Theory of multipulse averaging for spin systems with arbitrary nonequidistant spectra

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We introduce a rotating generalized coordinate frame, a concept necessary for a theoretical description of multipulse action on a spin system with an arbitrary nonequidistant spectrum. We consider the behavior of a nuclear spin system whose Hamiltonian includes the following: a) the principal interaction that forms the spectrum and consists of a Zeeman energy (interaction of the magnetic moments of the nuclei with the constant magnetic field) and a quadrupole energy (interaction of the electric quadrupole moments of the nuclei with the gradient of the crystal electric field); b) multiparticle spin-spin interactions that broaden the spectral lines; c) interaction with a multipulse rf field of arbitrary orientation. It is shown that any multipulse sequence acting on a spin system with a complex spectrum can be represented by a single-phase analog. The averaged Hamiltonian is constructed by using the method of canonical transformations and the Krylov-Bogolyubov-Mitropol'skiĭ averaging method. Principal attention is paid to examples of averaging of interactions that broaden NQR spectral lines.

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The idea of coherent averaging of interactions[1] for the purpose of narrowing down NMR spectral line has spawned various high-resolution techniques for solids.[2,3] One of the most effective and promising ones is multipulse rf action, with which it is possible to increase by several orders the sensitivity of the NMR method in the study of weak interactions in solids.[3] The theoretical description of such experiments is based on construction of the average Hamiltonian[2–4] by using the Magnus expansion and the conditions for periodicity and cyclicity of the pulsed action. The behavior of a spin system subject to such an action by pulsed rf fields is then described by the average Hamiltonian only at definite instants of time—after the termination of the pulse cycles. Many experimental facts agree well with the conclusions of the average-Hamiltonian theory. The main objects of the investigation are spin systems with a Zeeman, i.e., equidistant, spectrum.

The first application of the average-Hamiltonian theory to spin systems with nonequidistant spectra was reported in Refs. 5–7, devoted to calculation of the degree of line narrowing in the spectrum of NMR with quadrupole splitting and in the spectrum of NQR at axial symmetry of the electric field gradient. Various different pulse sequences were considered, as well as their modifications aimed at obtaining greater narrowing as measured by the second moments of the spectral lines. Attempts to explain the experimental NQR data[8] with the aid of the average-Hamiltonian theory in the particular case of a system of quadrupole nuclei with unity spin were made by calculation in Ref. 9 and experimentally and theoretically in Refs. 10 and 11.

It was recently established[12–16] that the average-Hamiltonian theory is subject to certain restrictions, due to the incorrect form of the average Hamiltonian in higher-order approximations (starting with the second),[15,16] as well as to the impossibility of describing the behavior of a spin system at times longer than T_2.[12–14]

A new approach to the description of the dynamics of equidistant-spectrum spin systems acted upon by arbitrary pulse sequences was proposed in Refs. 12–14, where a canonical-transformation method is used. In this approach it was possible to overcome the difficulties of the average-Hamiltonian theory and study the behavior of a spin system at any instant of time, including times much longer than T_2. In the case of NMR it was demonstrated that dipole-dipole interactions can be fully or partially averaged by various pulse sequences. Application of this approach to spin systems with nonequidistant spectra was restricted only to the case of NQR of nuclei with unity integer spin.[17,18]

A theoretical approach to the problem of averaging the interaction in periodic action on a spin system, based on the Krylov-Bogolyubov-Mitropol'skiĭ averaging method, was used in Refs. 15 and 16. This method yielded a correct expression for the average-Hamiltonian in all perturbation-theory orders, as demonstrated[15] for a spin system with equidistant spectrum. Nonstationary perturbation theory was used to investigated dipolar heteronuclear spin systems[19] and model systems (one-dimensional spin chains).[20]

Most studies of multipulse averaging deal thus with spin systems with equidistant spectra, describable by a Hamiltonian that includes linear functions of spin operators (NMR). This situation was apparently brought about by two circumstances connected with the equidistant character of the spectrum: 1) the transition to the interaction representation is equivalent to a transition to a rotating coordinate frame (RCF) and can be effected by a simple unitary transformation; 2) the action of the pulses reduces to rotation of the spin operators. For spin systems of quadrupole nuclei with arbitrary spin, the use of the new approaches to the problem of multipulse averaging meets with difficulties. Only for $J=1$ did the introduction of special operators[21] permit the solution of the problem of multipulse action on a quadrupole system to be reduced to the case of systems with equidistant spectra.[17,18]

Our present purpose is to construct a theory of multipulse averaging of interactions of spin systems with arbitrary nonequidistant spectra by using the method of canonical transformations and the Krylov-Bogolyubov-Mitropol'skiĭ averaging method.[22,23] The need for solving this problem is connected with the increased interest, on the one hand, in raising the sensitivity and the resolution in regions bordering on NMR (e.g., NQR), and on the other hand in investigations of relaxation processes by using multipulse methods.

1. TRANSFORMATION TO A ROTATING GENERALIZED COORDINATE FRAME (RGCF)

In the laboratory frame, the behavior of spin systems with arbitrary (equidistant or not) spectrum, formed by the Hamiltonian ($\mathscr{H}_0$) of the basic interaction, is described by the Neumann equation ($\hbar=1$)

$$i d\rho/dt=[\mathscr{H}(t),\ \rho(t)], \tag{1}$$

where $\rho(t)$ is the spin-system density matrix in the lab and

$$\mathscr{H}(t)=\mathscr{H}_0+\mathscr{H}_{\rm int}+\mathscr{H}_1(t). \tag{2}$$

In the general case the Hamiltonian $\mathscr{H}_0$ can consist of a Zeeman part ($\mathscr{H}_{\rm M}$) and a quadrupole part ($\mathscr{H}_Q$):

$$\mathscr{H}_M=-\gamma \mathbf{I}\mathbf{H}_0,\quad \mathscr{H}_Q=\frac{eQq_{zz}{}^0}{4J(2J-1)}\left[3I_z{}^2-I^2+\frac{\eta}{2}(I_+{}^2+I_-{}^2)\right], \tag{3}$$

where γ is the gyromagnetic ratio of the nuclei with spin J, while eQq^0_{zz} and η are the quadrupole-interaction constant and the asymmetry parameter of the electric field gradient (EFG). Depending on the relation between the Zeeman ($\|\mathscr{H}_M\|\sim\gamma H_0$) and the quadrupole ($\|\mathscr{H}_0\|\sim eQq^0_{zz}$) energies, one distinguishes between the following cases: 1) NMR ($eQq^0_{zz}=0$); 2) NMR with quadrupole splitting ($\gamma H_0 \gg eQq^0_{zz}$); 3) nuclear spin resonance ($\gamma H_0\sim eQq^0_{zz}$); 4) Zeeman effect in NQR ($\gamma H_0 \ll eQq^0_{zz}$), and 5) pure NQR ($\gamma H_0=0$).

The Hamiltonian $\mathscr{H}_{\rm int}$ of the particle system includes the single-particle interactions ($\mathscr{H}_{1\,\rm int}$), i.e., the interactions with the inhomogeneities of the magnetic and electric (intracrystalline) fields, the chemical shift, and others, as well as paired interactions ($\mathscr{H}_{2\,\rm int}$), i.e., direct dipole-dipole, indirect spin-spin interactions, and others.

The Hamiltonian of the interaction with a multipulse radiofrequency (rf) field that can in general have several frequencies is of the form

$$\mathscr{H}_1(t)=-\sum_p \gamma\mathbf{I}\mathbf{H}_{1p}\cos(\omega_p t+f_p{}^\psi(t))f_p(t), \tag{4}$$

where $f_p(t)$ and $f^\psi_p(t)$ are functions that reflect respectively the time of the appearance of the rf-field pulses and the changes of their phases at various applied frequencies ω_p. The carrier frequencies of the pulses ω_p can be close to or equal to the spin-system-spectrum frequencies determined by $\mathscr{H}_0$. All the spin operators will be considered in a basis in which the Hamiltonian $\mathscr{H}_0$ is diagonal. We introduce the projection operators $e_{mn}(\langle m'|e_{mn}|n'\rangle=\delta_{mm'}\delta_{nn'})$ (Ref. 24) and express in their terms the Hamiltonian $\mathscr{H}(t)$:

$$\begin{aligned}\mathscr{H}(t)=(\mathrm{Sp}\,1)^{-1}\sum_{mn}\omega_{mn}{}^0e_{mm}+\sum_{imn}G_{mn}{}^ie_{mn}{}^i\\+\sum_{i>j}\sum_{mn}\sum_{m'n'}D^{ij}_{mnm'n'}e_{mn}{}^ie^{j}_{m'n'}\\+\sum_p\sum_{mn}2\gamma H_{1p}I_{mn}{}^pf_p(t)\cos(\omega_pt+f_p{}^\psi(t))e_{mn}.\end{aligned} \tag{5}$$

The Hamiltonian $\mathscr{H}_0$ is expressed here in terms of the eigenfrequencies $\omega^0_{mn}=\lambda^0_m-\lambda^0_n$, where λ^0_m are the eigenvalues of $\mathscr{H}_0$ and $\mathrm{Sp}\,1=2J+1$.

We transform to the representation of the rotating generalized coordinate frame (RGCF)[25] with the aid of the operator

$$A=(\mathrm{Sp}\,1)^{-1}\sum_{mn}\omega_{mn}e_{mm}. \tag{6}$$

The spectrum of the operator A is defined as follows: The quantities ω_{mn} corresponding to the frequencies ω^0_{mn} at which the pulses are applied are chosen to be exactly equal to ω_p; the remaining frequencies are assumed equal to ω^0_{mn}. Transforming in Eq. (1) with the aid of the operator $u(t)=\exp(iAt)$ to the RGCF representation, i.e., substituting $\rho(t)=u^{-1}(t)\tilde\rho(t)u(t)$, we obtain

$$i d\tilde\rho/dt=[\tilde{\mathscr{H}},\ \tilde\rho(t)], \tag{7}$$

$$\tilde{\mathscr{H}}=\tilde{\mathscr{H}}_0+\mathscr{H}^{\rm sec}_{\rm int}+\tilde{\mathscr{H}}_1(t), \tag{8}$$

$$\tilde{\mathscr{H}}_0=(\mathrm{Sp}\,1)^{-1}\sum_{mn}\Delta_{mn}e_{mm}, \tag{8a}$$

$$\mathscr{H}^{\rm sec}_{\rm int}=\sum_i\sum_{mn}g_{mn}{}^ie_{mn}{}^i+\sum_{i>j}\sum_{mn}\sum_{m'n'}d^{ij}_{mnm'n'}e_{mn}{}^ie^{j}_{m'n'}, \tag{8b}$$

$$\begin{aligned}\tilde{\mathscr{H}}_1(t)=\sum_p\sum_{mn}I_{mn}{}^p\{\delta_{\omega_p,\omega_{mn}}\exp[if_p{}^\psi(t)]\\+\delta_{\omega_p,-\omega_{mn}}\exp[-if_p{}^\psi(t)]\}f_p{}^\varphi(t)e_{mn},\end{aligned} \tag{8c}$$

$$g_{mn}=G_{mn}{}^i(\delta_{mn}+\delta_{m\bar n}),$$

$$\begin{aligned}d^{ij}_{mnm'n'}=D^{ij}_{mnm'n'}[(\delta_{mn}+\delta_{m\bar n})(\delta_{m'n'}+\delta_{m'\bar n'})\\+(\delta_{mn'}+\delta_{m\bar n'})(\delta_{nm'}+\delta_{n\bar m'})],\end{aligned}$$

$$\bar m=-m,\quad \bar n=-n.$$

We have left out of (8) the terms that are nonsecular relative to $\mathscr{H}_0$ and contain rapidly oscillating factors with frequencies ω_{mn}. The frequency detunings Δ_{mn} are defined as $\Delta_{mn}=\Delta\omega^0_{mn}-\omega_{mn}$; δ_{mn} are Kronecker symbols; the pulse functions $f^\varphi_p(t)$ of an arbitrary pulse sequence with period t^p_c have a form similar to that in Ref. 14:

$$f_p{}^\varphi(t)=\sum_{i=1}^k\varphi_i{}^p\frac{\pi}{t_c{}^p}\delta(\sin x_i{}^p)+\varphi_0{}^p\delta(t),$$

$$x_i{}^p=\frac{1}{t_c{}^p}\left(t-\sum_{j=1}^it_j{}^p\right), \tag{9}$$

φ_0 and $\varphi_i^p = \gamma H_{1p} t w_i^p$ are respectively the angular durations of the first and of all the remaining pulses, $\delta(t)$ is the Dirac delta function, and $\delta(\sin x)$ is a generalized function.[26] Expression (9) takes into account the instants of the action of the pulses in the period t_c^p. The pulse functions $f_p^\psi(t)$ that determine the instants when the phases ψ_p^i of the pulses change are also determined by expression (9) subject to the substitutions $\varphi_0 \to \psi_0$ and $\varphi_p \to \psi_p$.

The introduction of the RGCF representation allows us thus to take into account the influence of a multifrequency multipulse action on a spin system with arbitrary nonequidistant spectrum, and separate the secular parts of the interactions. In Appendix 1 are given expressions for the secular parts of the Hamiltonians that describe the influence of the inhomogeneous broadenings and the dipole-dipole interactions in NQR when there is no axial symmetry of the EFG ($\eta \neq 0$). A quadrupole spin system is the most typical example of a system with arbitrary nonequidistant spectrum. In the particular case of an equidistant spectrum and in the absence of degeneracy, the RGCF representation reduces to the GCF representation in NMR.

2. CONSTRUCTION OF THE AVERAGED HAMILTONIAN FOR ARBITRARY PERIODIC PULSED ACTION

The action of periodic rf-field pulses on a spin system consists of a preparatory pulse and a multipulse sequence. The density matrix ($\rho_+(0)$) of the spin system immediately after the end of the action of the first (preparatory) pulse that takes the spin system out of equilibrium is the initial condition for Eq. (7) which describes the behavior of the spin system under the influence of a multipulse periodic action. We transform in (7) to the interaction representation in momenta and detunings, i.e., we make the substitutions

$$\tilde{\rho}(t) = L(t)\rho^*(t)L^{-1}(t), \tag{10}$$

$$L(t) = T\exp\left\{-i\int_0^t \left[(\mathrm{Sp}\,1)^{-1}\sum_{mn}\Delta_{mn}e_{mm} + \sum_p\sum_{mn} I_{mn}{}^p\{\delta_{\omega_p,\omega_{mn}} \times\exp[if_p{}^\psi(t')] + \delta_{\omega_p,-\omega_{mn}}\exp[-if_p{}^\psi(t')]\} f_p{}^\varphi(t')e_{mn}\right]dt'\right\}, \tag{11}$$

where the symbol T stands for time averaging. To simplify the subsequent calculations we confine ourselves to single-frequency multipulse action. We consider initially single-phase pulse sequences, and then show that the result of the action of arbitrary non-single-phase[1] multipulse sequences on a spin system with nonequidistant spectrum is equivalent to the result of the action of single-phase analogs of such sequences, as is the case in NMR.[13,14]

We consider the action of the operator $L(t)$ in the case of the single-phase pulse sequence MW-4 (Refs. 2 and 3) (pulsed spin-locking (PSL)) on an arbitrary transition $m_0 \to n_0$ (and $\bar{m}_0 \to \bar{n}0$ in the presence of degeneracy). During the time 2τ of the period, $L(t)$ can be represented as

$$L(2\tau) = \exp(-i\Delta^\omega\tau S_3)\exp(-i\Phi S_1)\exp(-i\Delta^\omega\tau S_3), \tag{12}$$

where Δ^ω and Φ are respectively the effective detuning and the effective angular duration of the pulse, and depend on the parameters of the excited transition:

$$\Delta^\omega = 2r\Delta/(2J+1), \quad \Phi = 2\varphi(KK^* + RR^*)^{1/2}. \tag{13}$$

Here r is the degeneracy multiplicity; $\Delta = \omega^0_{m_0n_0} - \omega = \omega^0_{\bar{m}_0\bar{n}_0} - \omega$; K, K^*, R, R^* and R^* are matrix elements of the operator (**II**) in the $\mathscr{H}_0$ representation, and the unity operator **1** determines the direction of the field $\mathbf{H}_i$.

The components of the Hermitian operator $\mathbf{S}(S_1, S_2, S_3)$, which are defined in Appendix 2, satisfy the commutation relations

$$[S_i, S_j] = iS_k,\ i, j, k = 1, 2, 3 \text{ and their cyclic permutation} \tag{14}$$

so that $L(2\tau)$ can be represented in the form

$$L(2\tau) = \exp\{-2i\omega_{\text{eff}}\mathbf{S}\tau\}. \tag{15}$$

The action of a single-phase multipulse sequence on a spin system with arbitrary nonequidistant spectrum over a period 2τ is thus equivalent to the action of an effective field whose magnitude and orientation are determined from the relations

$$\cos(\omega_{\text{eff}}\tau) = \cos\left(\frac{\Phi}{2}\right)\cos(\Delta^\omega\tau), \tag{16}$$

$$a_1 = \frac{\sin(\Phi/2)}{\sin(\omega_{\text{eff}}\tau)}, \quad a_2 = 0, \quad a_3 = \frac{\cos(\Phi/2)\sin(\Delta^\omega\tau)}{\sin(\omega_{\text{eff}}\tau)}. \tag{17}$$

In the particular case of spin $J = 1/2$ we have $\Delta^\omega \to \Delta$; $\Phi \to \varphi$, and relations (16) and (17) reduce to expressions (6) and (7) of Ref. 12.

The unitary transformation operator (11) expressed in terms of the introduced operators S_i ($i = 1, 2, 3$) is given by

$$L(t) = T\exp\left\{-i\int_0^t [-f(t')S_1 + \Delta^\omega S_3]dt'\right], \tag{18}$$

or, if (9), (16) and (17) are taken into account,

$$L(t) = T\exp\left\{-i\frac{\pi}{t_c}\theta\int_0^t \delta\left(\sin\frac{t'-\tau}{t_c}\pi\right)(\mathbf{aS})dt'\right\}, \tag{19}$$

where $\theta = 2\omega_{\text{eff}}\tau$ is the angular duration of the pulse of the effective field oriented along the axis $\mathbf{a}(a1, a2, a3)$.

Resolving $\mathscr{H}^{\text{sec}}_{\text{int}}$ into a secular part ($\mathscr{H}^0_{\text{int}}$) and a nonsecular part ($\mathscr{H}^m_{\text{int}}$, $m \neq 0$) relative to the operator $S_a = (\mathbf{aS})$ (see Appendix 3), which satisfy the commutation relations

$$[S_a, \mathscr{H}^m_{\text{int}}] = m\mathscr{H}^m_{\text{int}}, \tag{20}$$

and introducing the dimensionless time $\bar{t} = t/t_c$, we obtain for the density matrix an equation analogous to Eq. (6) of Ref. 14:

$$id\rho/dt = \varepsilon\left[\sum_m \chi_m(\bar{t})e^{-im\theta\bar{t}}V^m, \rho(\bar{t})\right]. \tag{21}$$

Here $\varepsilon = t_c\|\mathscr{H}_{\text{int}}\|$, $V^m = \mathscr{H}^m_{\text{int}}/\|\mathscr{H}_{\text{int}}\|$, and $\chi_m(\bar{t})$ is a periodic function with unity period.

The value of t_c in multipulse experiment is chosen such that $\varepsilon \ll 1$. In this case the right-hand side of (21) is proportional to the small parameter ε, and the entire equation takes the standard form.[22,23]

We shall not describe here the procedure for the canonical transformation of Eq. (21), since it is analogous for the spin system considered to the procedure of Ref. 14. On the one hand, this procedure yields, in any order in ε, the contributions to the time-independent averaged Hamiltonian, and on the other it provides an estimate of the contribution of the oscillating nonsecular terms to the absorption of the energy of the external fields by the system at an arbitrary ratio of ω_{eff} and $\omega_{\text{loc}} \propto \|\mathscr{H}_{\text{int}}\|$. To reach our aim of finding the averaged Hamiltonian it is convenient to use the Krylov-Bogolyubov-Mitropol'skiĭ averaging method.[15,22,23] Expanding the function $\chi_m(\bar{t})$ in a Fourier series

$$\chi_m(\bar{t}) = \sum_{n=-\infty}^{\infty} \chi_m^n e^{i2\pi nt}, \tag{22}$$

we obtain the averaged Hamiltonian (accurate to ε^2)

$$\bar{\mathscr{H}} = \varepsilon\chi_0 V^0 + \varepsilon^2 \sum_{n=-\infty}^{\infty} \sum_m \frac{\chi_m{}^n \chi_{-m}{}^n}{2(2\pi n + \theta m)} [V^{-m}, V^m]. \tag{23}$$

As shown in Ref. 15, the expression for the averaged Hamiltonian coincides with the mean Hamiltonian[3] only in first order in ε.

We proceed now to discuss a multipulse non-single-phase sequence and consider by way of example the sequences *MW*-2 (Refs. 2 and 3). In this case the behavior of the spin system is described in the RGCF by the equation

$$i d\tilde{\rho}/dt = [\Delta^\omega S_3 - f^\Phi(t) S_1 + \mathscr{H}_{\text{int}}^{\text{sec}}, \tilde{\rho}(t)], \tag{24}$$

where we have for the *MW*-2 sequence ($t_c = 4\tau$)

$$f^\Phi(t) = \Phi \frac{\pi}{t_c} \left[\delta\left(\sin \frac{t-\tau}{t_c} \pi\right) - \delta\left(\sin \frac{t-3\tau}{t_c} \pi\right) \right]. \tag{25}$$

The unitary transformation

$$\tilde{\rho}(t) = \exp\left\{ i \frac{\pi}{2\tau}(t-\tau) S_3 \right\} \tilde{\tilde{\rho}}(t) \exp\left\{ -i \frac{\pi}{2\tau}(t-\tau) S_3 \right\}, \tag{26}$$

yields

$$i \frac{d\tilde{\tilde{\rho}}}{dt} = \left[\left(\Delta^\omega + \frac{\pi}{2\tau} \right) S_3 - f^\Phi S_1(t) + \mathscr{H}_{\text{int}}^{\text{sec}}, \tilde{\tilde{\rho}}(t) \right], \tag{27}$$

$$\begin{aligned} S_1(t) &= \exp\left\{ -i \frac{\pi}{2\tau}(t-\tau) S_3 \right\} S_1 \exp\left\{ i \frac{\pi}{2\tau}(t-\tau) S_3 \right\} \\ &= S_1 \cos\left(\pi \frac{t-\tau}{2\tau} \right) + S_2 \sin\left(\pi \frac{t-\tau}{2\tau} \right). \end{aligned} \tag{28}$$

In the last expression we used the commutation relations (14). Taking the property $f(x)\delta[f(x)] = 0$ of generalized functions[26] into account, we get

$$S_1(t) f^\Phi(t) = S_1 \Phi \frac{\pi}{2\tau} \delta\left(\sin \frac{t-\tau}{2\tau} \pi \right) = S_1 f(t). \tag{29}$$

It can be seen from (27) and (29) that the action of the sequence *MW*-2 differs from the action of *MW*-4 by a detuning change $\Delta^\omega \to \Delta^\omega + \pi/2\tau$. In addition, the transformation (26) alters the initial condition, i.e., for the single-phase analog of *MW*-2 it will be produced, as it were, by a pulse shifted in phase by $\pi/2$.

In similar fashion it is possible to obtain single-phase analogs of the sequences *WHH*-4, *HW*-8, and others, as was done in Ref. 14 for NMR. When constructing single-phase analogs of an arbitrary multipulse sequence it must be recognized that the following parameters change: a) the period, b) the detuning, c) the initial conditions, i.e., the phases of the first pulse. The first two conditions determine the magnitude and direction of the effective field that acts on the system and has two components, the pulse field and the detuning field.

3. AVERAGING, BY MULTIPULSE ACTION, OF INTERACTIONS THAT BROADEN THE SPECTRAL LINES

It is clear from the theory expounded in the preceding section that multipulse action leads to two types of averaging of interactions describable by the Hamiltonian $\mathscr{H}_{\text{int}}$—general and selective. It is possible to choose (by a method described below) a pulse sequence that influences right away all the types of interaction, regardless of their nature. We call this general averaging. An example is pulsed spin locking (PSL) used in NMR.[2] On the other hand, in the NMR region there were proposed and are being used[2,3] various pulse sequences that average various interactions to different degrees. Such an averaging is called selective.[2] To obtain selective averaging when constructing pulse sequences of this type for spin systems with nonequidistant spectra, account must be taken of the actual structure of the secular parts of the interactions (see Appendix 1).

We shall show that in the presence of interactions of arbitrary type it is possible to construct a pulse sequence that satisfies the condition of spin-locking (the so-called spin "capture"). Namely, the magnetization vector taken out of its initial equilibrium does not change, under the action of a periodic (with period $t_c \ll T_2$) pulse sequence, its direction in a time $t \gg T_2$. The fact that the echo signals observed in each period do not drop to zero, i.e., the absence of total damping of the magnetization in a time $t < T_1$, is evidence of averaging of the interactions that broaden the line (with the exception of the natural line width connected with the finite lifetime of the energy levels on account, say, of thermal motion).

In NMR spectroscopy, PSL is of no interest for the study of weak interactions,[2] but is used to investigate relaxation processes.[27,28] In the case of spin systems with nonequidistant spectra, and particularly in NQR spectroscopy, the use of PSL is important not only for the study of relaxation but (as will be shown below) also to increase the sensitivity of the method.

We consider first the action of single-phase PSL with a constant arbitrary Φ (angular duration), ψ (phase) and Δ^ω (detuning, i.e., deviation from resonance conditions). We next describe the principle of selecting a universal PSL, in which the phase ψ can vary periodically.

It was established in the preceding section that the action of a multipulse sequence on a spin system is equivalent to the action of an effective field $\boldsymbol{\omega}_{\text{eff}}$ along the **a** axis, i.e., it is characterized by a Hamiltonian $-\omega_{\text{eff}}(\mathbf{aS})$. In the representation of this effective field, which is strong enough to exceed all the local fields, the spin system is described by the Hamiltonian (23). Clearly, the spin-locking state will be realized upon satisfaction of the condition

$$[\tilde{\rho}_+(0), \bar{\mathscr{H}}] = 0. \tag{30}$$

This condition means that the orientation of the magnetization of the spin system after the action of a preparatory pulse should coincide with the orientation **a** of the effective field produced by the multipulse sequence. The density matrix $\tilde{\rho}_+(0) = \rho_+(0)$ immediately after the action of the first pulse characterized by an angular duration Φ_0 and a phase ψ_0 can be calculated in the high-temperature approximation in the following manner:

$$\rho_+(0)=1-\beta e^{-i\Phi_0 S_0}\mathscr{H}_0 e^{i\Phi_0 S_0}, \quad \beta=1/kT, \tag{31}$$

$$\mathscr{H}_0=\sum_{m\neq|m_0|,|n_0|}\lambda_m{}^0 e_{mm}+{}^1/{}_2(\lambda_{m_0}{}^0+\lambda_{n_0}{}^0)\sum_{m=|m_0|,|n_0|}e_{mm}+\omega_{m_0n_0}S_3, \tag{32}$$

$$S_0=(\mathbf{bS}), \quad b_1=\cos(\psi-\psi_0), \quad b_2=\sin(\psi-\psi_0), \quad b_3=0. \tag{33}$$

Taking (32) and (33) into account, we obtain for $\rho_+(0)$

$$\rho_+(0)=1-\beta\Big[\sum_{m\neq|m_0|,|n_0|}\lambda_m{}^0 e_{mm} + \frac{1}{2}(\lambda_{m_0}{}^0+\lambda_{n_0}{}^0)\sum_{m=|m_0|,|n_0|}e_{mm}+\omega_{m_0n_0}(\mathbf{pS})\Big], \tag{34}$$

where the orientation of the unit vector **P** along which the magnetization is directed after the first pulse is determined in terms of the parameters of the rf field of the preparatory pulse:

$$p_1=b_2\sin\Phi_0, \quad p_2=-b_1\sin\Phi_0, \quad p_3=\cos\Phi_0. \tag{35}$$

Satisfaction of the conditions (30) requires satisfaction of the equalities

$$p_1=a_1, \quad p_2=a_2, \quad p_3=a_3. \tag{36}$$

Using (17), (33), (35), and (36) we obtain the connection that must hold between the parameters of the preparatory pulse and the pulse sequence in order to satisfy the conditions (36) and hence also (30). The phase difference $\psi - \psi_0$ should be a multiple of $\pi/2$, i.e., $\psi - \psi_0 = (2k+1)\pi/2$, where $k = 0, 1, 2$. We have then

$$\mathrm{tg}\,(\Phi/2)/\mathrm{tg}\,\Phi_0=\sin\Delta^\omega\tau. \tag{37}$$

Let us consider some particular cases. Let $\Phi_0 = \pi/2$, corresponding to the sequence $90_{\psi_0} - (\tau - \Phi_{\psi_0+\pi/2} - \tau)^n$; relation (37) holds at $\Delta^\omega = 0$, and Φ is arbitrary. Such a sequence does in fact produce PSL; the averaging of the interactions and the time of observation of the spin-echo signal envelope will in this case be maximal. We note that the use of such a sequence in NQR spectroscopy is quite promising because of the unique possibility of increasing the sensitivity and accuracy of tuning to the resonant frequency. Experiments[8,10,11] confirm this conclusion. Spin-echo signals at ^{14}N nuclei in both polycrystalline[8] and single-crystal[11] $NaNO_2$ are recorded up to times $\sim T_1$ ($\sim 3\times10^4$ msec).[11] The NQR line narrowing attainable in such experiments corresponds to values of the order of T_1/T_2. Investigations of ^{14}N nuclei in methylamine and sodium nitrite[10] using various multipulse sequences have shown that the greatest narrowing (from 1 kHz to 0.1–1 Hz) is observed when the chosen sequence parameters satisfy relation (37). This relation is satisfied also at $\Phi = \pi$ and $\Delta \neq 0$.

For non-single-phase pulse sequences, the effective-field orientation vector **a** can be arbitrarily directed.[14] To satisfy condition (30) in this case it is necessary to choose preparatory-pulse parameters such as to satisfy relations (36), when all $a_i \neq 0$. As shown in Refs. 2 and 3, the desirability of using non-single-phase multipulse sequences is dictated by the need for selective averaging of the interactions. The degree of averaging of various interactions depends on the choice of the sequence parameters that enter in the expressions for $\mathscr{H}^m_{\text{int}}$.

CONCLUSION

One of the main features of a spin system with an arbitrary nonequidistant spectrum is that the multipulse sequence acts on only one of the possible transitions, whereas in the case of equidistant spectra (NMR) all the transitions are simultaneously excited. The question is: will the averaging effect be the same when acting on different transitions? It turns out that if the parameters of the pulse sequence are so chosen that they correspond to the given transition, the averaging effect does not depend on the acted-upon transition. It was established that for any system it is possible to choose a pulse sequence that can lead to a spin-locking state and average any interaction. In selective averaging, the averaging of interactions for systems with complicated spectrum changes qualitatively. If the PSL state does not obtain in the action, none of the sequences can average the spectrum-line broadening factors for systems with nonequidistant spectra. A similar conclusion, based on the theory of the average Hamiltonian in the case of NQR (with axial geometry of the EFG), was arrived at earlier in Refs. 6 and 7. For systems with equidistant spectrum, the results of the described theory agree with the already established experimental data.[2,3] We note in conclusion that a similar approach to systems with complicated spectra can be used not only in the nuclear resonance region, but also in other radiospectroscopy regions, as well as for optical spectroscopy.

APPENDIX 1

When account is taken of the influence of inhomogeneous broadenings on the spectral lines of a quadrupole spin system, it is sufficient to take into account in the Hamiltonian (8b) at $\eta \neq 0$ only one term

$$\mathscr{H}^{\text{sec}}_{\text{inhom}}=\sum_{i_m}G_{mm}{}^i e_{mm}{}^i, \tag{A.1.1}$$

since the second term $\Sigma_{im} G^i_{m\bar{m}} e^i_{m\bar{m}}$ vanishes in the case of half-integer spins ($G^i_{m\bar{m}} = 0$), and for integer spins it vanishes because of the lifting of the degeneracy. In this case

$$G_{mm}{}^i=\frac{eQ\Delta q_{zz}{}^i}{4J(2J-1)}\Big\{3(I_{zi}{}^2)_{mm}-(I_i{}^2)_{mm} + \frac{\Delta\eta^i}{2}[(I_{+i}{}^2)_{mm}+(I_{-i}{}^2)_{mm}]\Big\},$$

$$\Delta\eta^i=(\Delta q_{xx}{}^i-\Delta q_{yy}{}^i)/\Delta q_{zz}{}^i, \quad \Delta q_{jj}{}^i=q_{jj}{}^i-q_{jj}{}^0, \quad j=x,\ y,\ z. \tag{A.1.2}$$

The operators I_i are chosen in a basis where $\mathscr{H}_Q$ is diagonal.

The secular part of the dipole-dipole interaction Hamiltonian that enters in (8) can be represented in the case $\eta\neq 0$ as

$$\begin{aligned}
\mathscr{H}^{\rm sec}_{dd} = &\sum_{i>j}\ \sum_{mm',m\neq m'}\left\{\frac{\gamma_i\gamma_j}{r_{ij}^{3}}\Big[(1-3\cos^2\theta_{ij})\right.\\
&\times\left(I^{zi}_{mm'}I^{zj}_{m'm}-\frac{1}{2}I^{i}_{mm'}I^{-j}_{m'm}\right)\\
&\left.-\frac{3}{4}\sin^2\theta_{ij}e^{-2i\varphi_{ij}}I^{+i}_{mm'}I^{+j}_{m'm}\Big]\, e^{i}_{mm'}e^{j}_{m'm}+\text{c.c.}\right\}\\
&+\sum_{i>j}\ \sum_{mm',m\neq m'}\left\{\frac{\gamma_i\gamma_j}{r_{ij}^{3}}\Big[(1-3\cos^2\theta_{ij})\left(I^{zi}_{m\bar{m}'}I^{zj}_{m'\bar{m}}-\frac{1}{2}I^{+i}_{m\bar{m}'}I^{-j}_{m'\bar{m}}\right)\right.\\
&\left.-\frac{3}{4}\sin^2\theta_{ij}e^{-2i\varphi_{ij}}I^{+i}_{m\bar{m}'}I^{+j}_{m'\bar{m}}\Big]\, e^{i}_{m\bar{m}'}e^{j}_{m'\bar{m}}+\text{c.c.}\right\}\\
&+\sum_{i>j}\ \sum_{mm'}\Big\{\gamma_i\gamma_j r_{ij}^{-3}(1-3\cos^2\theta_{ij})\\
&\times\left[\left(I_{mm}{}^{zi}I^{zj}_{m'm'}e_{mm}{}^{i}e^{j}_{m'm'}-\frac{1}{2}I_{m\bar{m}}{}^{+i}I^{-j}_{m'\bar{m}'}e_{m\bar{m}}{}^{i}e^{j}_{m'\bar{m}'}\right)+\text{c.c.}\right]\\
&-\frac{3}{2}\sin\theta_{ij}\cos\theta_{ij}\Big[\big(I_{mm}{}^{zi}I^{+j}_{m'\bar{m}'}e_{mm}{}^{i}e^{j}_{m'\bar{m}'}\\
&\qquad+I_{m\bar{m}}{}^{+i}I^{zi}_{m'm'}e_{m\bar{m}}{}^{i}e^{j}_{m'm'}\big)e^{-i\varphi_{ij}}+\text{c.c.}\Big]\\
&-\frac{3}{4}\sin^2\theta_{ij}\left(e^{-2i\varphi_{ij}}I_{m\bar{m}}{}^{+i}I^{+i}_{m'\bar{m}'}e_{m\bar{m}}e_{m'\bar{m}'}+\text{c.c.}\right)\Big\}.
\end{aligned}\qquad\text{(A.1.3)}$$

Expression (A.1.3) describes the secular part of homonuclear dipole-dipole interactions for half-integer spins. For heteronuclear interactions it is necessary to take into account in $\mathscr{H}^{\rm sec}_{dd}$ only the terms in the first curly brackets. The last circumstance reflects the well known phenomenon of "freezing" of dipole-dipole interactions for integer spins at $\eta\neq 0$ (Ref. 29).

Expressions for the seclar parts of the inhomogeneous broadening and of the dipole-dipole interactions in the case of axial symmetry of the EFG were obtained earlier in Refs. 6 and 30.

APPENDIX 2

The operatores S_i ($i = 1, 3, 4$) can be defined in general form as follows:

$$\begin{aligned}
S_1={}&{}^1/_2(KK^*+RR^*)^{-1/2}\big[R(e_{m_0n_0}e^{i\psi}+e_{\bar{n}_0\bar{m}_0}e^{-i\psi})\\
&+R^*(e_{n_0m_0}e^{-i\psi}+e_{\bar{m}_0\bar{n}_0}e^{i\psi})\\
&+K(e_{m_0\bar{n}_0}e^{i\psi}-e_{n_0\bar{m}_0}e^{-i\psi})+K^*(e_{\bar{n}_0m_0}e^{-i\psi}-e_{\bar{m}_0n_0}e^{i\psi})\big],\\
S_2={}&{}^1/_2(KK^*+RR^*)^{-1/2}\big[R(e_{\bar{m}_0\bar{n}_0}e^{-i\psi}-e_{n_0m_0}e^{i\psi})\\
&+R^*(e_{n_0m_0}e^{-i\psi}-e_{\bar{m}_0\bar{n}_0}e^{i\psi})\\
&-K(e_{m_0\bar{n}_0}e^{i\psi}+e_{n_0\bar{m}_0}e^{-i\psi})+K^*(e_{\bar{m}_0n_0}e^{i\psi}+e_{\bar{n}_0m_0}e^{-i\psi})\big],\\
S_3={}&(e_{m_0m_0}-e_{n_0n_0}+e_{\bar{m}_0\bar{m}_0}-e_{\bar{n}_0\bar{n}_0})/2.
\end{aligned}\qquad\text{(A.2.1)}$$

APPENDIX 3

For single-particle interactions $\mathscr{H}_{1\,\rm int}$ the resolution into secular and nonsecular parts relative to the operator S_a is of the form

$$\mathscr{H}^{\rm sec}_{1\,\rm int}=\sum_{l}\mathscr{H}^{l}_{\rm int},\ \mathscr{H}^{l}_{\rm int}\Rightarrow\sum_{i}\sum_{mm'}g^{i}_{mm'}K_{mm'},\quad l=0,\pm{}^1/_2,\pm 1.\qquad\text{(A.3.1)}$$

For paired interactions $\mathscr{H}_{2\,\rm int}$:

$$\mathscr{H}^{\rm sec}_{2\,\rm int}=\sum_{l}\mathscr{H}^{l}_{2\,\rm int},\qquad l=0,\pm{}^1/_2,\pm 1,\pm{}^3/_2,\pm 2,\qquad\text{(A.3.2)}$$

$$\mathscr{H}^{0}_{2\,\rm int}=\sum_{ij}\sum_{mm'}\sum_{nn'}\sum_{\lambda}d^{ij}_{mm'nn'}K^{\lambda i}_{mm'}K_{nn'},\qquad(\lambda=0,\pm{}^1/_2,\pm 1),\qquad\text{(A.3.3)}$$

$$\begin{aligned}
\mathscr{H}^{\pm 1/2}_{2\,\rm int}=\sum_{ij}\sum_{mm'}\sum_{nn'}d^{ij}_{mm'nn'}\{&K^{\mp 1/2 i}_{mm'}K^{0j}_{nn'}+K^{0i}_{mm'}K^{\mp 1/2 j}_{nn'}\\
&+K^{\pm 1/2 i}_{mm'}K^{\mp 1 j}_{nn'}+K^{\pm 1 i}_{mm'}K^{\mp 1/2 j}_{nn'}\},
\end{aligned}\qquad\text{(A.3.4)}$$

$$\begin{aligned}
\mathscr{H}_{2\,\rm int}^{\pm 1}=\sum_{ij}\sum_{mm'}\sum_{nn'}d^{ij}_{mm'nn'}\{&K^{\mp 1 i}_{mm'}K^{0j}_{nn'}+K^{0i}_{mm'}K^{\mp 1 j}_{nn'}\\
&+K^{\mp 1/2 i}_{mm'}K^{\mp 1/2 j}_{nn'}\},
\end{aligned}\qquad\text{(A.3.5)}$$

$$\mathscr{H}_{2\,\rm int}^{\pm 3/2}=\sum_{ij}\sum_{mm'}\sum_{nn'}d^{ij}_{mm'nn'}\{K^{\mp 1/2 i}_{mm'}K^{\mp 1 j}_{nn'}+K^{\mp 1 i}_{mm'}K^{\mp 1/2 j}_{nn'}\},\qquad\text{(A.3.6)}$$

$$\mathscr{H}^{\pm 2}_{2\,\rm int}=\sum_{ij}\sum_{mm'}\sum_{nn'}d^{ij}_{mm'nn'}K^{\mp 1 i}_{mm'}K^{\mp 1 j}_{nn'},\qquad\text{(A.3.7)}$$

where

$$\begin{aligned}
&K_{mn}{}^{0i}\\
&=\sum_{k}{}'\sum_{p}{}'e_{kk}e_{mn}{}^{i}e_{pp}+{}^1/_2\left(\sum_{k}{}''\sum_{p}{}''e_{kk}e_{mn}{}^{i}e_{pp}+4S_a e_{mn}{}^{i}S_a\right)\\
&K^{\mp 1/2 i}_{mn}\\
&={}^1/_2\sum_{k}{}'\sum_{p}{}''\{e_{kk}e_{mn}{}^{i}e_{pp}+e_{pp}e_{mn}{}^{i}e_{kk}\pm 2(S_a e_{mn}{}^{i}e_{kk}-e_{kk}e_{mn}{}^{i}S_a)\},\\
&K^{\pm 1 i}_{mn}\\
&={}^1/_4\sum_{k}{}''\sum_{p}{}''\{e_{kk}e_{mn}{}^{i}e_{pp}-4S_a e_{mn}{}^{i}S_a\pm 2(S_a e_{mn}{}^{i}e_{kk}-e_{kk}e_{mn}{}^{i}S_a)\},\\
&\qquad\sum_{k}{}'=\sum_{k\neq|m_0|,|n_0|},\qquad\sum_{k}{}''=\sum_{k=|m_0|,|n_0|}.
\end{aligned}$$

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