Mathematical modeling of spectra of nuclear magnetic resonance signals for investigation of condensed media in express mode

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Abstract. In article the necessity of developing a mathematical model for converting the recorded NMR signal using a modulation technique into the spectrum for new investigations is substantiated. The comparison of various methods for describing the shape of the registration NMR signals to determine the line structure and various practical tasks solve is performed. A mathematical model for to represent the NMR signal in the form of a spectrum, taking into account the features of its registration from condensed matter is developed. Spectra of calculated and experimental NMR signals are presented. Its comparison is carried out.

1. Introduction
The development of scientific and technological progress has led to the emergence of a large number of tasks, which need been solved during of the research and control of the state of condensed media [1-10]. The greatest difficulties are arising during the development of the fast and reliable methods for express control of the state of condensed media [1, 2, 8, 11-13]. Because after express control it is necessary to obtain the confirmation of identify deviation in the medium from the standard on high-resolution devices, which are located in a stationary laboratory [1, 5, 6, 8, 11-16]. For this reason, the measurements used for express control should not introduce changes in the physical structure and chemical composition of the test medium. The developed at the currently of optical [7, 16-26], electromagnetic [27-29] and ultrasonic [30, 31] devices for the research of the media row do not provide this condition. The fulfillment of these conditions for various media is possible only in case of use for express control of devices with the work principle is based on the phenomenon of nuclear magnetic resonance (NMR) [1, 11, 12, 32].

The conducted research are showed that during express control of the condensed medium state by NMR, the signal from its recorded with the using a modulation technique in a weak magnetic field in which the induction value is less than 0.1 T [1, 11, 12, 32]. Other methods of the NMR signal detecting in a weak magnetic field in a small-sized magnetic system of the device (the distance between the poles does not exceed 15 mm, the weight of the magnetic system design should not be more than 4 kg) do not allow the necessary measurement error (not more than 1 %). This error is need for the reliable results obtaining during research in express mode [1, 11, 12].

The lack of the adequate theoretical model is one of the drawbacks of the modulation technique using for express control of the condensed medium. It does not allow reproducing of the line shape of
the recorded NMR signal in a weak field and decoding the information contained in its. For example, to determine the signal structure or the components composition which are contained in the research medium. The conducted research have showed that this significantly limits of the possibility of express control of the condensed medium state in place of taking samples by NMR. One of the possible solutions to this problem is the used of spectral analysis of NMR signals. Therefore, the aim of this work is the developing a methodology that can reproduce the NMR signals spectra were recording in conditions of weak magnetic field modulation in the interpolar space of a small-sized NMR relaxometer. This will expand the possibilities of the small-sized NMR relaxometer using for express control of condensed media.

2. The equations of the nuclear magnetization vector motion in the conditions of a weak magnetic field modulation

The motion of the longitudinal and transverse components of the magnetization vector of the condensed medium in the detection coil of the NMR relaxation spectrometer is described by Bloch equations [33-35]:

\[
\begin{align*}
\frac{dM_x}{dt} + M_x / T_2 + \Delta \omega M_x &= 0 \\
\frac{dM_y}{dt} + M_y / T_2 - \Delta \omega M_y + \gamma H_1 M_z &= 0 \\
\frac{dM_z}{dt} + M_z / T_1 - \gamma H_0 / T_1 - \gamma H_1 M_y &= 0
\end{align*}
\] (1)

where \( \Delta \omega = \omega_0 - \omega_{nmr} \) is the frequency offset of the NMR signal detection circuit \( \omega_{nmr} \) from the magnetization precession frequency in the field \( H_0 \) (\( \omega_0 = \gamma H_0 \)), \( \gamma \) is the static nuclear magnetic susceptibility, \( T_1 \) and \( T_2 \) are the longitudinal and transverse relaxation times of the liquid medium, and \( t \) is the time.

In works of [33, 35] are presented the analytical solutions (1). The solutions (1) were obtained with the using of the variables replacement in the \( M_x \) and \( M_y \) components of the magnetization vector and the transition to a rotating coordinate system with frequency \( \omega_{nmr} \). These solutions were obtained for various conditions (fast passage through the resonance, fast adiabatic passage through the resonance, etc.) in which the NMR signal is recorded. In NMR spectrometers in the study of condensed matter in a stationary state, in most cases, a linear change in the magnetic field is used. For this change in the magnitude of the field \( H_0 \) in the new components of the magnetization vector \( u(t) \) and \( u(t) \) (absorption and dispersion) from solution (1) with fast adiabatic passage through the resonance, the following relations were obtained [33, 36-38]:

\[
\begin{align*}
u(t) &= v_0 \exp (- t / T_2^*) \cos (at^2/2) \\
u(t) &= u_0 \exp (- t / T_2^*) \sin (at^2/2)
\end{align*}
\] (2)

where \( a = \gamma \frac{dH}{dt} = \frac{\Delta \omega}{dt} \) is the rate of change of the magnetic field detuning, \( T_2^* \) is the effective transverse relaxation time, \( v_0 \) and \( u_0 \) are the maximum amplitudes of the recorded NMR absorption and dispersion signals.

The depending of the solved tasks during the investigation condensed media in NMR spectrometers are recorded the absorption or dispersion signals. The line shape of this signal is described with the using to (2) or to (3). In work of [33–40], for different media (which is the stationary condition) are presented the examples of the registered NMR signals (absorption and dispersion) for various media. These works also featured the calculated dependences of the signals of the obtained with the using to (2) and to (3) and is showed the correspondence of the theory with the experiment. The during of the comparing of the recorded NMR signals with the using a modulation technique from water that is both in stationary and in the flowing state with calculations are performed with the using to (2) and to (3) for the linear change in \( H_0 \), external then similarity is observed. For example, these dependencies for \( T=292.1 \) K are presented in fig. 1.

The analysis of the dependences are presented in fig. 1 shows that the line shape of the NMR signals for certain modulation parameters of the \( H_0 \) field is a set of peaks (“wigles”), whose amplitudes decay exponentially over time. For this reason, in [1, 33–40], to study various media that are both stationary and in the flowing state for the NMR signals of the recorded with the using of the
modulation technique, a method was proposed for determining the transverse relaxation time $T_2$ on the envelope decay. The envelope decay be described by the dependence $\exp(-t/T_2^*)$.

**Figure 1 (a, b, c).** The NMR signals from water: (a) and (b) - calculation with the using to (2) and to (3) - graphs 1, 2 and 3 correspond to the values $a^{1/2} T_2^*$: 0; 1; 2; (c) is the recorded NMR signal in a weak field ($B_0 = 0.074$ T) with using a modulation technique.

In this case, in accordance with the theory considered in [33–37], the values of $T_2$ are determined from the following relation:
\[
\frac{1}{T_2} = \frac{1}{T_2'} + \frac{\gamma \Delta H}{\pi}
\]  

(4)

where \(\Delta H\) is the inhomogeneity of the magnetic field in the area of the coil of registration of the NMR signal.

Due to the fact that the obtained results of determining \(T_2\) using (4) coincided within the measurement error with the values of \(T_2\) obtained on other devices, the authors of works to [33, 37, 38] came to the following conclusion. In case of need for line shape describe of the NMR signal, which is recorded with the modulation technique using of the modulation technique, can be applied of equation of (2) and (3). Further investigations in this direction have not been conducted.

To ensure the NMR signal registration from various nuclei with the magnetic moment are contained in the medium with the using of the modulation technique the generation field \(H_1\) of the autodyne detector is set to the maximum signal-to-noise ratio (S/N) in the weak magnetic field (induction value \(B_0 < 0.1 \text{ T}\)). In addition, the maximum value of S/N corresponds to \(\Delta \omega = 0\) (registration at the resonant frequency). In this case, many authors substituted the value \(\Delta \omega = 0\) in (1) and the equations system was simplified. The completed experiments showed that in the weak magnetic fields it is necessary in (1) to take into account the magnetic field in the modulation coil \(H_m\), which varies according to a given law. It is most expedient to use the following modulation mode of the magnetic field \(H\) in the interpolar space of the small-sized NMR spectrometer-relaxometer.

\[
H = H_0 + H_m \sin(\omega_m t)
\]  

(5)

where \(\omega_m\) is the modulation frequency.

In addition, in equations (1), it is also necessary to take into account the modulation of the weak magnetic field \(H_0\) in the magnetization of the investigation medium \(M\). The new relation for \(M\) must be written in the following form:

\[
M = \chi_0(H_0 + H_m \sin(\omega_m t))
\]  

(6)

In works [39, 40] the obtained after equations were considered in detail of equations (1), which are obtained after substituting in them to (6) and (5). It also substantiates the mathematical relationship for constructing the NMR waveform is recorded with the using of the autodyne detector:

\[
G(t) = F(t)(\frac{A}{A+B}u^a(t) + \frac{B}{A+B}u^d(t))^{1/2}
\]  

(7)

where \(u(t), u(t)\) are the absorption and dispersion signals, \(A\) and \(B\) are the coefficients that determine the contribution to the recorded NMR signal from the absorption and dispersion signals, and \(F(t)\) is the coefficient taking into account phase changes.

The completed experiments showed that the value of the dependence of the coefficient \(F(t)\) on time to obtain a correspondence between the results of the experiment and calculation, it is necessary to select for each case of the medium parameters change, the change of the temperature, the change in the ratio between the concentrations of the media (if the medium is a mixture), etc. This fact in the case of research in express mode of the unknown medium or the media mixture will lead to large time delays during the result obtaining or the errors during the results interpretation. The using of spectral analysis of NMR signals allows to exclude this problem during the express control.

3. The technique of the formation a spectrum of NMR signals and comparing the calculation results with experiment

On fig. 2 shows, as an example, the signals form of the absorption \(v(t)\) and dispersion \(u(t)\), as well as the NMR signal \(G(t)\) are obtained with the using to (1), (5), (6) and (7). Numerical solutions of equations (1) were obtained with the using of the Mathematica package for the magnetic fields and relaxation constants \(T_1\) and \(T_2\) corresponding to the experiment (\(T_1 = 1.47 \text{ s}; T_2 = 1.36 \text{ ms}; f_m = 10 \text{ Hz}; B_m = 0.52 \text{ mT}; N = 6.6 \times 10^{20} \text{ m}^{-3}; l = 1/2; \mu = 1.4 \cdot 10^{-28} \text{ J/T}; k = 1.38 \cdot 10^{-23} \text{ J/K}; B_0 = 74 \text{ mT}; T = 291.8 \text{ K}\)). The during a NMR signal registering in the weak magnetic field the parameters of the autodyne detector and the modulating magnetic field are adjusted to a maximum of S/N. In this case, the signals \(v(t)\) and \(u(t)\) participate in the formation of the NMR signal \(G(t)\).
Figure 2 (a, b, c). The calculation forms of NMR signals from water: (a) - absorption; (b) - dispersion; (c) - the total for the same contribution of the absorption and dispersion signals.

The spectra of the signals $v(t)$ and $u(t)$, which were obtained using relation (2) and (3) to describe their forms are presented on fig. 3.

To describe its shape, the following relation was used, which displays the NMR shape recorded in the experiment using a modulation technique:
\[ U = U_0 \exp\left(-\frac{t}{T^2}\right) \cos(\omega_0 t + \frac{1}{2} \gamma M H \cos(\omega_m t) t^2) \] (8)

In view of (5), relation (8) takes the following form:

\[ U = U_0 \exp\left(-\frac{t}{T^2}\right) \cos(\omega_0 t + \frac{1}{2} \gamma H_m \omega_m \cos(\omega_m t) t^2) \] (9)

The analysis of the obtained dependences in fig. 2 shows that they are reflect the physical processes essence corresponding to the experiment. But our additional calculations showed flowing. In the above description of \( G(t) \) for NMR signal form, which was considered of the authors number during its is recorded with the using of other methods, with the increasing \( t \) the across every phase \( T_m/2 \) is the phase change in the line form of \( G(t) \) on \( \pi/2 \) and the sequential decrease of the peaks amplitude. In the experiment, every half period \( T_m/2 \) of the \( H_0 \) modulation field, the same NMR signal is recorded. This discrepancy between theory and experiment and the previously noted difficulties with the choice of the coefficient \( F(t) \) do not allowed the full volume are presented the experimental results. Therefore, to compare the experimental results with the theory is not entirely correctly. This is confirmed by spectra analysis are presented on fig. 3. The signals spectra of absorption (fig. 3.a) and dispersion (fig. 3.b) do not correspond to the experimental spectrum. Also does not correspond to the experimental spectrum, the signal spectrum is presented on fig. 4.

Figure 3 (a, b). The Spectra of NMR signals from water: (a) is absorption; (b) is dispersion.
Figure 4. The spectrum of the NMR signal from water when describing its shape by relation (9).

Figure 5 (a, b). The spectra from an experimental NMR signal recorded from water: (a) is amplitude; (b) is phase.
Figure 6 (a, b). The spectra from the calculated NMR signal for water: (a) is amplitude; (b) is phase.

Therefore, we propose to use the discrete Fourier transform for the description of the calculated NMR signals (absorption, dispersion, and G(t)):

\[ y_k = \sum_{n=0}^{N-1} x_n e^{-j2\pi kn/N} \]  

where \( n = 0, 1, 2, ..., N - 1 \), \( x_n \) is the input data sequence, \( N \) is the number of elements of the input data sequence \( x_n \).

The harmonics of the spectrum are located on the frequency axis with a discrete \( \Delta f = f_s / N \), where \( f_s \) is the sampling frequency of the original sequence \( x \). The sampling rate is determined as follows. Let \( \tau \) be the duration of the NMR signal. Then \( f_s \) can be calculated using the following relation:

\[ f_s = \frac{N}{\tau} \]  

In the case when \( N \) is a power of two, DFT is calculated using the FFT (Fast Fourier Transform) algorithm, which is much faster than a discrete Fourier transform and requires less computational resources.

The discrete Fourier transform is symmetric with respect to the Nyquist frequency equal to \( f_s / 2 \), which allows us to combine harmonics with the numbers \( (N/2-k) \) and \( (N/2+k) \). As a result combining harmonics, we obtain a one-sided complex spectrum with frequencies from 0 to \( f_s / 2 \), which
corresponds to the indices \( k = 0 \ldots (N/2-1) \). The scaled one-sided complex spectrum of a discrete input sequence \( x_n \) is determined by the expression:

\[
y_k = \begin{cases} 
y_0 & k = 0 \\
\sqrt{2} \frac{y_k}{N} & k = 1, 2, \ldots, \frac{N}{2} - 1 
\end{cases}
\]

In relation (12), the operation in brackets \([N/2] \) means rounding to the nearest smallest integer. Accordingly, the amplitude spectrum \( S \) is the modulus of the one-sided complex spectrum, the phase spectrum \( P(f) = \arg y_k \) is its argument, where \( f = k \Delta f \).

The spectra (amplitude and phase) of an NMR signal recorded from a water sample obtained using relations (10) - (12) are presented on fig. 5. The spectra from the calculated waveform of the NMR signal of water (fig. 2.c) is presented on fig. 6.

The spectra analysis are presented on fig. (5 and 6) shows that proposed the method proposed by us for modeling of NMR signals spectra allows to obtain the good concurrency between theoretical and experimental data. This allows to apply it for efficient express control of condensed media.

4. Conclusion

In results of the performed experiments was be established that the developed method for modeling the NMR signal spectra with using to (10) - (12) has no restrictions on the used. For its application necessary to register the NMR signal from a medium (containing nuclei with magnetic moments), for example, on the resonant frequency, on example of protons. The experimental spectrum of the NMR signal is received. Further is necessary to calculate the spectra of absorption and dispersion signals with the using numerical solution (1) taking into account the measured values of the relaxation constants \( T_1 \) and \( T_2 \). The using equation to (7) and choosing for it of the weight coefficients (A and B) can formed a total spectrum. This spectrum should coincided with the experimental spectrum. The values of the weight coefficients (A and B) will determined the contribution of the absorption and dispersion signals to the structure of the NMR signal. Taking into account the fact that during the registering of the NMR signal with a maximum signal-to-noise ratio, the absorption signal is always larger than the dispersion signal [33, 37–40], the weight coefficients are determining of uniquely.

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