Dynamic NMR frequency shift in the inverted state

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The motion of the nuclear magnetization in the inverted state under the conditions of the dynamic NMR frequency shift is investigated. The conditions under which the NMR line has different shapes in the equilibrium and inverted states are found. It is shown that the line width changes considerably during the quasistationary transient process.

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The first experiments on the investigation of the motion of the nuclear magnetization in the inverted state under the conditions of the dynamic NMR frequency shift were performed recently.[1] Theoretically, the characteristics of the NMR of a ferromagnet in the inverted state have already been investigated by Ignatchenko and the present author,[2] but the effects that arise under the conditions of the dynamic frequency shift (DFS) were not considered in that investigation. The purpose of the present paper is to investigate these effects.

Let the nuclear magnetization $\boldsymbol{\mu}$ be switched over at zero time $t = 0$ into the inverted (or a nearly inverted) state (the Z component $m = \mu_Z/\mu = -1$). Let us consider the precession of $\boldsymbol{\mu}$ under the action of a weak microwave field h at $t > 0$. The equations of motion of the nuclear magnetization are given in, for example, Ref. 3 (the equations (4)). We shall assume that the longitudinal-relaxation time T_1 is significantly longer than the characteristic damping time of the natural oscillations of the transverse nuclear magnetization. If now the field h is sufficiently small, then a quasistationary transient process is realized in the system of nuclear spins[2]: the tranverse component $\boldsymbol{\mu}_\perp$ of the nuclear magnetization executes small forced oscillations under the action of the microwave field, while the Z component relaxes according to the simple law:

$$m(t) = 1 - 2\exp(-t/T_1). \tag{1}$$

The expression describing $\boldsymbol{\mu}_\perp(t)$ coincides with the solution obtained in Refs. 3 and 4 for the case of small oscillations near the ground state if we make the following substitution:

$$m = 1 \to m = m(t). \tag{2}$$

Let us consider the absorption P of the microwave-field energy during the quasistationary process. Using (2) and the steady-state solution obtained earlier,[3,4] we find a general expression describing the absorption line shape:

$$P \sim F(\Delta, m) = \frac{m(t)\Phi'}{(1 - D\Phi'')^2 + (D\Phi')^2},$$
$$\Phi = \Phi' - i\Phi'' = \int_{-\infty}^{\infty} \frac{g(\delta)\,d\delta}{i(\delta + \Delta) + \Gamma_n}, \quad D = D_0 m(t). \tag{3}$$

Here D_0 is the maximum dynamic NMR frequency shift, $\delta = \omega_n - \langle\omega_n\rangle$, $\Delta = \langle\omega_n\rangle - \omega$, ω_n is the unshifted NMR frequency, ω is the frequency of the microwave field, $g(\delta)$ is a prescribed distribution function, and $\Gamma_n = 1/T_2, T_2$ being the transverse nuclear relaxation time. Usually, in magnetic materials we have $\Gamma_n \ll \Gamma$, where Γ is the halfwidth of the function $g(\delta)$; therefore, in the absence of a DFS (i.e., for $D \ll \Gamma$) the NMR line shape is described by the function g. For $D \ll \Gamma$, we can, by repeating the analysis, performed earlier,[4] of the expression (3), verify that the NMR signal should be observed at the shifted frequency $\omega = \langle\omega_n\rangle - D$, and obtain the following approximate expression for the halfwidth ζ of the NMR line:

$$\zeta = \pi D^2 g(-D) + \Gamma_n. \tag{4}$$

In the steady ($m = 1$) state, the behavior of the NMR line as D_0 increases depends essentially on the form of the function g, i.e., on the NMR line shape in the absence of a DFS. If for $D_0 \ll \Gamma$ the original NMR line falls off at the wings more rapidly than the Lorentz function (i.e., if $g(\delta) < \Gamma/\pi\delta^2$), then it narrows down as D_0 increases; in the opposite case the NMR line broadens as D_0 increases, while in the case of the Lorentz distribution function the NMR line remains unchanged as D_0 increases. The function $g(\delta)$ can have the most diverse forms in real magnetic materials, but it is always a truncated function. Therefore, there always exists some critical value D_c such that $g(\delta) \equiv 0$ for $|\delta| > D_c$. Thus, as predicted earlier,[5] the NMR line narrows down to the value Γ_n at sufficiently high values of $D_0 (D_0 \gg D_c)$. On the other hand, the situation can be quite exotic in the intermediate region $\Gamma \lesssim D_0 < D_c$: the NMR signal narrows down, broadens, or remains unchanged, depending on the form of the original NMR line.

Let us now consider the shape of the NMR line in the inverted (i.e., $m = -1$) state. Let $D_0 = 0$ initially. Then the expression (3) describes an inverted NMR signal (in the absence of nonresonance electronic absorption the microwave-field energy is not absorbed, but amplified[2]). As m relaxes, the amplitude of the nuclear signal decreases to zero, and then (in the region $m > 0$) there appears a "normal, upward-directed" NMR signal that increases continuously to its steady-state level. Let us note that, for $D_0 = 0$, the frequency and shape of the NMR line remain invariant during the quasistationary process.

Now let $D_0 \neq 0$. It is clear from the expressions (3) that, for $D_0 \neq 0$, the amplitude, frequency, and shape of the NMR line change in the general case. To analyze the general pro-

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perties of this phenomenon, let us consider the modification of the function $F(\Delta, m)$, that occurs when the signs of m and Δ are changed. We can, by making the substitution $\tilde{\delta} = -\delta$ in the integral (3) and assuming that $g(-\delta) = g(\delta)$, verify that

$$F(-\Delta, -m) = -F(\Delta, m). \quad (5)$$

This indicates that, upon the inversion of the nuclear magnetization (upon the induction of the transition $m \to -m$) under DFS conditions, the NMR signal turns over, and its frequency shifts in the opposite direction: if in the equilibrium state the NMR is observed at $\omega = \langle\omega_n\rangle - D_0$, then after the inversion it is observed that $\omega = \langle\omega_n\rangle + D_0$. Let us emphasize that the NMR line shape does not depend on the sign of m, and, consequently, it remains unchanged after the inversion. Thus, if, for example, the DFS leads to a narrowing of the NMR line in the equilibrium ($m = 1$) state, the line will turn over, but remain narrowed upon the inversion (i.e., on going over into the $m = -1$ state). As m relaxes, the quantity D increase from $-D_0$ to D_0; correspondingly, the NMR frequency decreases monotonically from $\omega = \langle\omega_n\rangle + D_0$ to $\omega = \langle\omega_n\rangle - D_0$. In the process, the line width varies nonmonotonically. Let us denote the value of ζ for $m = 1$ by ζ_0. If $\zeta_0 < \Gamma$, then the line broadens to its unperturbed width 2Γ as m (<0) tends to zero, but again narrows down to the original width $2\zeta_0$ as m (>0) increases to unity. If $\zeta_0 > \Gamma$, then, conversely, the NMR signal narrows down in the region $m<0$, and then broadens in the region $m>0$. (Let us note that in this case the most intense signal may be observed at $|m|<1$, and not at $|m|=1$ if the signal amplification on account of the line narrowing exceeds the attenuation due to the factor $m(t)$ in the expression (3).

Notice that the equality (5) is valid only for symmetric distribution functions $g(\delta)$. If $g(\delta)$ is asymmetric, then the NMR line shape will depend not only on the magnitude, but also on the sign, of m. It is clear from the expression (4) that, in the equilibrium ($m = 1$) state, the variation of the NMR line width as D_0 increases is governed by the behavior of the left wing of the function $g(\delta)$; in the inverted ($m = -1$) state, by the behavior of the right wing of $g(\delta)$. Thus, if the original NMR line (i.e., the line for $D_0 \ll \Gamma$) is asymmetric, then the line shape may, as D_0 increases, vary differently or even contrariwise in the equilibrium and inverted states (i.e., $\zeta > \Gamma$ in the equilibrium, and $\zeta \leqslant \Gamma$ in the inverted, state, or vice versa). It is possible that it is precisely this situation that obtained in the experiments of Bun'kov *et al.*[1]

Let us now briefly discuss the conditions of applicability of the steady-state solution. Firstly, the expression (1) for $m(t)$ will be valid only at sufficiently low values of h; the corresponding inequality can easily be derived in much the same way as is done in Ref. 2. Secondly, the natural oscillations of the transverse nuclear magnetization attenuate over a period of time $\sim 1/\xi$; therefore, the quasistationary transient process is possible only when $1/\zeta \gg T_1$. Let us recall that $1/\zeta \leqslant T_2$; and what is more, as a rule, $1/\zeta \ll T_2$, and therefore the condition $1/\zeta \ll T_1$ is usually clearly fulfilled. In conclusion, let us note the following. For small deviations of the nuclear magnetization from the equilibrium configuration,[3,4] the free-precession signal, like the response to a δ-pulse influence for any linear system, is a Fourier transform of the absorption-line shape. This is, naturally, valid for the inverted state as well. Therefore, the NMR line in the inverted state can be determined from the shape of the free-precession signal following the action of a short microwave pulse that turns the nuclear magnetization through an angle φ close to π (the experiments reported in Ref. 1 were performed in this way). The NMR line shape for the intermediate values of $m = m_0(-1 < m_0 < 1)$ can be studied with the use of two pulses: the first pulse transfers the nuclear magnetization into the inverted state ($\varphi_1 \approx \pi$); then at the moment of time t_0 ($m(t_0) = m_0$) the second pulse deflects the nuclear magnetization through a small angle $\varphi \ll 1$, after which the free-precession signal should be observed.

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[1]Yu. M. Bun'kov, M. Punkkinen, and E. E. Yulinen, Zh. Eksp. Teor. Fiz. **74**, 1170 (1978) [Sov. Phys. JETP **47**, 615 (1978)].
[2]V. A. Ignatchenko and V. I. Tsifrinovich, Zh. Eksp. Teor. Fiz. **69**, 1243 (1975) [Sov. Phys. JETP **42**, 635 (1975)].
[3]V. I. Tsifrinovich and I. V. Krasnov, Zh. Eksp. Teor. Fiz. **78**, 1760 (1980) [Sov. Phys. JETP **51**, 883 (1980)].
[4]V. I. Tsifrinovich, Fiz. Tverd. Tela (Leningrad) **23**, 3521 (1981) [Sov. Phys. Solid State **23**, 2047 (1981)].
[5]E. A. Turov and M. I. Kurkin, in: Problemy magnitnogo rezonansa (Problems of Magnetic Resonance), Nauka, Moscow, 1978, p. 271.

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