Wing shapes of magnetic-resonance spectra and adiabatic invariants in a spin system

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(Submitted 22 September 1992)
Zh. Eksp. Teor. Fiz. **103**, 1070–1077 (March 1993)

It is shown that the exponential form of the wings of the magnetic-resonance spectra observed in experiments over many years are due to the onset of an adiabatic invariant in the system under the conditions corresponding to observation of the wings. The approach developed made it also possible to analyze the magnetization loss produced when a system is acted upon by a system of adiabatic pulses.

McArthur, Hahn, and Valstedt[1] were the first to demonstrate by experiment that the Fourier spectrum of the thermal correlation function (TCF) of the magnetization component longitudinal with respect to the external magnetic field has wings in the form of a simple exponential; it was named a dipole-fluctuation spectrum (DFS). The result of Ref. 1 was quite surprising in light of the then prevailing convictions that the absolute majority of the TCF observed by the magnetic-resonance method have spectra close to Gaussian or Lorentzian. The results of Ref. 1 were subsequently repeatedly confirmed experimentally for different objects and by different procedures (see, e.g., Refs. 2–5).

The exponential shape of the spectrum wings was first described by us on the basis of a statistical theory.[6] Furthermore, a system of nonlinear integrodifferential equations yielded[5] an exponential wing shape for TCF spectra and an estimate of the exponent. So far, however, the physical causes of the exponential form of the frequency asymptotes of the TCF spectra remain unclear.

We show in the present paper that the exponential form of the frequency asymptotes is due to the onset, in the spin system, of an adiabatic invariant under conditions corresponding to the observation of spectrum wings. The presence of an adiabatic invariant makes it possible to explain the physics of the experimental results[2–5] by resorting to the general theory developed in mechanics[7] for adiabatic invariants. In addition, it was possible to analyze, on the very same basis, the magnetization losses incurred when adiabatic pulses act on a system.

It is known that the motion of a magnetic moment in magnetic field of variable direction is regarded as adiabatic[8] if the rate of change of the field direction is much smaller than the field itself. Under these conditions the magnetic moment follows up the field. Owing to this property, adiabatic pulses have by now found extensive use in the practice of synchronous rotation of magnetic moments situated in different magnetic fields.[9–12] We show in the present paper that the magnetization losses induced by the action of adiabatic pulses on a spin system are exponentially small. The arguments of the exponentials were calculated for typical magnetic-field variation cases.

We consider thus a magnetic moment located in a constant magnetic field and an RF field rotation in a perpendicular plane. One of these fields, or both simultaneously, is modulated in accord with a certain law. The magnetic field acting on the magnetic moment consists, in a rotating coordinate frame (RCF), if two slowly varying orthogonal components: a longitudinal detuning field $\omega_{\parallel}(t)$ and a transverse field $\omega_{\perp}(t)$ with amplitude equal to that of the RF field. We change to a comoving coordinate system, with a $\bar{z}$ axis directed along the instantaneous direction of the effective field $\Omega(t)$, which makes at the instant t an angle $\theta(t)$ with the z axis of the RCF:

$$\Omega^2(t) = \omega_{\parallel}^2(t) + \omega_{\perp}^2(t), \qquad \theta(t) = \operatorname{arctg} \frac{\omega_{\perp}(t)}{\omega_{\parallel}(t)}. \tag{1}$$

The change of the magnetic-moment projection $[\mu_{\bar{z}}(t)]$ on this axis, initially directed along the constant external magnetic field, is described by the equation[13]

$$\mu_{\bar{z}}(t) = \mu_0 - \int_{-\infty}^{t} \dot{\theta}(t_1) \int_{-\infty}^{t_1} \dot{\theta}(t_2) \cos[\varphi(t_1) - \varphi(t_2)]\, \mu_{\bar{z}}(t_2) dt_1 dt_2, \tag{2}$$

where

$$\varphi(t) = \int_0^t \Omega(t')dt', \quad \dot{\theta}(t) = \frac{d}{dt}\theta(t) = \frac{\dot{\omega}_{\perp}(t)\omega_{\parallel}(t) - \omega_{\perp}(t)\dot{\omega}_{\parallel}(t)}{\Omega^2(t)}. \tag{3}$$

Let us find the value of the projection $\mu_{\bar{z}}(t)$, assuming that the adiabaticity condition

$$|\theta(t)/\Omega(t)| \ll 1 \tag{4}$$

is met. Under these conditions $\mu_{\bar{z}}(t)$ varies very little and, assuming the projection to be constant, we take $\mu_{\bar{z}}(t)$ outside the integral sign. Integrating and transforming with allowance for the symmetry of the integrand to interchange of the temporal variables, we get

$$\mu_{\bar{z}} \approx \frac{1}{2}\mu_0 \left| \int_{-\infty}^{t} dt_1 \exp[i\varphi(t_1)]\, \dot{\theta}(t_1) \right|^2. \tag{5}$$

We can now use in detail the analogy between our problem and the above references[7] to adiabatic invariants. The role of the slowly varying parameter λ of Ref. 7 is played by the angle θ characterizing the direction of the instantaneous field in the RCF. To make complete the analogy with the problem of the harmonic oscillator with slowly varying frequency,[7] we assume that $\Omega(t) = \gamma H_0 = \omega_0$ as $t \to -\infty$ and as $t \to \infty$, changing slowly (compared with ω) near ω_0 at other times $|\Omega(t) - \omega_0| \ll \omega_0$. Note that since the spin ener-

 1063-7761/93/030526-04$10.00

gy in an instantaneous field is determined by the relation $E = \mu\Omega\cos\theta'$, the adiabatic invariant will be $\cos\theta'$ (or the proportional quantity $\mu_{\tilde{z}} = \mu\cos\theta'$), since[7]

$$\partial E/\partial\cos\theta' = \Omega,$$

θ' is the angle between the direction of the instantaneous field and the magnetic moment.

Replacing in (3) and (5) the lower integration limit by $-\infty$, and the upper by ∞, we obtain

$$\mu_{\tilde{z}}(\infty) - \mu_0 = -\frac{1}{2}\mu_0|\Phi|^2, \quad (6)$$

$$\Phi = \int_{-\infty}^{\infty} dt_1 \exp[i\varphi(t_1)]\,\dot{\theta}(t_1)dt_1. \quad (7)$$

Following Ref. 7, we replace the integration variable t by φ:

$$dt = \frac{dt}{d\varphi}d\varphi = \frac{d\varphi}{\Omega(t(\varphi))}.$$

Now

$$\Phi = \int_{-\infty}^{\infty} \frac{\dot{\theta}(t(\varphi))}{\Omega(t(\varphi))} e^{i\varphi}d\varphi. \quad (8)$$

This formulates the problem of the accuracy with which the adiabatic invariant is conserved. The integrand in (8) has no singular points on the real axis. We now regard φ as a complex variable and shift the integration path from the real axis to the upper half-plane of this variable. The contour is then linked with singular points of the integrand and envelops them. Let φ_0 be the singular point closest to the real axis, i.e., the point with the smallest positive imaginary part. Note that this point is either a pole of $\dot{\theta}$ or a zero of Ω.

The main contribution to the integral (8) comes from the vicinity of the point:

$$\Phi \propto \exp(-\operatorname{Im}\varphi_0), \quad (9)$$

where

$$\varphi_0 = \int^{t_0} \Omega(t)dt, \quad (10)$$

t_0 is the coordinate of the singular point on the complex-variable plane, the lower integration limit can be chosen to be a real value of t; the imaginary part of interest to us is independent of the real. It is most convenient to integrate along a segment parallel to the imaginary axis from the point t_0 to the point $\tau = t_0 + i\tau_0$ since the important part in the exponent is $\operatorname{Im}\varphi_0$:

$$\operatorname{Im}\varphi_0 = \operatorname{Im}\int_{t_0}^{t_0+i\tau} \Omega(t)dt. \quad (11)$$

We investigate now the magnetization lost by the action of adiabatic pulses on the system. We assume that the field modulation is governed by

$$\omega_{\parallel}(t) = \Delta + bf(t), \qquad \omega_{\perp} = \text{const} \ll |\Delta| \quad (12)$$

with a function $f(t)$ of two types

$$\text{a)}\ f(t) = 1/\operatorname{ch}(\alpha t),$$
$$\text{b)}\ f(t) = \exp(-\alpha^2 t^2). \quad (13)$$

Substituting (13) in (7) we find that the sought nearest singular point is determined by a zero of the denominator, i.e., by the equation

$$\omega_{\parallel}^2(t) + \omega_{\perp}^2 = 0, \quad (14)$$

the approximate solutions of which in the two chosen cases are

$$\text{a)}\ \alpha t_0 = i\left(\frac{\pi}{2} - \frac{b}{\Delta}\right) \pm \frac{b\omega_{\perp}}{\Delta^2} + O(\Delta^{-3}),$$
$$\text{b)}\ \alpha t_0 = i\ln^{1/2}\frac{\Delta}{b} \pm \omega_{\perp}\left(2\Delta\ln^{1/2}\frac{\Delta}{b}\right)^{-1} + O(\Delta^{-2}). \quad (15)$$

We obtain a pair of closely located branch points, which coalesce as $\Delta \to \infty$. Integrating in (11) and retaining only the principal terms, we get

$$\text{a)}\ \Phi \propto \exp\left[-\frac{\Delta}{\alpha}\left(\frac{\pi}{2} - \frac{b}{\Delta}\right) + \frac{b}{\alpha}\ln^2\frac{\Delta}{b} - \frac{\pi\omega_{\perp}^2}{4\alpha\Delta} + \ldots\right],$$
$$\text{b)}\ \Phi \propto \exp\left[-\frac{\Delta}{\alpha}\left(\ln^{1/2}\frac{\Delta}{b} - \ldots\right) - \frac{\omega_{\perp}^2}{2\alpha\Delta}\left(\ln^{1/2}\frac{\Delta}{b} + \ldots\right)\right]. \quad (16)$$

Note that in some cases of practical importance the integrals (7) can be calculated exactly. Thus, for example, for the two modifications of adiabatic-pulse inversion, proposed in Refs. 8 and 9, we have

$$1)\ \omega_{\parallel}(t) = \omega_1\operatorname{th}(\alpha\omega_1 t), \qquad \omega_{\perp} = \omega_1/\operatorname{ch}(\alpha\omega_1 t), \quad (17)$$

$$2)\ \omega_{\parallel}(t) = \omega_1\operatorname{tg}(\alpha\omega_1 t), \qquad \omega_{\perp}(t) = \omega_1 = \text{const}. \quad (18)$$

For both cases we obtain the same result:

$$\Phi = \alpha\int_{-\infty}^{\infty}\left[\frac{e^{i\varphi}}{\operatorname{ch}(\varphi\alpha)}\right]d\varphi = \pi\operatorname{ch}^{-1}\frac{\pi}{2\alpha}. \quad (19)$$

The causes of the obtained equality of the losses (19) for different time dependences of the fields $\omega_\perp$ and $\omega_\parallel$ are the following. The quantity Φ is determined in final analysis by an integral of a function that depends on the phase φ acquired by the magnetic moment upon rotation around the effective field $\Omega(t)$, and one and the same integrand can be obtained for a different choice of $\omega_\perp(t)$ and $\omega_\parallel(t)$, provided the form of the dependence of $\dot{\theta}/\Omega$ on φ is preserved; this corresponds, of course, to a strictly defined connection between them. Thus, the result (19) turns out to be a consequence of the relation

$$\omega_{\perp}(\varphi) = \omega_{\parallel}(\varphi)\operatorname{sh}(\alpha\varphi).$$

Another functional dependence will lead to other results.

Expression (19), when substituted in (6), determines the magnetization loss following the action of an ideal pulse. Under real conditions, however, the pulses become inevitably shortened, so that the main loss occurs at the "on" and "off" instants. An estimate of this loss, which has a power-law dependence on α, is given in Refs. 8, 11, and 12.

By way of example of the investigation of the frequency asymptote of the TCF spectrum, consider the shape of the absorption-line wing. Unfortunately, unlike in the preceding examples, the variation, with time, of the local magnetic field acting on the spin in a solid-state multispin system cannot be described by some simple function. An approximation quite popular for magnetic resonance is a description of the local field by a random function of the time.[14] In addition, as usual, we confine ourselves to the $\omega_\perp$ approximation linear in the field. The absorption will be determined from the change of the projection of the magnetic moment on the RCF axis. Equation (2) changes now into the equation

$$\mu_z(t) = \mu_0 - \omega_\perp^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \cos[\Psi(t_1) - \Psi(t_2)]\, \mu_z(t_2). \tag{20}$$

In the approximation assumed $\omega_\perp$ is conserved only in the pre-exponential factor $\dot{\theta}/\Omega$, while the terms with $\omega_\perp$ are left out of the exponents of (8) and (11). By the same token, φ and φ_0 are replaced by Ψ and Ψ_0:

$$\Psi(t) = \int_0^t \omega_\parallel(t')dt', \qquad \Psi_0 = \int^{t_{00}} \omega_\parallel(t)dt, \tag{21}$$

where t_{00} is determined by the solution of the equation $\omega_\parallel(t) = 0$. Note finally that in Eq. (20) the field $\omega_\perp$ is turned on at the instant $t = 0$. In accordance with the statistical theory widely used in magnetic resonance,[6,13,14] we shall assume that the local magnetic field acting on the spin is a Gaussian random function of time $\xi(t)$. Recognizing that the longitudinal-field modulation is due exclusively to local fields, we choose $\omega_\parallel(t)$ in the form $\Delta + \xi(t)$. It is known that a Gaussian process is fully defined by a correlation function

$$\langle \xi(t)\xi(t+\tau)\rangle = \langle \xi^2\rangle g(\tau). \tag{22}$$

In addition, $\Psi(t)$ will also be a Gaussian random function of time. Thus[14]

$$\langle \cos[\Psi(t_1) - \Psi(t_2)]\rangle = \exp[i\Delta(t_1 - t_2)]G(t_1 - t_2), \tag{23}$$

where

$$G(t) = \exp[-\langle \xi^2\rangle \int_0^t dt' \int_0^{t'} dt'' g(t'')].$$

Since $\mu_z(t)$ varies slowly under the considered conditions, we take $\mu_z(t)$ outside the integral sign in (20). After an averaging and some simple transformations we get

$$\langle \mu_z(t)\rangle = \mu_0 - \mu_0\omega_\perp^2 \int_0^t (t-\tau)G(\tau)e^{i\Delta\tau}d\tau. \tag{24}$$

Finally, extending the integration limits to infinity, we obtain Anderson's expression[14] for the absorption-line shape

$$G(\Delta) = \int_{-\infty}^{\infty} e^{i\Delta t}G(t)dt. \tag{25}$$

An asymptote of the spectrum (25) as $\Delta \to \infty$ in the absence of singular points on the real axis of the function $G(t)$ can be obtained[6] by the saddle-point method. The equation for the saddle point is

$$i\Delta = \langle \xi^2\rangle \int_0^t g(\tau)d\tau. \tag{26}$$

For the spin system of a solid it was proposed in Ref. 14 to approximate the correlation of a random field by the Gaussian

$$g(t) = \exp(-t^2/\tau_c^2), \tag{27}$$

and in Ref. 15 by the function

$$g(t) = 1/\mathrm{ch}^2(t/\tau_c). \tag{28}$$

In the first case an estimate of the wings by the saddle point yields[6]

$$G(\Delta) \propto \exp[-\tau_c \Delta \ln^{1/2}(2\Delta/\langle \xi^2\rangle \tau_c)]. \tag{29}$$

In the second case the integrals are calculated in explicit form[16]

$$G(\Delta) = 2^{\nu-1}\tau_c\Gamma\left(\frac{\nu}{2} + \frac{1}{2}i\Delta\tau_c\right)\Gamma\left(\frac{\nu}{2} - \frac{1}{2}i\Delta\tau_c\right)/\Gamma(\nu), \tag{30}$$

where $\nu = \langle \xi^2\rangle \tau_c^2$ and Γ is the gamma function.

For a longitudinal magnetic field dependence, specified by functions $f(t)$ and $g(t)$ and different from those in the above example, we can find the coordinates of the singular points and determine the arguments of the exponentials in the corresponding asymptotic expressions by solving Eq. (14) or (26). Note that in the above examples a dependence on the detuning is encountered in the exponents in two forms: Δ and $\Delta \ln^{1/2} \Delta$. Each form of the exponent is determined by the properties of the slowly varying field $\omega_\parallel(t)$, namely by the behavior of the function $f(t)$ or $g(t)$ on the complex-variable plane. If the function becomes infinite at a finite distance τ_0 from the real axis, the singular-point coordinate determined by Eqs. (14) and (26) as $\Delta \to \infty$ will approach this value, while the exponent will approach $\Delta\tau_0$. If, however, the function becomes infinite only at an infinite distance then the singular point t_0 will move away as $\Delta \to \infty$, leading to an additional dependence on the detuning and to an exponent $\Delta \ln^\beta \Delta$.

Thus, the magnetic losses following the action of ideal adiabatic pulses, and the form of the NMR absorption line on the wing depend exponentially on the ratio of the detuning to the rate of change of the field α or of $1/\tau_c$. This dependence illustrates, with the magnetic-moment motion known from mechanics as the example, the exponential smallness of the variation of the adiabatic invariants ($\mu_{\bar{z}}$ in the considered case) for motion of systems with slowly varying parameters. The exponential dependence is replaced by a power law only if the singular points of the functions $f(t)$, $g(t)$, and $\Omega(t)$ are located on the real axis [for example the instants of turning on the pulses, the inflection point for functions of the type $g(t) = \exp(-|t|/\tau_c)$].

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Translated by J. G. Adashko