

$$Ae^{x_0^2 M_2} = 2x_0 M_2(\omega - x_0 M_2). \qquad (16)$$

Solving this equation in an approximate way for large ω, we find

$$g(\omega) = \frac{1}{\sqrt{4\pi\sqrt{M_2}\,\omega \ln^{1/2}(2\omega\sqrt{M_2}/A)}} \exp\left\{-\frac{\omega}{\sqrt{M_2}}\ln^{1/2}\left(\frac{2\omega\sqrt{M_2}}{A}\right)\right\}. \qquad (17)$$

We note in conclusion that the "modulation" contribution to the local field plays the dominant role, according to the results presented above, in the formation of the exponential asymptotic function. This contribution also determines the asymptotic behavior of the rest of the correlation functions. The incorporation of this contribution into the dipole fluctuation spectrum[1] gave rise to an exponential frequency dependence with an exponent closely matching the exponent obtained experimentally.

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