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HIGH-FREQUENCY SUSCEPTIBILITIES OF THE GAUSSIAN TYPE

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When we investigate substances by means of the magnetic resonance methods (NMR, EPR), the investigated sample is located in a static and high frequency magnetic field. In a vector model describing those phenomena the motion of the magnetic polarization vector in a simultaneous action of both fields is investigated.

In the present paper the time dependent differential equation of the magnetic polarization motion vector is formulated. We take into account both the longitudinal and the transversal effects and it is further shown that under certain simplification of the so-called slow transition through the resonance point $dJ_z/dt=0$ and the conditions $\omega_t=$const, $\Delta\omega=$const, there sets in, after a certain amount of time when $t\to\infty$, a fixed state of the system, corresponding to a stational solution of the magnetic polarization vector components. Those stational components enable us to define the value and the form of the dispersion $\varkappa'$ and the absorption $\varkappa''$ high-frequency susceptibility, described by the gaussian function.

ВЫСОКОЧАСТОТНЫЕ ВОСПРИМЧИВОСТИ ГАУССОВСКОГО ТИПА

При исследовании материалов с помощью магнитного резонанса (НМР, ЭПР) изучаемый образец помещается в высокочастотное магнитное поле. В работе приводится векторная модель, описывающая эти явления, на основе которой исследуется движение вектора магнитной поляризации при одновременном действии обоих полей.

В данной работе выведены зависящие от времени дифференциальные уравнения, описывающие движение вектора магнитной поляризации, которые учитывают как продольные, так и поперечные эффекты. Показано также, что так называемый медленный переход через резонансную точку $dJ_z/dt=0$ и условие $\omega_t = const.$, $\Delta\omega = const$ после истечения определенного времени $t\to\infty$ приводит к определенному состоянию системы, соответствующему стационарному решению для составляющих вектора магнитной поляризации. Эти стационарные составляющие позволяют определить значение и форму дисперсии $\varkappa'$ и поглощения $\varkappa''$ высокочастотной восприимчивости, описанной при помощи гауссовской функции.

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I. INTRODUCTION

Bloch arranged in his fundamental paper [1] concerning the Nuclear Magnetic Resonance (NMR) a system of differential mobility equations, describing the dynamic properties of the magnetic polarization in the system of paramagnetic nuclei. Similar equations, formally identical with those of Bloch, may be used also for the description of the paramagnetic system of spins by the Electron Paramagnetic Resonance (EPR). The difference between the two descriptions is only in the value of the gyromagnetic ratio existing in Bloch's equations. In Bloch's equations there is an assumption that the magnetic polarization vector is able to orientate only in two directions — a parallel and an antiparallel one according to the statical magnetic field direction. Such equations are therefore suitable for describing twolevel spin systems.

Bloch's equations are of a halfclassical character, therefore we add to the terms describing the influence of the external magnetic field on the magnetic polarization vector the terms of relaxation, which express phenomenologically the interaction between the spin system with its neighbourhood (lattice) and the interaction of the spins in the system with one another. In a certain analogy with the phenomenon of dielectric polarization, Bloch expressed those terms versus time in an exponentially decreasing form. Under certain conditions of the experimental arrangement the solution of the system of Bloch's equations is possible and enables us to define and to express the value and the form of dispersion and absorption of high-frequency susceptibility. In case of a weak saturation of the sample those susceptibilities are described by a lorentzian curve.

In the paper presented we shall begin with a similar halfclassical model and make the differential mobility equations, the solution of which, under certain conditions steady by the practical arrangement of the experiment, makes it possible to express the dispersion and absorption high-frequency susceptibility. Under the condition of weak saturation their form will be described by a gaussian curve.

II. THE MOBILITY EQUATIONS

When a paramagnetic sample is located in a static magnetic field, then the magnetic polarization is

$$\boldsymbol{J}_s = \varkappa_s \boldsymbol{B}_0 , \qquad (1)$$

where $\varkappa_s$ is the volume static susceptibility. If — besides the static magnetic field $\boldsymbol{B}_0$, usually oriented in the Z axis direction — there acts upon the sample also a high frequency circular polarized magnetic field $\boldsymbol{B}_1$ rotating in the XY plane with a frequency ω, the magnetic polarization vector under the action of the two fields performs a rather complicated motion, which can be described by the equation

$$\mathrm{d}\boldsymbol{J}/\mathrm{d}t = \gamma\,(\boldsymbol{J}\times\boldsymbol{B}) \qquad (2)$$

where $\boldsymbol{B} = \boldsymbol{B}_1 + \boldsymbol{B}_0$ is the resulting magnetic field. Under certain conditions there sets in during the magnetic resonance the absorption of the high frequency energy in the sample, which in the vector model manifests itself as an overturn of the vector $\boldsymbol{J}$. To have the possibility of the experimental observation of the phenomenon, the sample must continually absorb the energy and so it is necessary to remove continually the energy absorbed by the sample to the neighbourhood of the sample by a certain mechanism.

There exist two kinds of such a mechanism:

a) the spin lattice interaction, where the system delivers the energy to the lattice neighbourhood and which from a macroscopical point of view can be characterized by a constant of the spin-lattice interaction T_{sm};

b) the spin-spin interaction, where the individual spins (particles of the sample) exchange the energy with each other, can be characterized by, as a constant of the spin—spin interaction T_{ss}.

From the quantum mechanical theory of the relaxation processes it follows that both constants, T_{sm} and T_{ss}, are connected with the velocity of the magnetic polarization changes, where there is valid

$$T_1 = T_{sm}\,; \;\; 1/T_2 = 1/T_{ss} + 1/2T_{sm} ,$$

where T_1 is the constant of the longitudinal relaxation, characterizing the velocity of changes of the Z-component of the magnetic polarization and T_2 is the constant of the transversal relaxation, characterizing the velocity of changes of the J_x, J_y components. If we assume the relaxation of mechanisms, equation (2) in a scalar expression takes the form

$$\frac{\mathrm{d}J_x}{\mathrm{d}t} = \gamma(\boldsymbol{J}\times\boldsymbol{B})_x + \left(\frac{\mathrm{d}J_x}{\mathrm{d}t}\right)_{\mathrm{rel}} \qquad (3a)$$

$$\frac{\mathrm{d}J_y}{\mathrm{d}t} = \gamma\;\boldsymbol{J}\times\boldsymbol{B})_y + \left(\frac{\mathrm{d}J_y}{\mathrm{d}t}\right)_{\mathrm{rel}} \qquad (3b)$$

$$\frac{\mathrm{d}J_z}{\mathrm{d}t} = \gamma(\boldsymbol{J}\times\boldsymbol{B})_z + \left(\frac{\mathrm{d}J_z}{\mathrm{d}t}\right)_{\mathrm{rel}} . \qquad (3c)$$

Now there remains to be determined the form of the relaxation terms. We assume that the magnetic polarization vector can have according to the static field only two positions — a parallel and an antiparallel one. The external static field causes a nonequal occupation of the two energy levels of the system as a consequence of validity of the Boltzmann distribution.

Let N_1 be the number of spins in the energy state 1 and N_2 in the other. The Z-component of the magnetic polarization J_z is proportional to the difference of occupation of the two states according to the relation

$$J_z = \mu_0 \gamma \hbar \, (N_1 - N_2) = \mu_0 \gamma \hbar n \, ,$$

where $n = N_1 - N_2$ is the difference of occupation of the two states and as a consequence of relaxation we have (see for example [2]):

$$\frac{dn}{dt} = -\frac{1}{T_1}(n - n_s) \text{ and } \left(\frac{dJ_z}{dt}\right)_{rel} = -\frac{1}{T_1}(J_z - J_s) \, , \tag{4}$$

where J_s is the magnetic polarization in the equilibrium state. The relation (4) is the searched relaxation term. Bloch in his classical paper assumed the components to the magnetic polarization J_x, J_y to have also the same analytical expression. This is not valid in general, but the components J_x, J_y are influenced also by another kind of interaction, than that of the J_z component. But between the form of the absorption line $g(\Omega)$ and the relaxation components of magnetic polarization $J_l(t)_{rel}$, where $l = x, y$, there exists an insignificant universal coherence in the form (see [3], [4])

$$J_l(t)_{rel} = \int_{-\infty}^{\infty} g(\Omega) \, . \, e^{i\Omega t} \, d\Omega \tag{5}$$

where $\Omega = \omega - \omega_0$. When the spectral line $g(\Omega)$ has to be a curve of a gaussian form, then from relation (5) it results that the $J_l(t)_{rel}$ must have the form

$$J_l(t)_{rel} = J_l(0) \, . \, e^{-t^2/2T_2^2} \text{ or } \frac{dJ_l(t)_{rel}}{dt} = -\frac{t}{T_2^2} J_l(t)_{rel} \, . \tag{6}$$

The mobility equations for the magnetic polarization (3a), (3b), (3c), with respect to (4) and (6), are then

$$\frac{dJ_x}{dt} = \gamma(\boldsymbol{J} \times \boldsymbol{B})_x - \frac{t}{T_2^2} J_x$$

$$\frac{dJ_y}{dt} = \gamma(\boldsymbol{J} \times \boldsymbol{B})_y - \frac{t}{T_2^2} J_y$$

$$\frac{dJ_z}{dt} = \gamma(\boldsymbol{J} \times \boldsymbol{B})_z - \frac{1}{T_1}(J_z - J_s)$$

or in a vectorial expression

$$\frac{d\boldsymbol{J}}{dt} = \gamma(\boldsymbol{J} \times \boldsymbol{B}) - \frac{t}{T_2^2}(J_x \boldsymbol{i} + J_y \boldsymbol{j}) - \frac{1}{T_1}(J_z - J_s) \, \boldsymbol{k} \, , \tag{7}$$

were $\boldsymbol{i}$, $\boldsymbol{j}$, $\boldsymbol{k}$ are the unitary vectors in the laboratory system S.

III. THE SOLUTION OF THE MOBILITY EQUATIONS

It is advantageous to search the solution of equations (7) in the rotational system S', (X', Y', Z'), chosen by us so that the Z-axis fuses $Z \equiv Z'$ and the X' axis lies permanently in the direction of the rotating vector $\boldsymbol{B}_1$. Further we suppose that at the time $t = 0$ there were valid $X \equiv X'$ and $Y \equiv Y'$. From the point of view of the rotating system S' therefore we have

$$\boldsymbol{B}_0 = B_0 \, . \, \boldsymbol{k}'$$

$$\boldsymbol{B}_1 = B_1 \, . \, \boldsymbol{i}'$$

$$\boldsymbol{\omega} = \omega \, . \, \boldsymbol{k}'$$

$$\boldsymbol{J}_r = u\boldsymbol{i}' + v\boldsymbol{j}' + J_z \boldsymbol{k}'$$

where u, v, J_z are the components of the magnetic polarization vector in the rotating frame. By transformation of equation (7) to S' we obtain the expression

$$\frac{dJ_r}{dt} = \gamma \boldsymbol{J}_r \times \left[\left(B_0 + \frac{\omega}{\gamma}\right) \boldsymbol{k}' + B_1 \boldsymbol{i}'\right] -$$

$$-(u\boldsymbol{i}' + v\boldsymbol{j}') \frac{t}{T_2^2} - \frac{1}{T_1}(J_z - J_s) \, \boldsymbol{k}'$$

or in the components

$$\frac{du}{dt} = \Delta\omega \, . \, v - \frac{t}{T_2^2} u \tag{8a}$$

$$\frac{dv}{dt} = -\Delta\omega \, . \, u - \frac{t}{T_2^2} v - \omega_1 J_z \tag{8b}$$

$$\frac{dJ_z}{dt} = \omega_1 \, . \, v - \frac{1}{T_1}(J_z - J_s) \tag{8c}$$

where in the adaptation of these relations we used

$$\omega_0 = -\gamma B_0$$

$$\omega_1 = -\gamma B_1$$

$$\Delta\omega = \omega - \omega_0 \, .$$

The general solution of equations (8a, 8b, 8c) in the analytically closed form does not exist. Therefore we will search for the solution in a special case, responsible for certain experimental conditions. Under the condition of slow transition through the resonance point

$$\frac{dJ_z}{dt} = 0 \, , \tag{9}$$

respectively, $J_z = J_z^s = \text{const}$ and under the conditions $\omega_1 = \text{const}$, $\Delta\omega = \text{const}$ and the conditions $\lim_{t\to\infty} u(t) = u_s$, $\lim_{t\to\infty} v(t) = v_s$, there are a fixed state of the system, corresponding to a stational solution of the equations (8a, 8b, 8c) denoted u_s, v_s, J_z. To solve equations (8a, 8b, 8c) we will proceed as follows: We will multiply equation (8b) with an imaginary unit "i" and add it to equation (8a). With respect to condition (9) the third equation (8c) for the present will not be considered. If we put

$$J_+ = u + \mathrm{i}v\,, \tag{10}$$

then after some rearrangement we obtain the equation

$$\frac{\mathrm{d}J_+}{\mathrm{d}t} + \left(\frac{t}{T_2^2} + \mathrm{i}\Delta\omega\right) J_+ + \mathrm{i}\omega_1 J_z^s = 0\,,$$

which has the solution

$$J_+(t) = J_+(0)\,.\,A(t) - \mathrm{i}\omega_1 J_z^s F(t)\,, \tag{11}$$

where $J_+(0)$ is the value $J_+(t)$ at the time $t=0$ and where is

$$A(t) = \exp\left(-\frac{t^2}{2T_2^2} - \mathrm{i}\Delta\omega t\right)$$

$$F(t) = \int_0^t \exp\left(-\frac{t\tau}{T_2^2} - \frac{\tau^2}{2T_2^2}\right).\,\mathrm{e}^{-\mathrm{i}\Delta\omega\tau}\,\mathrm{d}\tau\,.$$

The stational solution of equation (11) is

$$J_+^s = u_s + \mathrm{i}v_s = \lim_{t\to\infty} J_+(t) = J_+(0)\lim_{t\to\infty} A(t) - \mathrm{i}\omega_1 J_z^s \lim_{t\to\infty} F(t)\,.$$

From the analysis of this solution there results

1) partly that for $t\to\infty$, the value $\lim_{t\to\infty} A(t)$ strongly converges to zero and therefore the first term can be omited

2) partly that the value not converging to zero of the second term limit makes marked contributions near the upper boundary of the integral, also by condition $\tau \to t$, and therefore we can write with sufficient precision (see [5])

$$\lim_{t\to\infty} F(t) \doteq \lim_{\substack{\tau\to t\\ t\to\infty}} F(t) = \int_0^\infty \exp\left(-\frac{\tau^2}{2T_2^2}\right).\,\mathrm{e}^{-\mathrm{i}\Delta\omega\tau}\,\mathrm{d}\tau =$$

$$= \sqrt{2}\,.\,T_2\left[\frac{\sqrt{\pi}}{2} - \mathrm{i}aP(a)\right]\exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right)$$

where $a = \frac{\sqrt{2}}{2}\,T_2\Delta\omega$, $P(a) = \sum_{n=0}^{\infty} \frac{a^{2n}}{(2n+1)\,.\,n!}$, "$n$" is a whole positive number $n = 0, 1, 2, \ldots$.

The stational solution has then the expression

$$J_+^s = -\left[\omega_1 J_z^s \Delta\omega T_2^2 P(a) + \mathrm{i}\,\frac{\sqrt{2\pi}}{2}\,\omega_1 J_z^s T_2\right]\exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right).$$

This expression under condition (9) and equation (8c) after the algebraical rearrangement for the stational components of the magnetic polarization vector takes the form

$$u_s = -\,\omega_1 T_2^2 J_s \Delta\omega P(a)\,\frac{1}{s+1}\exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right) \tag{12a}$$

$$v_s = -\sqrt{\frac{\pi}{2}}\,\omega_1 T_2 J_s\,\frac{1}{s+1}\exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right) \tag{12b}$$

$$J_z^s = \frac{1}{s+1}\,J_s \tag{12c}$$

where we denoted

$$s = \sqrt{\frac{\pi}{2}}\,\omega_1^2 T_1 T_2 \exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right). \tag{12d}$$

IV. HIGH FREQUENCY SUSCEPTIBILITIES

The transmission from a clockwise frame system S' to a laboratory frame system S mediates the transformer relations

$$J_x = u_s\,.\cos\omega t + v_s\,.\sin\omega t \tag{13a}$$

$$J_y = -\,u_s\,.\sin\omega t + v_s\,.\cos\omega t \tag{13b}$$

$$J_z = J_z^s\,. \tag{13c}$$

So far we have considered the rotation motion of the high frequency (HF) field amplitudes B_1 and with equal frequencies ω. The vector sum of both turning fields in each case of the time "t" is $\boldsymbol{B}_x = i\, 2B_1 \cos \omega t$. Near the resonance point only one of the two turning fields will be used, which has a corresponding orientation with the direction of the free precession of the magnetic polarization vector. Thus the effect of the harmonically variable, linear by polarized magnetic field B_x is the same as the effect of the circular polarized field of amplitude B_1, turning in the plane XY with the frequency ω. We will write the HF field B_x in the complex form as $B_x^c = 2B_1 \cdot e^{i\omega t}$ and the component magnetic polarization vector in the X axis orientation as $J_x^c = \varkappa B_x^c$, where $\varkappa = \varkappa' + i\varkappa''$ is a complex susceptibility, having the dispersion $\varkappa'$ and the absorption $\varkappa''$ term. Then the real part of the magnetic polarization is

$$J_x = \mathrm{Re}\,[\varkappa B_x^c] = 2B_1\varkappa' \cos \omega t - 2B_1\varkappa'' \sin \omega t$$

and comparing it with (13a) we give

$$\varkappa' = \frac{u_s}{2B_1} = -\frac{1}{2}\,\varkappa_s T_2^2 \Delta\omega P(a)\,\frac{1}{s+1}\exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right) \tag{14}$$

$$\varkappa'' = -\frac{v_s}{2B_1} = \frac{1}{2}\sqrt{\frac{\pi}{2}}\,\varkappa_s T_2 \omega_0\,\frac{1}{s+1}\exp\left(-\frac{1}{2}\,T_2^2\Delta\omega^2\right). \tag{15}$$

In this modification we have used the relations

$$J_s = \varkappa_s B_0\,; \qquad \omega_1 = -\gamma B_1\,; \qquad \omega_0 = -\gamma B_0\,.$$

From the relations (14) and (15) it results that both susceptibilities depend on the factor "s" and according to relation (12c) also on the frequency HF field ω_1, or on the amplitude B_1, respectively. With the increasing value of ω_1 the value of the factor "s" increases and the value of the expression $1/(s+1)$ decreases the values of the quantities $\varkappa'$ and $\varkappa''$ decreases as well. This phenomenon is called the saturation of magnetic resonance. For small amplitudes of ω_1, for which there applies $\omega_1^2 T_1 T_2 \ll 1$, or $s \ll 1$, respectively and the saturation is neglected, therefore we can write with sufficient precision

We indicate with the sign $x = T_2\Delta\omega$ and define the functions $g_1(x) = x\exp\left(-\frac{1}{2}x^2\right)$, $g_2(x) = \exp\left(-\frac{1}{2}x^2\right)$, then the HF susceptibilities are

$$\varkappa' = -\frac{1}{2}\,\varkappa_s T_2 \omega_0 P(a) \cdot g_1(x)\,,$$

$$\varkappa'' = \frac{1}{2}\sqrt{\frac{\pi}{2}}\,\varkappa_s T_2 \omega_0 g_2(x)\,.$$

The functions $g_1(x)$, $g_2(x)$, which characterizes the form of susceptibilities are called the curves of the gaussian type.

V. CONCLUSION

The physical meaning of the susceptibilities $\varkappa'$ and $\varkappa''$ is partly that $\varkappa'$ expresses the part of the magnetic polarization created with the HF field B_x, which is in phase with this field and $\varkappa''$ expresses the part of the magnetic polarization, whose phase is shifted against that field by about $\pi/2$. Further $\varkappa'$ by means of the polynomical $P(a)$ depends twice as much on $\Delta\omega$, or ω, respectively and that is why in analogy with optics we can use the "dispersion susceptibility". On the other hand, if we calculate the density absorption of the HF energy in the sample during the period $2\pi/\omega$, we obtain

$$w = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} \frac{1}{\mu_0}\,|B_x \cdot \mathrm{d}J_x| \doteq \frac{2\omega_0 B_1^2}{\mu_0}\,\varkappa''$$

and that is why we call $\varkappa''$ also absorption susceptibility.

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