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The Line Shape of a Two-Level System with a Fluctuating Frequency

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Abstract—An expression is derived for describing the transformation of the line shape in a two-level system with a fluctuating resonance frequency ω. In contrast to the existing approaches, the obtained expression is not based on any assumption regarding the distribution of frequencies ω. It is shown that, under conditions of a dichotomous random process when the resonance frequency ω randomly assumes one of two values, as well as under conditions of the Gauss–Markov and Lorentz–Markov random processes describing the frequency fluctuations, the derived expression reduces to well-known results. The transformation of the line shape of a two-level system described by the plateau-shaped Abragam curve is considered as an example.

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1. INTRODUCTION

The model of a two-level system with a frequency stochastically fluctuating over time has found a wide application in various fields of solid-state physics (nuclear magnetic resonance (NMR) spectroscopy [1–14], nonlinear optical spectroscopy [15–19], problems of decoherence and phase relaxation of states in quantum computers [20–22], etc.). This model is described by the Kubo–Anderson equation [2, 3]

$$\dot{x} = -i\omega(t)x, \tag{1}$$

where $\omega(t)$ is the random function of time.

The formal time-averaged solution of Eq. (1) can be written as

$$\langle x(t)\rangle = \left\langle x(0)\exp\left(-i\int_0^t \omega(t')dt'\right)\right\rangle, \tag{2}$$

where $\langle\ldots\rangle$ denotes averaging over all possible outcomes of a random process.

The function $\langle x(t)\rangle$ describes the linear response of the two-level system (in nuclear magnetic resonance, this function is called the free precession decay [1]), and in the case of stationary stochastic processes, the Fourier image of function (2) describes the shape of the absorption line of the two-level system [1, 17–19, 23].

The analytical solution of Eq. (1) is known when the resonance frequency ω randomly assumes two values ±Δ (the dichotomous random process) [10–13, 15]. An averaging algorithm for expression (2) was proposed in [1, 3, 24] for the case where the resonance frequency ω randomly assumes n possible values $\omega_1, \omega_2, \ldots, \omega_n$. In the classical works by Kubo and Tomita [23] and Klauder and Anderson [5], the following expression was derived for $\langle x(t)\rangle$ in a Gauss–Markov random process:

$$\langle x(t)\rangle = \exp\{-\sigma^2\tau_0^2(e^{-\nu_c t} - 1 + \nu_0|t|)\}. \tag{2a}$$

Here, σ is the variance of the random process and $\tau_0 = \nu_0^{-1}$ is the correlation time that describes random variations in the frequency ω.

The Fourier image of function (2) (the line shape) is described by the expression

$$f(\omega) = \frac{\exp(\sigma^2\tau_0^2)}{2\pi\sigma}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(\sigma\tau_0)^{2n} \times \frac{\sigma\tau_0 + n/\sigma\tau_0}{(\sigma\tau_0 + n/\sigma\tau_0)^2 + (\omega/\sigma)^2}. \tag{3}$$

In the absence of random fluctuations of the resonance frequency ω (the "rigid" two-level system, $\sigma\tau_0 \gg 1$), the function $f(\omega)$ transforms into a Gaussian function [23]. In the other extreme case of very rapid fluctuations in ω ($\sigma\tau_0 \ll 1$), the function $f(\omega)$ transforms into a Lorentzian function [23]. This transformation of the line shape correctly qualitatively describes the so-

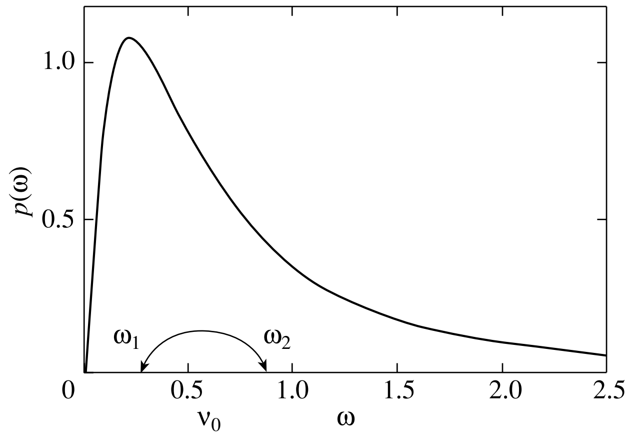

Fig. 1. Schematic representation of the distribution function $p(\omega)$ of all possible frequencies ω.

called effect of thermal line narrowing [1, 19]. However, the line shape $f(\omega)$ of the rigid two-level system is far from Gaussian in many solids, which is a significant hindrance for practical use of relationship (3).

In this study, we obtained a solution to Eq. (1) which does not rest on any assumption regarding the explicit form of the line shape $f(\omega)$ of the rigid two-level system.

2. THE LINE SHAPE OF A TWO-LEVEL SYSTEM

We assume that the distribution of all possible values of the frequency $\omega(t)$ in Eq. (1) is described by the function $p(\omega)$ and that the jumps from one allowed frequency (ω_1) to another allowed frequency (ω_2) are independent of each other and homogeneously distributed over time with the density ν_0 ($\nu_0 dt$ determines the average number of jumps within the time interval dt) (Fig. 1).

For the stochastic process under consideration, the solution to Eq. (1) can be easily obtained using the method of differentiation formulas, which was described in detail in the review by Loginov [25]:

$$\frac{d}{dt}\langle x_k\rangle = -\nu_0\langle x_k\rangle + \nu_0\langle x_0\rangle\langle\alpha^k\rangle + \left\langle \alpha^k\frac{\partial x_0}{\partial t}\right\rangle. \quad (4)$$

Here, $x \equiv x_0$ and

$$\alpha^k = [i\omega(t)]^k, \quad (5)$$

$$x_k = \alpha^k x_0. \quad (6)$$

After substituting Eq. (1) into expression (4), we derive the equation

$$\frac{d}{dt}\langle x_k\rangle = -\langle x_{k+1}\rangle - \nu_0\langle x_k\rangle + \nu_0\langle\alpha^k\rangle\langle x_0\rangle. \quad (7)$$

The Laplace transform of Eq. (7) leads to the expression

$$z\bar{x}_k - \langle x_k(0)\rangle = -\bar{x}_{k+1} - \nu_0\bar{x}_k + \nu_0\overline{\langle\alpha^k\rangle\langle x_0\rangle}, \quad (8)$$

where

$$\overline{\langle\alpha^k\rangle\langle x_0\rangle} = \int_0^\infty e^{-zt}\langle\alpha^k\rangle\langle x_0\rangle dt, \quad (9)$$

$$\bar{x}_k = \int_0^\infty e^{-zt}\langle x_k\rangle dt. \quad (10)$$

Then, we introduce the designation $l = (z + \nu_0)^{-1}\, l$ and rewrite Eq. (10) in the form

$$\bar{x}_k = l[\langle x_k(0)\rangle - \bar{x}_{k+1} + \nu_0\overline{\langle\alpha^k\rangle\langle x_0\rangle}]. \quad (11)$$

By assuming that the stochastic process is a stationary process and using Eq. (11), we obtain

$$\bar{x}_0 = \frac{p(z)}{1-\nu_0 p(z)}, \quad (12)$$

where

$$p(z) = \int_0^\infty \frac{p(\omega)d\omega}{z + i\omega + \nu_0}. \quad (13)$$

In practice, it is sometimes convenient to use relationship (13) rewritten in the form

$$p(z) = \int_0^\infty e^{-(z+\nu_0)t}G(t)dt, \quad (14)$$

where $G(t)$ is the Fourier image of the function $p(\omega)$:

$$G(t) = \int_0^\infty e^{-i\omega t}p(\omega)d\omega. \quad (15)$$

The resulting expression (12) describes the line shape of the two-level system for an arbitrary distribution function $p(\omega)$ of the frequency ω.

3. DISCUSSION

Now, we consider the application of relationship (12) to several types of distribution functions $p(\omega)$.

(1) When $\nu_0 = 0$ and $p(\omega) = \delta(\omega - \Delta)$, relationships (12) and (13) lead to the well-known result [1]:

$$\bar{x}(z) = \frac{1}{z + \Delta}, \quad (16)$$

$$\langle x(t) \rangle = \cos(\Delta t). \quad (17)$$

(2) When $p(\omega) = \frac{1}{2}\delta(\omega + \Delta) + \frac{1}{2}\delta(\omega - \Delta)$, from relationships (12) and (13), we again obtain the well-known result [10–13]:

$$\bar{x}(z) = \frac{z + \nu_0}{z(z + \nu_0) + \Delta^2}. \quad (18)$$

The Laplace transform of relationship (18) leads to the expression [10–12]

$$\langle x(t) \rangle = e^{-\nu_0 t}\left[\left(\frac{\nu_0}{R}\right)\sinh(Rt) + \cosh(Rt)\right], \quad (19)$$

where $R^2 = \nu_0^2 - \Delta^2$.

(3) In the case where the distribution function of possible values $\omega(t)$ is a Lorentzian function,

$$p(\omega) = \frac{\sigma}{\pi(\omega^2 + \sigma^2)}, \quad (20)$$

from relationships (12) and (13), it follows that [1, 2, 10, 24]

$$\langle x(t) \rangle = \exp(-\sigma t). \quad (21)$$

Therefore, in the case of the Lorentzian distribution function of frequencies $\omega(t)$, random fluctuations of the frequency $\omega(t)$ do not affect the line shape of the two-level system. This remarkable result was first noted in [2, 10, 24]. It is interesting to note that the Lorentzian function (20) is the limiting case of the Pareto–Levy distributions, i.e., the distributions for which only the first moment of the distribution a finite quantity [26].

(4) Let us consider the case where the distribution function of all possible values $\omega(t)$ is described by a Gaussian function:

$$p(\omega) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{\omega^2}{2\sigma^2}\right). \quad (22)$$

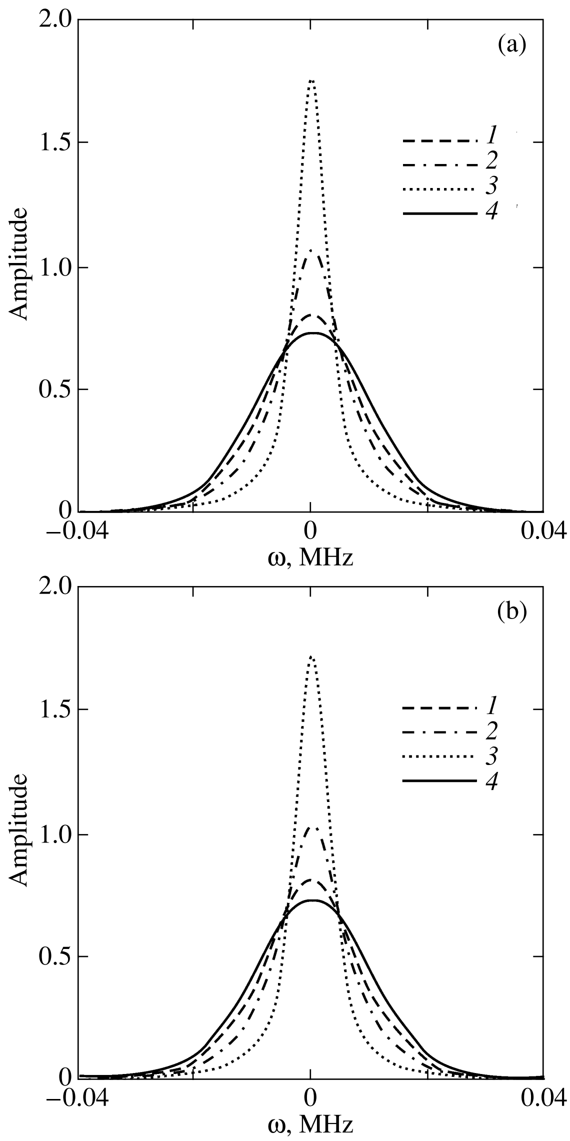

Fig. 2. Thermal transformations of the line shape (Gaussian curve) according to (a) relationship (23) and (b) relationship (3) for the parameters $\sigma = 10^{-2}$ MHz; $\nu_0 = 1.2 \times 10^7\exp\{-25\ [\text{kJ mol}^{-1}]/kT\}$ MHz; and T = (*1*) 136, (*2*) 144, and (*3*) 152 K. Curve *4* shows the Gaussian distribution (22).

After substituting this expression into relationships (13) and (12), we obtain

$$\bar{x}(z) = \frac{\dfrac{\sqrt{\pi/2}}{\sigma}\operatorname{erfc}\left[\dfrac{(z + \nu_0)}{\sigma\sqrt{2}}\right]}{\exp\left[-\dfrac{(z + \nu_0)^2}{2\sigma^2}\right] - \sqrt{\dfrac{\pi}{2}}\dfrac{\nu_0}{\sigma}\operatorname{erfc}\left[\dfrac{(z + \nu_0)}{\sigma\sqrt{2}}\right]}. \quad (23)$$

The results of the calculations performed using relationships (3) and (23) are presented in Fig. 2. It can be

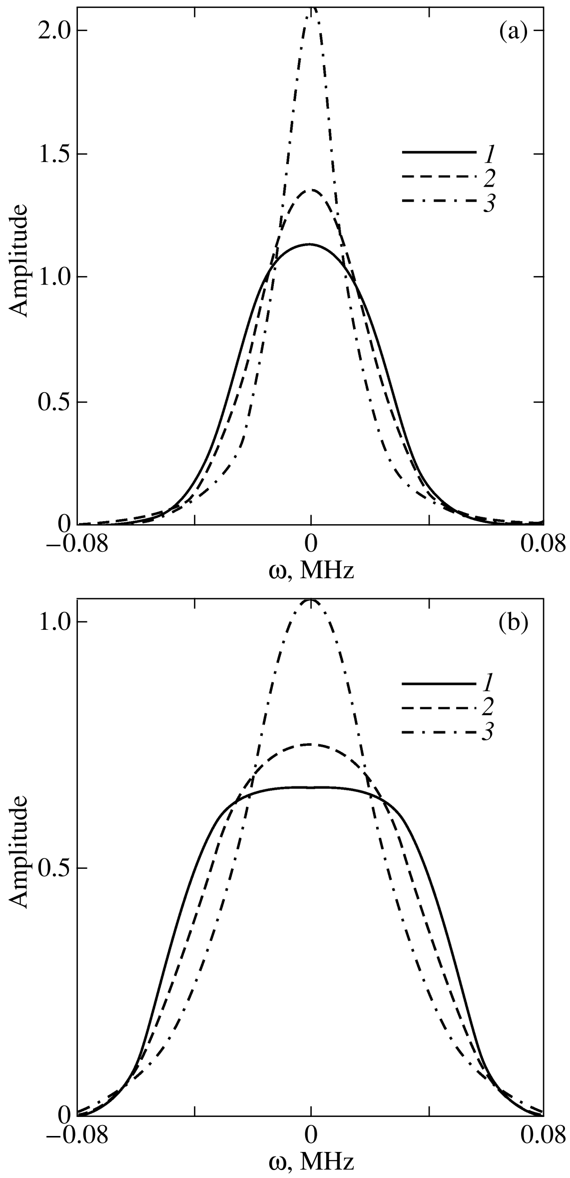

Fig. 3. Thermal transformations of the line shape with the free precession decay described by relationship (24) (Abragam curve) for the parameters $\sigma = 10^{-2}$ MHz; $\nu_0 = 1.2 \times 10^7 \exp\{-25[\mathrm{kJ\ mol^{-1}}]/kT\}$ MHz; T = (*1*) 136, (*2*) 144, and (*3*) 152 K; and b = (a) 3σ and (b) 5σ.

seen from the curves depicted in Fig. 2 that, for the Gaussian function describing the distribution of all possible values $\omega(t)$, relationships (3) and (23) lead to the same results.

(5) In his classical monograph [1], Abragam proposed to use a plateau-shaped function instead of a Gaussian function for describing the free precession decay in solid-state NMR; that is,

$$G(t) = \exp\left(-\frac{\sigma^2 t^2}{2}\right)\frac{\sin(bt)}{dt}. \qquad (24)$$

We carried out calculations of the thermal variations in the line shape for a two-level system with the use of function (24) and with allowance made for relationships (14) and (12). The results of these calculations are presented in Fig. 3. A comparison of the curves depicted in Figs. 2 and 3 demonstrates that the thermal variations in line shape depend substantially on the form of the function describing the distribution of all possible frequencies $\omega(t)$.

In conclusion, we note that the theory presented in this paper does not depend on the specific form of the frequency distribution function $p(\omega)$ and makes it possible to consider a series of yet-unsolved problems, in particular, problems in the physics of solid-state NMR. We would like to point out some of these problems. It is interesting to investigate transformations of the NMR line shape of water molecules in crystal hydrates. At present, these transformations are analyzed using relationship (18) (or relationship (19)) [11], i.e., without regard for the intermolecular dipole–dipole interactions of magnetic moments of protons from different water molecules. In [12], this interaction was investigated phenomenologically, with changing z in relationship (18) by $z + T_2^{-1}$. This formal change disregards the thermal averaging of intermolecular dipole–dipole interactions of magnetic moments of protons, which can lead to errors in experimental values of the activation energy of thermal motion of water molecules. Moreover, it would be of interest to investigate the problem of transformations of the line shape in a two-level system for other distribution functions $p(\omega)$ of the Pareto–Levy type, which describe the anomalous diffusion and reorientation processes in solids [26].

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