

Actual Problems of Computer Parametric Identification of the NMR and NQR spectra: a Review

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Determining a computer model of a spin echo to simulate its amplitude and obtain information about the magnitudes and orientations of the local magnetic field, the direction of the gradient of the crystalline electric field in a sample, is an important task. The paper considers a number of topical issues that enable solving the problem of computer parametric identification of the NMR and NQR spectra. Analysis of the data presented in literature revealed several software programs for simulation of the shapes of NQR lines associated with quadrupole interactions of nuclei in powder solids. It has been established that many computer programs for modeling NMR/NQR experiments developed over the past four decades can be categorized as follows: NMR analytical tools (usually implemented in Mathematica), specialized applications (for example, NOESY spectrum simulator), application programming interfaces, API; the generic NMR modeling program. The available means of computer simulation of the spin echo are described in regard with obtaining information about its amplitude, the magnitude and orientation of the local magnetic field, and the direction of the gradient of the crystalline electric field in the sample. Considerable attention is paid to the imitation of accurate NMR/NQR spectra using the fast diagonalization procedure, as well as an effective averaging scheme for Olderman, Straw, Grant powders. The conducted analysis revealed that Quadrupolar Exact Software (QUEST) is one of the most accurate programs for modeling quadrupole nuclei of powder samples under static conditions. The QUEST spectral simulation is based on summation in the full quadrupole Hamiltonian. This theory is valid and holds for all transitions and at an arbitrary direction of the magnetic field. When modeling the NQR spectra, it is necessary to use low Larmor frequency (~ 0.0001 MHz), but not equal to 0. This is due to the fact that the pure NQR peaks are infinitely sharp and, therefore, it is difficult to summarize them if they appear between the bins in the histogram. Since the calculations in QUEST are performed in units of the absolute frequency, when using a very narrow spectral window, the required accuracy in the frequency values of each bin in the histogram may be missing.

Keywords: Computer parametric identification, Modeling, Spectrum, Spin, NQR, NMR.

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1. INTRODUCTION

Pulsed excitation of nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) is widely used in physics to study internal electric fields, as well as during the study of non-equilibrium states of nuclear spins (relaxation processes) [1, 2]. In particular, the spin echo phenomenon provides the most convenient and accurate measurements of relaxation times, the study of the structure of crystals, and is also the basis of modern NMR tomographs and NQR radiospectrometers [3-5]. In addition, the phenomenon of spin echo is important in the physical models of solid-state quantum computers.

The analysis of the experimental picture of a quadrupole spin echo in a magnetic field is important while studying local electric fields in crystals. In stationary experiments with a change in the time interval between radio-frequency pulses, the amplitude of the spin echo, under constant external or local magnetic field, experiences "slow beatings", the frequency of which is determined by the Zeeman splitting. The basic models for calculating the spin-echo amplitude envelope were developed as early as in the mid-50s and formed the basis of most NMR spectrometers that have a number of approximations. In particular, the resulting formulas for calculating the spin echo intensity given in these models are valid provided $\omega_1 \tau \ll 1$, where $\omega_1 = \gamma H_{rf}$, γ is the gyromagnetic ratio, H_{rf} is the magnetic field

strength, τ is the duration of the radiofrequency pulse. However, in NQR spectrometers, a perceptible signal is observed only under the condition $\omega_1 \tau \sim 1$ [3]. That is, the limits of application of these formulas have not yet been analyzed in detail, and a mathematical model of quadrupole spin echo has not been formulated, which would provide the opportunity to receive information about the physical properties of substances and the orientation of the local magnetic field based on a comparison of experimental data with simulation results.

In addition, since some nuclei have a small quadrupole moment (for example, the nitrogen nucleus compared to the bismuth nucleus), the quadrupole resonance frequencies and the intensity of the spin echo signals are miserable, therefore, the development of NQR spectrometers that are more efficient than the existing ones, is of particular relevance. The importance of the task of measuring and analyzing the amplitude envelope of a nuclear quadrupole spin echo in nitrogen compounds is due to the need to develop effective means of control and safety in transport, customs control, etc. Solving the task of calculating the spin echo amplitude in the case of low frequencies of the main stationary Hamiltonian, which determines the system of nuclear spin levels, and a strong radiofrequency field, requires improvement of the existing analytical models for describing quantum systems with periodically time dependent Hamiltonians. Most of these models are bulky and limited in practical use in the

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range close to resonance.

That is why the design of a spin echo computer model, which would simulate its amplitude and derive information about the magnitudes and orientations of the local magnetic field and the direction of the gradient of the crystalline electric field in a sample, is an important task.

2. THE METHODS OF COMPUTER PARAMETRIC IDENTIFICATION OF THE NMR AND NQR SPECTRA

The analysis of literature data enabled us to identify several available programs that can be used to simulate the shapes of the NQR lines associated with quadrupole interactions of nuclei in powder solids. Typically, they are divided into two classes.

The modeling programs of the first class use in their analysis a density matrix. Examples of such programs include GAMMA, SIMPSON and SPINEVOLUTION, which are mainly used to calculate data in the time interval and to simulate sequences of excitation pulses. The simulation time of a specific experiment or spectrum using these programs may take from a few minutes to several days. These software products can also be used to simulate a magnetic spin angle (MSA) NMR, to test different sequences of excitation pulses or to simulate multidimensional experiments with NMR.

The second class of modeling programs uses simple mathematical expressions to directly calculate the resonance frequencies, which significantly reduces the simulation time. Examples of such programs are WSOLIDS, DMFit and QuadFit. The latter specializes in modeling the NMR spectra with distributed parameters, which is useful when analyzing amorphous solids. To efficiently generate simulation spectrums, all these programs use formulas derived from second-order perturbation theory to calculate the effect of quadrupole interaction on Zeeman energy levels.

Currently, with the rapid growth of computer processing power, the calculations of the NMR spectra for small spin systems can be performed using diagonalization methods (i.e. "precise" methods). Thus, second-order perturbation theory is no longer the only convenient analysis instrument.

2.1 Theoretical Substantiation of Mathematical Models of Decay of Free Induction and Spin Echo

Traditional stationary methods of observing NMR and NQR are now almost completely superseded by pulsed Fourier spectroscopy. Pulsed NQR observation methods are widely used to solve various problems of solid state physics.

In the pulsed NMR method, besides spectral characteristics, additional information is obtained from the results of measuring the relaxation times T_2 and T_1 , which are the result of the interaction inside the spin system (this process is characterized by the transverse relaxation time T_2) and other degrees of freedom in the lattice (this is the spin-lattice relaxation time T_1). These parameters characterize the dynamics of the lattice and spins. Using stationary methods, it is

hardly ever possible to determine the actual time T_2 .

The impulse NQR method consists in observing the response of a nuclear spin system (induction or echo signals) to a short and powerful radiofrequency pulse or a series of pulses [3-5]. The radiofrequency pulse causes the precession of the nuclear magnetization vector, which disappears after a period $T_2^* = 1/\delta$ (δ is the width of the absorption line). This makes possible the reduction of the multicomponent spectrum observation time comparing with the stationary method, the resonance spectrum of which is recorded by continuous transit of frequency at low power of the excitation generator.

By irradiating a sample with a radiofrequency field at a resonance frequency $\omega = \omega_0$ in a rotating coordinate system, the magnetic moment vector \vec{M} is influenced by an effective field $\vec{H}_{eff} = \vec{H}_1$, directed along the axis x' (Fig. 1). Therefore, in this system \vec{M} will rotate around an axis x' in a plane $Z'OY'$ with an angular frequency $\omega_1 = \gamma H_1$. When the field \vec{H}_1 is turned on for a short time t_p , the moment vector will turn at an angle

$$\theta = \omega_1 t_p = \gamma H_1 t_p.$$

The pulse duration must be chosen according to the condition $\theta = \omega_1 t_p = \pi/2$, i.e.

$$t_p = \frac{\pi}{2\gamma H_1}.$$

Under this condition, after the completion of pulse impact, the moment will be oriented along the axis y' . Such a pulse is called a 90-degree, or $\pi/2$ -pulse. After \vec{H}_1 is turned off, the magnetic moment will be fixed in the moving system. In the laboratory coordinate system, it will precess at an angular frequency $\omega = \gamma H_0$, keeping its orientation perpendicular to \vec{H}_0 .

If the sample is in a coil, the axis of which lies in the XOY plane, an electromotive force (e.m.f.) resulting from the spin precession, will be induced in it, which can be observed in free induction decrease. If all spins were independent and precessed at the same frequency, e.m.f. would remain constant. However, due to interaction with the environment, frequencies of the spins differ. The frequency distribution of spins is in the form of a resonant line. Therefore, phase unbalance of spins in the plane XOY occurs and the signal drops to zero. The mathematical model of the signal free induction decay (FID) can be represented by the exponential dependence

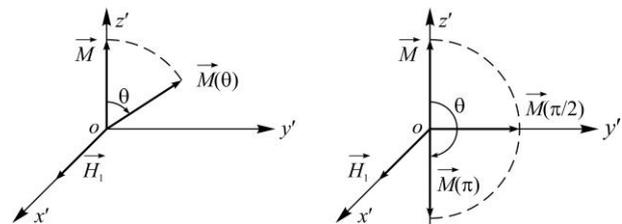


Fig. 1 – Influence on a sample of a radiofrequency field at a frequency $\omega = \omega_0$

$$M_1 = M_0 e^{-t/T_2}.$$

If one writes down FID and applies the Fourier transformation of the decay function

$$J(\omega) = \int_{-\infty}^{\infty} G(t) e^{-i\omega t} dt,$$

the spectral line is obtained.

To observe the spin echo, Khan et al. used imitative expansion of the resonance line by creating a significant inhomogeneity of the magnetic field in the sample ΔH_0 , which corresponds to the frequency interval $\Delta\omega = \gamma\Delta H_0$. If $1/\gamma\Delta H_0 = T'_2 \ll T_2$, the signal decay will occur much faster according to the expression $\exp(-t/T'_2)$, since it will be determined by the effective relaxation time $T'_2 \ll T_2$:

$$\frac{1}{T'_2} = \frac{1}{T_2} + \frac{1}{T'_2} = \frac{1}{T_2} + \gamma\Delta H_0.$$

Let us discuss the formation of a spin echo. After the action of $\pi/2$ -pulse for better understanding we will consider the total vector \vec{M} , as one consisting of three spins and directed along the axis y' of the moving coordinate system (Fig. 3).

For a time interval equal to several T_2 , the phase will be unbalanced in a plane of XOY. We assume that the spin «2» precesses at a Larmor frequency $\omega_0 = \gamma H_0$, while the frequencies of the spins «1» and «3» are $\omega_1 > \omega_0 > \omega_3$. The application of a π -impulse after a time τ will cause the rotation of each of the vectors by 180° around the axis x' . As a result, the vector orientation will change to the opposite – the «slow» vector will be ahead, and the «fastest» vector will be behind. In such a situation, the vectors will come in-phase after the time of 2τ from the beginning of the cycle, and we will get the echo signal (Fig. 4).

Carr and Parcel suggested to apply π -pulses through intervals of $\tau, 3\tau, 5\tau, \dots, (2n-1)\tau$, to call forth the occurrence of echo pulses at $t = 2\tau, 4\tau, \dots, 2n\tau$. Their amplitude will decrease exponentially with the time of transverse relaxation T_2 , which can be determined (Fig. 4).

When observing quadrupole spin echo in polycrystalline samples, a 90°-pulse commonly refers to the shortest pulse at a given voltage of a high-voltage source, when the maximum induction drop is observed. Similarly, the 180°-pulse gives a minimal induction decay. The observation of the NQR signals in the intervals between pulses of the radiofrequency field allows us to avoid many of the difficulties associated with the presence of the radiofrequency field. However, if frequency of pulse repetition in pulsed methods is sufficiently high, the spin system does not have time to absorb energy between pulses. The intensity of the echo signal drops. This effect is called saturation.

A mathematical model of a cyclic spin-echo sequence can be described by the dependence [3]:

$$S = k\rho(1 - e^{-T_n/T_2})e^{-T_E/T_2},$$

where S is the amplitude of the signal after Fourier transformation, k is the proportionality factor, ρ is the spin density in the research sample, T_R is the sequence repeat time, T_E is the spin echo duration.

The principles of constructing equipment for observing spin echo in magnetic and quadrupole resonances have much in common [3-5]. Since the NQR lines are wider than NMR ones in liquids, the installation for observing quadrupole spin echo should provide more powerful radiofrequency pulses. In addition, to search for weak quadrupole echo signals, it is necessary to have a receiver tunable over a wide frequency range.

To observe spin echo in solids, the condition $t_p < T_2$ must be met. Otherwise, the induction signal after the impact of the 1-st pulse does not have time to go out before the formation of the echo signal. When observing the latter from various nuclei, it is necessary to change the pulse duration, since the condition of the 90°-pulse has the form (for $\eta = 0$):

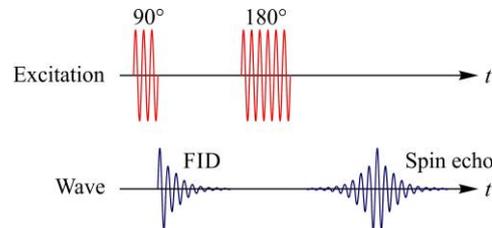


Fig. 2 – NQR signal in the form of FID and spin echo

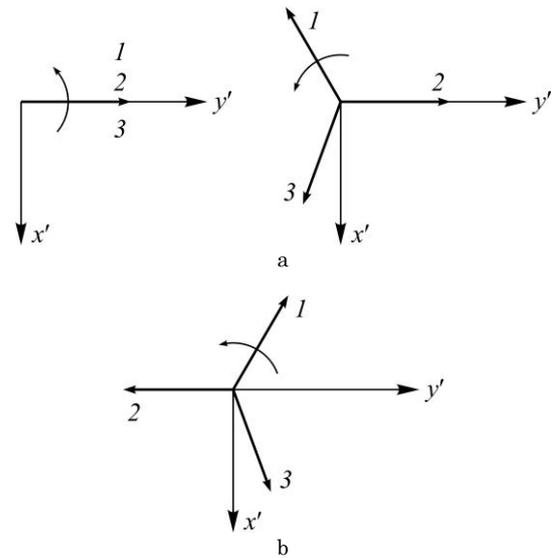


Fig. 3 – Change in the magnetic moments of the spin system: after the action of the $\pi/2$ -pulse (a); after the action of the π -pulse (b)

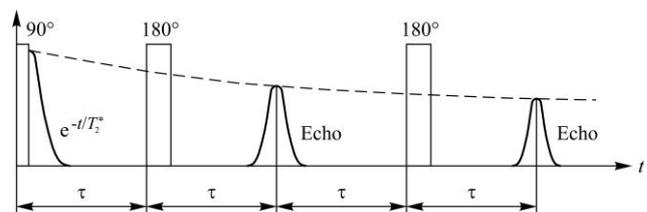


Fig. 4 – Spin echo formation process

$$\alpha\gamma H_1 t_p = \pi/2,$$

where $\alpha = \sqrt{I(I+1) - m(m+1)}$, I is the nuclear spin, m is the magnetic quantum number for low energy level, t_p is the pulse duration. If $I = 3/2$, then $\alpha = \sqrt{3}$; if $I = 5/2$, then $\alpha = 2\sqrt{2}$. Usually, when a spin echo is observed in solids, $t_p \sim 1-4 \mu\text{s}$ is taken, and the amplitude of the RF pulse reaches several kilovolts. The “dead” time of the receiver after exposure to a powerful pulse at its input should not exceed 3-5 μs . Theoretical foundations of pulsed methods of radiospectroscopy are given in the works [1-6].

Usually, to determine the picture of a phenomenon, it is considered that the axis of the coil with a radio frequency field is oriented in parallel to the axis x of the electric field gradient tensor. Under real conditions, the coil axis is oriented randomly with respect to the principal axes of the tensor of the electric field gradient. Then the effective RF field along the axis x will be written as

$$H_x = H_1 \sin\theta \cos\varphi,$$

where θ is the angle between the direction H_1 and axis z , φ is the azimuthal angle.

Accordingly, the component of the RF field along the axis y is equal to:

$$H_y = H_1 \sin\theta \sin\varphi.$$

These two components excite transitions between levels of NQR. Therefore, in the general case, the angles θ and φ will be included in the formula for the conditions of 90°-pulses.

2.2 Software

With the ever increasing complexity of NMR methods and software, numerous simulations have become an integral part of modern research. Usually, they are necessary for obtaining structural parameters from data, the development of new experiments and theoretical studies. This particularly refers to continuous NMR, where most programs use the magic-angle spinning (MAS) and ^1H -splitting to obtain high-resolution spectra, while various methods of chemical shift anisotropy (CSA) are used to reconstruct the averaged interactions of dipole and chemical anisotropy [7]. These methods usually generate a homogeneous Hamiltonian, which depends on time and requires the use of numerical methods every time, when experiments need to be accurately simulated [8]. As a rule, such experiments have been developed and interpreted from the point of view of the first several orders of the average Hamiltonian theory (AHT), which can often be used to obtain approximate solutions [7].

However, although AHT is a fairly powerful analytical apparatus, it is not always possible to apply it because of its insufficient accuracy. In continuous NMR, analytical descriptions of experiments occur more frequently. However, numerical simulation in many cases does not lose its importance, for example, when studying non-ideal pulses, various effects generated by a strong coupling and relaxation, as well as in single-

scan 2D-experiments [7].

Guided by the requirements of experimental NMR, in the past four decades, many computer programs for modeling NMR experiments have been developed [7]. Most of this software can be easily attributed to one of the following categories: NMR analytical tools (usually implemented in Mathematica), specialized applications (for example, NOESY spectrum simulator), application programming interfaces (APIs), generic NMR modeling programs. The last ones are called generic, since they can be used to simulate experiments with a wide spectrum of pulse sequences and spin systems, and therefore have the function of a virtual NMR-spectrometer. In addition, unlike the API, the modeling program must have a convenient high-level interface.

Despite all the advantages, only a few types of software available so far are suitable for modeling general experiments with NMR. As a result, several years ago, the development of new methods, in particular in solid state NMR, was often combined with the development of new problem-oriented software.

The analysis of the literature shows that ANTIOPE was the first common software for simulating NMR. The program is still supported and distributed by its author (J.S. Waugh). It has recently acquired a particularly user-friendly interface and experienced other significant changes since the release of the first version. The API-type package GAMMA, which appeared shortly after ANTIOPE, developed as a library of C++ classes and methods, intended for the development of simulation applications [8]. Despite the fact, that GAMMA greatly facilitates the development of software for modeling, a significant number of tools are often required. The package has been widely used for many years to simulate NMR and EPR experiments. A similar API (BlochLib) has been developed recently, which uses efficient numerical libraries for its basic computations and is superior to GAMMA in terms of efficiency [7]. Currently the most popular in the solid-state NMR simulation package is SIMPSON [7]. It is designed as a high-level API, where modeling is guided by an input file written in a scripting language. SIMPSON does not require compilation and cumbersome software codes to perform simulations. The main application of this tool is the simulation of MAS experiments. Overall, this provides a trade-off between efficiency, convenience and versatility.

The above-mentioned three qualities are the most important characteristics, which are required by the general NMR/NQR simulation program. Versatility is achieved by using the approaches of GAMMA, BlochLib and, to a lesser extent, SIMPSON.

However, an interface that requires writing C++ code for a complex API platform is unlikely to be convenient in most cases. In addition, for the effective propagation of the density matrix using the complex MAS experiment with multiple pulse sequences, it is necessary to calculate and process a complex collection of propagators. GAMMA, BlochLib and SIMPSON have limitations in such features. Moreover, the effectiveness of any simulation depends on the efficiency of computational methods and algorithms on which the modeling package relies, and is independent of the user. If these methods include only enough basic set of

algorithms, creating a simple interface for such a package is relatively easy. However, if these methods include a large library of highly efficient and often specific algorithms, then their integration into a unified general NMR simulation program with a user-friendly interface presents a significant problem, which is added to the problem of developing methods themselves and creating libraries.

In an attempt to solve this problem, the SPINEVOLUTION tool was developed – a general NMR modeling program that implements a number of new calculation methods and methodological approaches to it. Despite the fact that SPINEVOLUTION was developed specifically for modeling solid-state MAS experiments, it can also be used in the context of NMR-spectroscopy, in particular, for solving various optimization problems. The program has a convenient interface based on text files, where the pulse sequences are determined in the natural non-algorithmic form of the description of NMR experiments.

Computational methods and algorithms, which are largely responsible for the high performance of multi-spin calculations in SPINEVOLUTION, are based on Chebyshev decomposition to calculate propagators, thus, are able to use Hamiltonian diagonalizations. Another g-COMPUTE method, which generalizes the previously known COMPUTE and c-COMPUTE algorithms, combines efficient expansion of spectral lines with powder averaging. This makes it possible to use the c-COMPUTE algorithm for multivariate experiments of unlimited spectrum width. SPINEVOLUTION version 4.3 is compatible with most operating systems (Windows, Mac OS X, Linux) [9].

In an NMR experiment, each data point is obtained by observing the magnetization of the sample after it undergoes a certain sequence of radiofrequency (RF) excitation pulses. In real experiments, a pulse program is used to set up the spectrometer to generate such sequences. In modeling, they usually write a program which algorithmically describes which propagators should be calculated, and how they should be manipulated in order to specify the necessary sequence of pulses (as for example in GAMMA and SIMPSON).

SPINEVOLUTION is designed as an application and not as an API, so the user does not need to program. This is partially achieved using the classical approach to represent a sequence of pulses. Such a methodology provides a sufficiently simple interface and almost unlimited internal flexibility for analyzing the problem, organizing data and choosing calculation algorithms in the most efficient way. The user can choose the most convenient description of the sequence of pulses, can indicate the need to calculate powder averaging and relaxation processes. These parameters affect the efficiency and accuracy of the simulation. The interface provides the ability to perform a thorough check of the obtained data for compliance, facilitates the detection of configuration errors and significantly increases the convenience and reliability of the program [7].

The program enters the main input text file, which is edited by the user according to a template. It can be either autonomous or refer to other files describing the details of the simulation. Thus, the same pulse se-

quences and parameter files can be used to create new models. The interface is also well suited for use with an external system shell (Pearl, MATLAB, etc.).

2.3 Universal Modeling Applications

Spectral modeling is an effective means to optimize data collection sequences. The VeSPA package (Versatile Simulation, Pulses and Analysis Package) is an integrated set of open source applications in Python, which allows users to perform the following manipulations: synthesize RF pulses, study scenarios of collecting MRS data using multiparameter spectral modeling and rising the efficiency of analyzing MRS data from GE and Siemens scanners [10].

Programs in VeSPA are integrated using a SQLite database (standard in the Python distributive), which allows you to exchange objects and results of MR-data. Programs are built on the basis of adaptation and expansion of three programs: MatPulse, GAVA and SITools, respectively [7, 8]. The modeling is based on the GAMMA modeling library (Fig. 5) [8]. VeSPA integrated this resource using SWIG to make it possible to obtain the necessary data directly in Python, without the need to attract external resources [7].

The interactive graphical interface of VeSPA enables simultaneously working with data in several separate windows. The most important parameters of the configuration of the excitation pulses and the setting of important functions for the synthesis and analysis of resonance spectrums are combined into the following groups:

- RFPulse – pulse concatenation, scaling, inversion of poles and export to graphic and special formats of the manufacturer;
- Simulation – a graphical interface for simulating the excitation by a sequence of pulses, full dialog boxes for managing the database, outputting to the manufacturer's graphic and data formats (LC Model, Siemens Metabolite Report);
- Analysis – HLSVD signal analysis, control deconvolution.

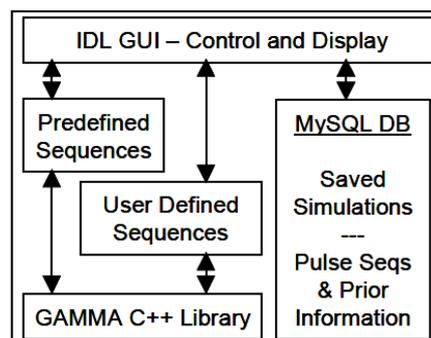


Fig. 5 – Functional diagram of the GAVA environment, implemented on the basis of the SQLite database and the GAMMA library

The fit of the least-squares baseline of the metabolite is repeated with an estimate of the wavelet baseline. In all applications, the results can be shared between VeSPA users through XML import and export.

The pulses specified in RFPulse can be used to form

excitation sequences in Simulation, and the simulation results can be used to analyze spectral lines or selection of metabolites. The results obtained in VeSPA applications are accessed through browsers of MR results objects from the SQLite database. The databases also include integrated, predefined spectral modeling algorithms, designing RF excitation pulses and determining the optimal pulse sequences. Unfortunately, it is difficult to find fast and at the same time convenient software for modeling with satisfactory accuracy of NMR/NQR spectra in open access [11]. From the review, it was found that one of the most accurate is the program for modeling quadrupole cores of powder samples under static conditions – Quadrupolar Exact SofTware (QUEST).

In particular, QUEST is designed to simulate accurate NMR/NQR spectra using the fast diagonalization procedure in the GNU Scientific Library, as well as an effective Aderman, Solum, and Grant (OSG) powder averaging scheme. Thus, diagonalization and NMR calculations are performed for a large number of crystal orientations, after which linear interpolation is performed in accordance with the ASG procedure to complete averaging of the powder. The GUI contains a central graph of the resonance spectrum with the ability to configure the above-indicated parameters.

3. IMITATION OF RESONANCE SPECTRA IN QUEST SOFTWARE

3.1 Fundamentals of Theoretical Analysis in QUEST Software

As a rule, for quadrupole nucleus, the main interactions that affect the resonance spectrum are quadrupole interaction and magnetic shielding. These interactions include quantities that can be represented as second-rank tensors ("tensors"), which are especially convenient for representing NQR interactions in three-

dimensional space [11].

The quadrupole interaction occurs due to the interaction of the electric quadrupole moment of the nucleus (Q) with the electric field gradient (EFG) on the nucleus. The tensor EFG is symmetric and has three components: $|V_{33}| \geq |V_{22}| \geq |V_{11}|$.

Since the EFG satisfies the Laplace equation (i.e. $V_{11} + V_{22} + V_{33} = 0$), the value of the quadrupole interaction can be represented by two parameters: the quadrupole coupling constants (C_Q) and the quadrupole asymmetry parameter (η). In QUEST, these parameters are defined as follows:

$$C_Q = \frac{eV_{33}Q}{\eta},$$

$$\eta = \frac{V_{11} - V_{22}}{V_{33}},$$

where C_Q is the measure of quadrupole interaction, and η is the asymmetry parameter of the EFG tensor (with-in from 0 to 1), what determines the asymmetry of the EFG tensor (for $\eta = 0$, a symmetric tensor).

In QUEST, the C_Q and η values are indicated above the spectrum, which can be simulated by changing the mentioned data (Fig. 6a). In QUEST, the chemical shift tensor can be used as the EFG tensor, which is represented using the three main components (δ_{ii}) in the sequence: $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. For setting the chemical shift tensor, three corresponding parameters are used: isotropic chemical shift δ_{iso} , interval Ω and offset K (Fig. 6b) determined by the formulas [11]:

$$\delta_{iso} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3},$$

$$\Omega \cong \delta_{11} - \delta_{33},$$

$$K = \frac{3(\delta_{22} - \delta_{iso})}{\Omega}.$$

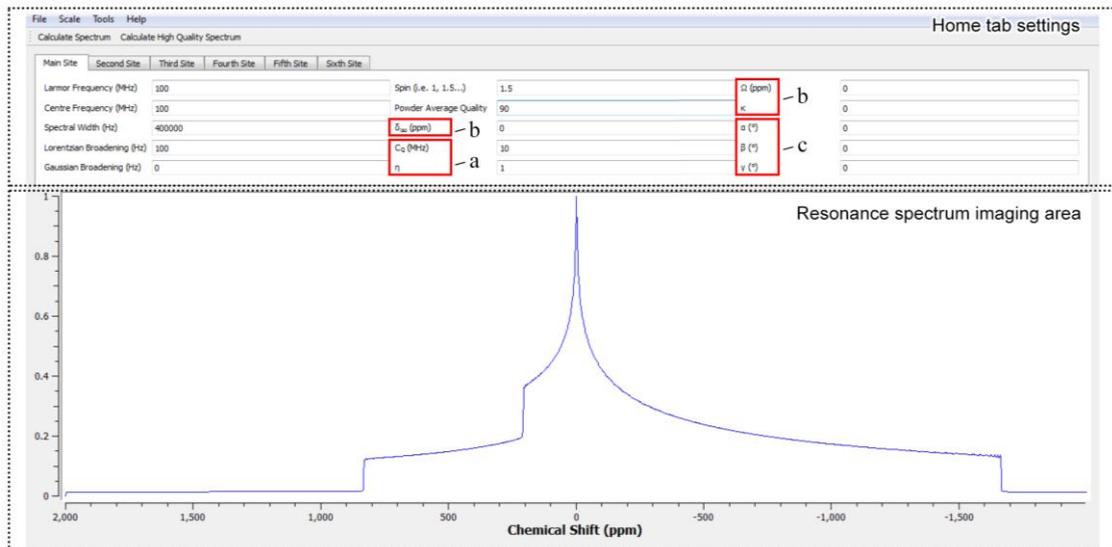


Fig. 6 – Graphic interface of the QUEST software environment: C_Q and η (a) parameters; δ_{iso} , Ω and K (b) parameters; parameters α , β and γ (c) [11]

The relative orientation of the systems of the main axis of two tensor values mentioned above also affects

the resonance frequency [11]. A common way to determine the relative orientation between different coordi-

nate systems is to use Euler angles. In QUEST, the "ZYZ" system is adopted, where the chemical shift tensor is positioned in the direction of the EFG tensor (δ_{ii} along V_{ii}), and then turned off this EFG reference system. First, the chemical shift tensor rotates around δ_{11} at the Euler angle α , the next turn occurs around new orientation δ_{22} at the Euler angle β and, finally, the new orientation δ_{33} according to the Euler angle γ takes place. The location of these parameters in the QUEST interface is shown in Fig. 6. This process can be represented by rotating the magnetic field at a distance from the chemical shift tensor along the rotation matrix. The orientation of the constant magnetic field to calculate the EFG in this case is preserved:

$$R(\alpha, \beta, \gamma) = \begin{bmatrix} \cos\alpha \cos\beta \cos\gamma - \sin\alpha \sin\gamma & \sin\alpha \cos\beta \cos\gamma + \cos\alpha \sin\gamma & -\sin\beta \cos\gamma \\ -\cos\alpha \cos\beta \sin\gamma - \sin\alpha \cos\gamma & -\sin\alpha \cos\beta \sin\gamma + \cos\alpha \cos\gamma & \sin\beta \sin\gamma \\ \cos\alpha \sin\beta & \sin\alpha \sin\beta & \cos\beta \end{bmatrix}$$

3.2 Representation of the Zeeman Quadrupole Hamiltonian

A special feature of QUEST, which makes it unique with respect to other programs for modeling spectral lines, is the way of quadrangular interaction processing. QUEST uses the complete quadrupole Hamiltonian, which can be expressed as follows [11]:

$$\hat{H}_Q = \frac{C_Q}{4I(2I-1)} \begin{bmatrix} \frac{1}{3} \sqrt{6} (3\hat{I}_z^2 - I(I+1))V_0 + (\hat{I}_z \hat{I}_+ + \hat{I}_+ \hat{I}_z)V_{-1} \\ -(\hat{I}_z \hat{I}_- + \hat{I}_- \hat{I}_z)V_{+1} + \hat{I}_+^2 V_{-2} + \hat{I}_-^2 V_{+2} \end{bmatrix},$$

where the spherical tensor components are expressed as [11]:

$$\begin{aligned} V_0 &= 3\sqrt{1/6}V_{zz} \\ V_{+1} &= -V_{xz} - iV_{yz} \\ V_{-1} &= V_{xz} - iV_{yz} \\ V_2 &= \frac{1}{2}(V_{xx} - V_{yy}) + iV_{xy} \\ V_{-2} &= \frac{1}{2}(V_{xx} - V_{yy}) - iV_{xy}, \end{aligned}$$

and the orientation dependence of the quadrupole Hamiltonian is calculated using the expressions [11]:

$$\begin{aligned} V_{xx} &= \frac{1}{2}(3\sin^2\theta - 1 - \eta\cos^2\theta\cos 2\phi) \\ V_{yy} &= \frac{1}{2}(-1 + \eta\cos 2\phi) \\ V_{zz} &= \frac{1}{2}(3\cos^2\theta - 1 - \sin^2\theta\cos 2\phi) \\ V_{xy} = V_{yx} &= \frac{1}{2}\eta\cos\theta\sin 2\phi \\ V_{xz} = V_{zx} &= -\frac{1}{2}\sin\theta\cos\theta(3 + \eta\cos 2\phi) \\ V_{yz} = V_{zy} &= \frac{1}{2}\eta\sin\theta\sin 2\phi. \end{aligned}$$

It is much more convenient to represent the Hamiltonian in the matrix form, where all the matrix elements can be calculated analytically using the expectation values of various operators in the quadrupole

Hamiltonian. The expressions given below include the influence of a magnetic field and chemical shift [11]

$$\begin{aligned} \langle m | \hat{H}_{ZQ} | m \rangle &= -\nu_0(1 + \delta_{zz}) + \frac{\sqrt{6}C_Q}{12I(2I-1)}(3m^2 - I(I+1))V_0 \\ \langle m \pm 1 | \hat{H}_{ZQ} | m \rangle &= \frac{\pm C_Q}{4I(2I-1)}((2m \pm 1)\sqrt{I(I+1) - m(m \pm 1)})V_{\mp 1} \\ \langle m \pm 2 | \hat{H}_{ZQ} | m \rangle &= \\ &= \frac{C_Q}{4I(2I-1)}(\sqrt{I(I+1) - m(m \pm 2)}\sqrt{I(I+1) - m(m \pm 1)})V_{\mp 2} \\ \langle m \pm 3 | \hat{H}_{ZQ} | m \rangle &= 0. \end{aligned}$$

The above expressions show that the Zeeman states ($m = 3/2, 1/2, \dots$) are not real eigenstates of this Hamiltonian, since there are non-zero behind-diagonal elements. For this reason, the approximation of a high field, under certain circumstances, appeared to fail. The Hamiltonian should not contain off-diagonal elements, therefore QUEST diagonalizes this matrix, and its eigenvalues (which are energy levels) are used directly to calculate the resonance frequencies of all transitions with non-zero transition probability (this model also well describes overtones and NQR transitions). To calculate the intensities eigenvectors are used, and real nuclear eigenfunctions are expressed as [11]:

$$|n\rangle = \sum_{m=-I}^I a_{nm} |m\rangle,$$

where the coefficient a_{nm} corresponds to the m -th component of the n -th eigenvector.

Proceeding from this, one can easily calculate the intensity of the lines of the NQR spectrum (the square of the magnitude of the expected value of the operator I_x in the case of a coil located perpendicular to the direction of the magnetic field).

The maximum intensity value will correspond to the case of the coil oriented perpendicularly to the direction of the external field. However, when using the MAS probe slight deviations are possible, since in this case the spectrometer coil is oriented at an angle of 54.74° , and not at 90° . Therefore, when studying nuclei with spin -1 on the Tools tab, an additional parameter was added to change the angle of inclination. Potentially, this can be very useful in modeling the NMR spectra of overtones. The effect of changing the angle of the coil is carried out by adding a certain fraction of the operator I_Z .

A secular approximation was used to calculate the effect of the chemical shift tensor (provided that change of the eigenstates is only facilitated by the chemical shift tensor component, aligned with the applied field) [11]:

$$\delta_{zz} = \delta_{11}\sin^2\vartheta\cos^2\phi + \delta_{22}\sin^2\vartheta\sin^2\phi + \delta_{33}\cos^2\vartheta.$$

3.3 Powder Averaging and Expansion of Spectral lines

The increase in the processing speed of spectrum in QUEST is achieved due to the optimized implementa-

tion of the Alderman, Solum, and Grant spatial mosaic algorithm [11]. According to this algorithm, powder averaging is performed for an ensemble of points above the pyramid instead of a hemisphere. This pyramid is divided into many triangles (each of which is a crystalline orientation), where the resonance frequency is calculated at each vertex of the triangle. The resonance frequency for the residual space can be interpolated based on these three frequencies. Such an approach provides two advantages: cosines and sines do not need to be calculated, since they can be approximated using simple expressions, and secondly, fewer crystal orientations can be used, since the residual space can be interpolated.

Calculations of powder averaging in QUEST are performed at the vertices of each triangle, and the space between them is interpolated.

Unless the chemical shift anisotropy (CSA) is taken into account, it is only necessary to perform averaging over one edge of this pyramid, which significantly reduces the calculation time. If we take into account the CSA and, if the tensors do not coincide, it will be necessary to perform powder averaging over all four edges of the pyramid. The factor limiting the time of performing the calculation in QUEST, appears to be the calculation of not only one resonance frequency, but all frequencies that determine the resonance spectrum. At the beginning of the calculations, two indicators of these actions will appear: the first shows the actual NMR calculation, while the second shows the binnig of all frequencies (data addition from the next N pixels of the matrix takes place, while increasing the sensitivity in N times, the spatial resolution experiences the N time drop).

Algorithm of spreading spectral lines in QUEST is based on Lorentz and Gauss convolutions. They are calculated by distributing the signal intensity of a single histogram cell into all cells [11]:

$$I_L = \frac{I}{1 + \frac{4(v - v_0)^2}{L_B^2}},$$

$$I_G = I \exp\left[-\frac{4 \ln(2)(v - v_0)^2}{G_B^2}\right],$$

where I_L is the Lorentz line intensity at a given frequency ν , I_G is the Gauss line intensity at a given frequency ν , v_0 is the resonance frequency for peak intensity I , L_B is the magnitude of the expansion of the Lorentz line; G_B is the magnitude of the expansion of the Gauss line.

3.4 The Basis of the Analysis and Modeling of Spectrum Using QUEST

QUEST is able to read spectral files of the standard Bruker format (i.e. TOPSPIN) [11]. To be more specific, QUEST reads only *.1r and *.procs files. In order to open the spectrum, it is necessary to open the folder containing the spectrum and select the *.1r file; the *.procs file automatically finds the QUEST software if it is in the same directory. The *.1r file contains a series of binary integer numbers representing the signal

intensity, whereas the *.procs file contains all other necessary information (transmitter frequency, width of the spectrum, number of data points, etc.).

The QUEST software enables calculating all resonance transitions, and therefore the spectral window is set manually when necessary. This can be done by adjusting the parameters of central frequency and spectral width. The size of the spectral width also affects the calculation time.

For nucleus with significant quadrupole interactions and possessing several NMR-active isotopes with similar gyromagnetic ratios, such as bromo-79/81 or rhenium-185/187, different layers of powder for different isotopes can overlap. This entangles the modeling of spectrum, because chemical shifts are related to only one isotope. To eliminate this effect, one can change the reference frequency, which is used to calculate the chemical shifts. This function should be used while maintaining the NMR spectrum of one isotope that was experimentally associated with another isotope. Alternatively, if the experimental spectrum is loaded, there is also an additional option to set the reference frequency.

By default, the experimental and calculated spectra are normalized to an intensity equal to unity. If there are obvious differences in the experimental spectrum, this can greatly reduce the intensity of the wider spectrum elements, which have a practical interest in the experimental spectrum. Thus, it is necessary to increase the scale of the experimental spectrum. In addition, it is possible to save or read the parameters used to create the QUEST simulation spectrum with the "Save" or "Read" option of the QUEST parameter files on the File menu tab. The parameter files in QUEST are the text files containing information about the Larmor frequency, center frequency, L_B , G_B , δ_{iso} , average powder quality, sample rotation angle, spectrum width, C_Q , α , β , γ , η , Ω and κ in sequential order.

Examples of simulation of resonance spectrums with the use of the QUEST software environment are shown in Fig. 7-Fig. 9. QUEST allows to simulate up to six objects. To configure the parameters of other objects it is necessary to select the new tabs. Additional settings (chemical shift and parameters of the EFG tensor, rotation angle, Larmor frequency and relative intensity) are available for the first object. If the relative intensity is set to "0", then no other calculations are performed. By default, the main position has a relative intensity of 100 %. An example of modifying several positions using the QUEST software is shown in Fig. 7.

The tab "Tools" menu contains options that facilitate the operation with several objects, in particular for some elements, such as bromine or rhenium, there are various isotopes with similar NMR parameters. In these cases, if the quadrupole interaction is noticeable, both isotopes can be observed in the same window. For this reason, it is possible to combine several objects; thus, the selected parameters for the second object are automatically calculated based on the corresponding parameters of the first one. Chlorine, titanium, copper, bromine, indium and rhenium are added to the spin pairs. On the tab "Tools" of the menu there is a possibility to "disconnect" objects that were connected to each other, or remove the experimental spectrum.

During modeling of the NQR spectra, it is necessary to use a small Larmor frequency (~ 0.0001 MHz), but not equal to 0. This is due to the fact that the pure NQR peaks are infinitely sharp and, therefore, difficult to add if they appear between the bins on the histogram. Since the calculations in QUEST are performed in terms of the absolute frequency, while using a very narrow spectral window, there may be a lack of the necessary accuracy in the frequency values of each bin in the histogram. In addition, when the spectrum is stored in the Bruker TOPSPIN format, information on the chemical shift, not on the resonance frequency is used. Thus, the spectra can be saved only if they are calculated in the chemical shift mode, and not in the resonance frequency mode.

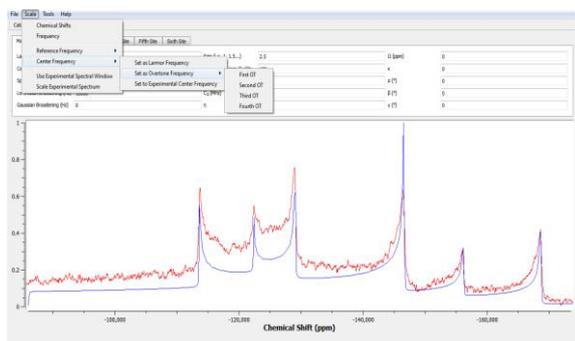


Fig. 7 – QUEST graphical user interface, which demonstrates the $^{185/187}\text{Re}$ NMR spectrum simulation and its comparison with the experimental spectrum obtained at 11.7 T [12]

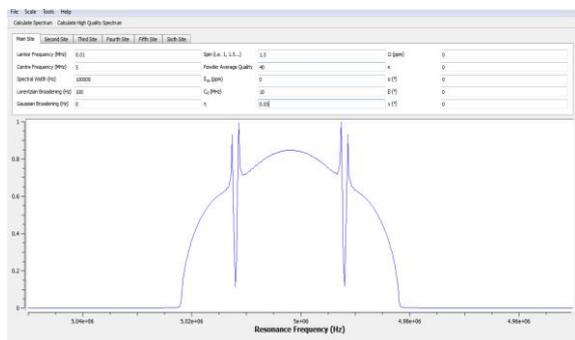


Fig. 8 – Simulation of the Zeeman effect in the NQR for a nucleus with spin $3/2$. The asymmetry parameter can be determined from the positions of the dips [13, 14]

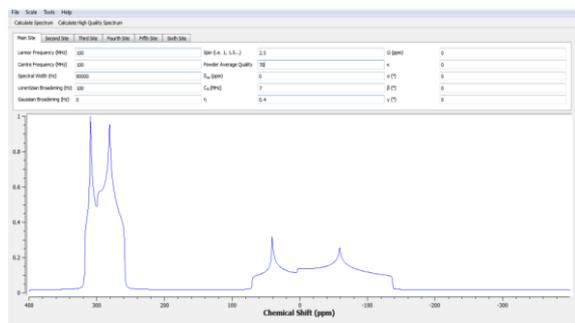


Fig. 9 – QUEST graphical user interface that shows a simulation of several positions for a spin pair $^{47/49}\text{Ti}$ [11, 13]

QUEST uses several C/C++ libraries for research. The function "gsl_eigen_hermv" from the GNU Scientific Library was used to diagonalize the effective Zeeman-

man-quadrupole Hamiltonian matrix [13]. This is a free C library developed for scientists that provides an optimized diagonalization procedure and hundreds of other procedures.

It is also possible to change the coil angle for all spins, for example, this enables simulating the Zeeman NQR perturbation spectrum of spin $3/2$ nucleus, where the coil angle is usually parallel to the magnetic field (Fig. 8) [13, 14].

As it is already mentioned, the QUEST spectral modeling is based on summation in the complete quadrupole Hamiltonian. This theory is valid and holds for all transitions and with an arbitrary position of the magnetic field. Fig. 10 shows the particular case of a nucleus with spin $3/2$ with a C_Q of 10 MHz and an axially symmetric gap ($\eta = 0$) when the Larmor frequency is changed.

In Fig. 10 ($\nu_0 = 100$ MHz), a typical NMR spectrum is observed for a nucleus with spin $3/2$ with an intense central transition (from $1/2$ to $-1/2$) in the center which is not affected by the first-order quadrupole interaction. The interval between two adjacent transitions (from $3/2$ to $1/2$ and from $-1/2$ to $-3/2$), which are much wider and largely invariant depending on the magnetic field, shrinks in NMR mode. On the other hand, the width of the central transition increases sharply with decreasing magnetic field. When the value of ν_Q is equivalent to the value of ν_0 (5 MHz), the spectrum starts losing features, typical of quadrupole-perturbed NMR spectrums (for example, there is no "step" observed in the central transition). When $\nu_0 = 2$ MHz, three overtone transitions (from $3/2$ to $-1/2$, from $1/2$ to $-3/2$ and from $3/2$ to $-3/2$) appear in the spectrum and overlap with "allowed" NMR-transitions. Further, when $\nu_0 = 0$ MHz, they are combined with NMR transitions to form the "allowed" NQR transition (from $\pm 1/2$ to $\pm 3/2$). This type of analysis together with the analysis of magnetic resonance frequencies, carried out by Bane and Hasavna [11], is crucial for understanding both NQR and NMR.

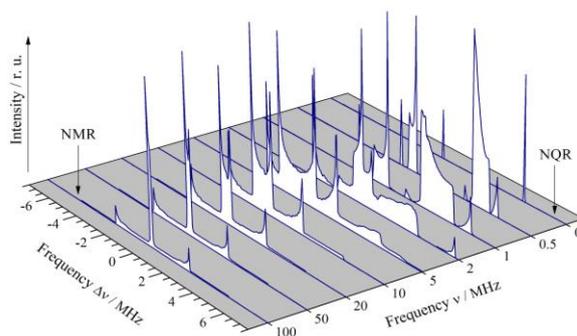


Fig. 10 – Spectral modeling in QUEST of nucleus with a spin of $3/2$ with an axially symmetric EFG tensor and $C_Q = 10$ MHz with increasing Larmor frequency from 0 to 100 MHz. There is a progression from NQR in high field NMR. Simulation with ν_0 from 5 MHz corresponds to $\nu_0 = \nu_Q$

4. CONCLUSIONS

As a result of the performed analysis it can be stated that there is no publicly available and user-friendly software that accurately describes the mathematical

models of the Zeeman quadrupole Hamiltonian and the chemical shift anisotropy. In NQR, the quadrupole interaction is dominant, and when conducting experiments on real samples with quadrupole nucleus, the intermediate region is uncertain, hence common practice using perturbation theory to analyze spectrums under certain circumstances may be unacceptable.

It is established that the Quadrupolar Exact Soft

ware (QUEST) software is the most suitable for computer parametric identification of NMR and NQR spectrums. Such a choice is also justified when it is required to identify complex multiplet spectra, thin structure of which is associated with a complex crystal structure, in particular, the presence of EFG $\eta \neq 0$. The latter confirms the possibility of effectively using QUEST to study all possible quadrupole Zeeman interactions.

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Актуальні проблеми комп'ютерної параметричної ідентифікації ЯМР та ЯКР спектрів: огляд

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Визначення комп'ютерної моделі спінового відлуння з метою моделювання його амплітуди та отримання інформації про величини і орієнтації локального магнітного поля, напрям градієнта кристалічного електричного поля в зразку є важливим завданням. У роботі розглядається ряд актуальних питань, що уможливають розв'язання задачі комп'ютерної параметричної ідентифікації ЯМР та ЯКР спектрів. З аналізу літературних даних встановлено кілька доступних програм, які можуть бути використані для імітації форм ліній ЯКР, зв'язаних з квадрупольними взаємодіями ядер в порошкових твердих тілах. Встановлено, що впродовж останніх чотирьох десятиліть було розроблено безліч комп'ютерних програм моделювання експериментів ЯМР/ЯКР, які можна віднести до наступних категорій: аналітичні інструменти ЯМР (як правило, реалізовані в Mathematica), спеціалізовані прикладні програми (наприклад, імітатор спектрів NOESY), інтерфейси прикладного програмування API, загальні програми моделювання ЯМР. Описано доступні засоби комп'ютерного моделювання спінового відлуння з метою отримання інформації про його амплітуду, величини і орієнтації локального магнітного поля, напрям градієнта кристалічного електричного поля в зразку. Значна увага приділена імітації точних спектрів ЯМР/ЯКР із використанням процедури швидкої діагоналізації а також ефективної схеми усереднення порошоків Олдермана, Солома, Гранта. З проведеного огляду визначено, що однією з найбільш точних є програма моделювання квадрупольних ядер порошкових зразків у статичних умовах – Quadrupolar Exact Software (QUEST). В основі спектрального моделювання QUEST лежить додавання в повному квадрупольному гамільтоніані. Дана теорія справедлива та виконується для всіх переходів і при довільному положенні магнітного поля. При моделюванні спектрів ЯКР необхідно використовувати невелику Ларморову частоту (~ 0.0001 МГц), але не рівну 0. Це пов'язано з тим, що чисті піки ЯКР є нескінченно різкими і, відповідно, їх важко додати, якщо вони з'являються між бінами на гістограмі. Оскільки розрахунки в QUEST виконуються в одиницях абсолютної частоти, при використанні дуже вузького спектрального вікна може бути відсутня необхідна точність у значеннях частоти кожного біну в гістограмі.

Ключові слова: Комп'ютерна параметрична ідентифікація, Моделювання, Спектр, Спін, ЯКР, ЯМР.