

Suppression of spin-spin width of the resonance line of a nonequidistant NMR spectrum with the aid of RF pulses

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The possibility is investigated of narrowing down simple lines of a nonequidistant spectrum with the aid of various pulse sequences. An analysis is made of pulse sequences, consisting of 90-degree (or close to them) RF pulses used in the study of an equidistant spectrum, and concrete recommendations are made with respect to the choice of the optimal parameters of these sequences in the nonequidistant case. New RF pulse sequences are proposed that eliminate most completely the dipole-dipole widths of simple lines. It is shown that the second moment, due to the dipole interaction, of a simple line of a nonequidistant spectrum can be decreased by a factor 25-30 if the parameters of the sequence are optimized.

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1. INTRODUCTION

The existence of a strong dipole-dipole interaction between nuclei is the main obstacle to the study of weaker interactions in solids, such as the chemical shift, indirect spin-spin interactions, and others. By now NMR experiments have come into wide use, in which a system of spins polarized in a constant magnetic field is subjected to definite sequences of pulses of a strong RF field for the purpose of effectively eliminating the spin-spin broadening of resonance lines.^[1-9] In the case of an equidistant spectrum it was found possible to prepare the spin system in such a way as to eliminate the dipole-dipole interactions that make the decisive contribution to the line shape.

For a nonequidistant spin spectrum, the study of the possibilities of strong narrowing was carried out only theoretically and it was shown that when experiments of the Lee-Goldburg type^[10] are performed on a single simple line it is possible to decrease effectively the second moment by an approximate factor of seven,^[11] while in the "time-reversal" procedure^[12,13] the decrease is by a factor 25-30.^[14] Our purpose was to investigate the possibilities of narrowing down simple lines of a nonequidistant spectrum with the aid of various pulse sequences consisting of 90-degree pulses or sequences that can be reduced to them.¹⁾ We shall follow where possible the review^[7] of the pulse sequences most widely used in high-resolution NMR for the investigation of systems with equidistant spin spectra.

2. GENERAL RESULTS

We confine ourselves to the case when the eigenvalues m_i of the operator I_i^z of the spin i are sufficiently good quantum numbers. We introduce the projection operators q_{mn}^i , which are directly connected by the relation

$$\langle m_i' | q_{mn}^i | n_i' \rangle = \delta_{m_i', m_i} \delta_{n_i', n_i} \sum_{m, n} q_{mn}^i = q_{mn}^i \quad (1)$$

with the eigenfunctions $|m_i\rangle$ of the single-particle spin Hamiltonian \mathcal{H}_i^0 :

$$\mathcal{H}_i^0 = \sum_{m=-I}^I \varepsilon_m q_{mm}^i \quad (2)$$

The Hamiltonian of the considered system of spins polarized in a constant magnetic field directed along the z axis is written in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i^k + \mathcal{H}_d^{(k)}, \quad \mathcal{H}_0 = \sum_i \mathcal{H}_i^0 \quad (3)$$

where the operator \mathcal{H}_0 describes the energy spectrum of the system, \mathcal{H}_i^k describes the interaction with the alternating field of the k -th pulse, and $\mathcal{H}_d^{(k)}$ is the secular part of the dipole-dipole interaction operator. It is assumed that the frequency spectrum consists of only simple lines and that they are well resolved, i.e., that for all $m \neq n$

$$|\omega_m - \omega_n| \gg \omega_d, \quad \omega_m = (\varepsilon_{m+1} - \varepsilon_m) / \hbar, \quad (4)$$

where ω_d is the line width due to the dipole-dipole interaction.

For the considered spin systems we have

$$\mathcal{H}_d^{(k)} = \sum_{i>j} B_{ij} \left\{ 2 \sum_{m, n=-I}^I m n q_{mm}^i q_{nn}^j - \frac{1}{2} \sum_{k=-I}^I A_k^2 (q_{k+1,1}^i q_{k, k+1}^j + q_{k, k+1}^i q_{k+1, k}^j) \right\}, \quad (5)$$

$$B_{ij} = \frac{1}{2} \gamma^2 \hbar^2 r_{ij}^{-3} (1 - 3 \cos^2 \theta_{ij}), \quad A_k = [I(I+1) - k(k+1)]^{1/2}. \quad (6)$$

Here r_{ij} , θ_{ij} , φ_{ij} are the spherical coordinates of the vector \mathbf{r}_{ij} that joins the positions of the two spins i and j . The second moment of the resonance line, corresponding to the transitions $m_0 \leftrightarrow m_0 + 1$, at the frequency ω_{m_0} , due to $\mathcal{H}_d^{(k)}$, is determined by the formula^[11]

$$\hbar^2 M_2 = (2B + 2C + 2D) \sum_{i>j} B_{ij}^2 / (2I+1), \quad (7)$$

where we introduce for convenience the notation

$$B = (1 + \frac{1}{2} A_{m_0}^2)^2, \quad C = \frac{1}{2} (A_{m_0+1}^2 + A_{m_0-1}^2), \quad (8)$$

$$D = [\frac{1}{2} I(I+1) (2I+1) - 1].$$

Assume that the system in question is acted upon by a series of RF pulses at one of the resonance frequencies ω_{m_0} of the system, and let the amplitude of each pulse H_k lie in a plane perpendicular to the axis, let its duration be $\delta_k \ll \omega_d^{-1}$ and let $|h_k| = |\gamma h H_k| \gg \hbar \omega_d$, where γ is the gyromagnetic ratio. In this case transitions are excited only between a definite pair of levels, so that in good approximation we retain in the Hamiltonian of the interaction with the alternating field only the part

$$\mathcal{H}_d^k = \frac{1}{2} A_m h_k (q_{m_0-1, m_0} \exp\{-i(\omega_0 t + \varphi_k)\} + q_{m_0 m_0+1} \exp\{i(\omega_0 t + \varphi_k)\}), \quad (9)$$

which is responsible for the resonant transitions at the frequency ω_{m_0} ; here φ is the angle between the field direction and the z axis.

The inequality $|h_k| \gg \hbar \omega_d$ corresponds to the case of a strong RF field, which is therefore best taken into account as fully as possible. This can be done by changing over to the interaction representation (IR) with the aid of the unitary operator^[14]

$$R = \exp\left\{i\hbar^{-1} \sum_n \varepsilon_n q_{nm} t\right\}, \quad (10)$$

in which the Hamiltonian $\mathcal{H}_0 + \mathcal{H}_d^k$, which we shall consider as the principal one, does not depend explicitly on the time. In the case of an equidistant spectrum ($\varepsilon_m = \hbar \omega_0 m$) the IR is equivalent to a transition to a coordinate frame rotating with a frequency ω_0 .

In the IR, the total Hamiltonian takes the form

$$\mathcal{H}^* = R \mathcal{H} R^{-1} = \mathcal{H}_{\text{const}}^* + \mathcal{H}_d^{(k)} + \mathcal{H}_{it}^*, \quad (11)$$

where

$$\mathcal{H}_{\text{const}}^* = \frac{1}{2} I_m \omega_k \hbar (q_{m_0+1, m_0} e^{-i\varphi_k} + q_{m_0, m_0+1} e^{i\varphi_k}) \quad (12)$$

does not depend on the time, and \mathcal{H}_{it}^* is that part of the operator $R \mathcal{H}_d^k R^{-1}$, which oscillates at a frequency $2\omega_m$, and can be neglected. Therefore in the absence of a pulse we have $\mathcal{H}^* = \mathcal{H}_d^{(k)}$, and the interval δ_k of the pulse action we have $\mathcal{H} \approx \mathcal{H}_{\text{const}}^*$, since by virtue of the condition $\delta_k \ll \omega_d^{-1}$ the dipole-dipole interaction can be neglected. The action of such a pulse in the IR is equivalent to the transformation

$$P_{n, m_0}(\theta) = \exp[-i\theta_k (n_k I^{m_0})], \quad (13)$$

$$I^{m_0} = I_x^{m_0} x_0 + I_y^{m_0} y_0 = \frac{1}{2} A_m (q_{m_0-1, m_0} + q_{m_0, m_0+1}) x_0 + \frac{1}{2} i A_m (q_{m_0, m_0-1} - q_{m_0-1, m_0}) y_0, \quad (14)$$

where I^{m_0} is that part of the spin operator I which is responsible for the resonant transitions, x_0 , y_0 , and n_k are unit vectors in the respective directions of x , y , and φ_k , and $\theta_k = H_k \delta_k$.

Let the function $|t\rangle$ describe the state of the system at the instant of time t and let it be known for a certain instant t_0 . Following^[7], we determine the state of the system at the instant of time

$$t_0 + \sum_{k=1}^n \tau_k,$$

where τ_k is the interval between the $k+1$ -st and the k -th pulses,

$$\begin{aligned} \left| t_0 + \sum_{k=1}^n \tau_k \right\rangle &= \left\{ \prod_{k=1}^n [\exp(-i\mathcal{H}_d^{(k)} \tau_k) P_{n, m_0}] \right\} |t_0\rangle \\ &= \left(\prod_{m=1}^n P_{n, m_0} \right) \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_d^k \tau_k) \right\} |t_0\rangle. \end{aligned} \quad (15)$$

We have put here

$$\mathcal{H}_d^k = \left(\prod_{i=1}^k P_{n, m_0} \right)^{-1} \mathcal{H}_d^{(k)} \left(\prod_{i=1}^k P_{n, m_0} \right). \quad (16)$$

If n pulses make up a cycle, i. e., if

$$\prod_{i=1}^n P_{n, m_0} = 1,$$

then the following relation holds:

$$|t_0 + T\rangle = \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_d^k \tau_k) \right\} |t_0\rangle, \quad (17)$$

where

$$T = \sum_{k=1}^n \tau_k$$

is the time of the cycle.

Upon application of N cycles with a time $T \ll \omega_d^{-1}$ the system evolves over long times NT under the influence of the effective Hamiltonian $\overline{\mathcal{H}}$ ^[5, 15]

$$|t+t_0\rangle \approx \exp(-i\overline{\mathcal{H}}t) |t_0\rangle, \quad (18)$$

which is described in first-order approximation by the formula

$$\overline{\mathcal{H}} = \frac{1}{T} \sum_{k=1}^n \mathcal{H}_d^k \tau_k. \quad (19)$$

In the case of an equidistant spectrum, many pulse sequences that produce $\overline{\mathcal{H}} = 0$ have been proposed, meaning that in the given approximation the free-precession signal has under the conditions $\overline{\mathcal{H}} = 0$ an infinite duration and accordingly its Fourier transform has a narrow width. Our earlier investigations^[11, 14] have shown that in the case of nonequidistant spectra the use of pulse sequences that excite only one of the resonance frequencies of the system can not eliminate completely the dipole-dipole interactions (it is impossible to obtain $\overline{\mathcal{H}} = 0$). This is the consequence of the fact that such an excitation "shakes up" only part of the dipole-dipole interactions. Therefore the main task of the present paper is to find sequences that produce an effective Hamiltonian that makes a minimal contribution to the second moment.

As already noted, formula (19) for $\overline{\mathcal{H}}$ is valid only in first-order approximation. In our case, however, it turns out that the contribution from $\overline{\mathcal{H}}$ does not vanish, but on the contrary remains predominant in the dipole-

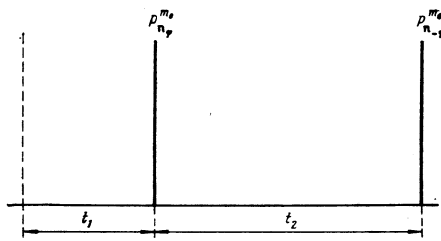


FIG. 1.

dipole width, while the succeeding approximations do not lead to a noticeable change of the results. We shall therefore confine ourselves henceforth to the investigation of the first-order approximation.

To understand the effective Hamiltonian that describes a system acted upon by various pulse sequences in the case of nonequidistant spin spectra, we consider the simplest cycle consisting of two 90-degree pulses, shown in Fig. 1. $P_{n_0}^{m_0}$ denotes a 90-degree pulse at a frequency ω_{m_0} with magnetic field lying in the xy plane at an angle φ to the x axis.

In this case we obtain with the aid of (19), (16), (13), and (5)

$$\bar{\mathcal{H}} = \frac{t_1}{t_1+t_2} \mathcal{H}_d^{(1)} + \frac{t_2}{t_1+t_2} \mathcal{H}_d^{(\varphi)}, \quad \mathcal{H}_d^{(\varphi)} = \mathcal{H}_d + \mathcal{P}^{(\varphi)} + \mathcal{Q}^{(\varphi)}. \quad (20)$$

The Hamiltonian $\mathcal{H}_d^* = \mathcal{H}_d^*(ij) + \mathcal{H}_d^*(ji)$ is the secular part of the operator $\mathcal{H}_d^{(\varphi)}$,

$$\begin{aligned} \mathcal{H}_d^*(ij) &= \frac{1}{2} \sum_{i>j} B_{ij} \left\{ 2 \sum_{m,n} mnq_{nm}^i q_{nn}^j - \sum_k A_k^2 q_{k+i,k}^j q_{k+i,k}^j \right. \\ &+ 2 \sum_m m (q_{m_0, m_0}^i - q_{m_0+1, m_0+1}^j) q_{mm}^i + \left(1 + \frac{1}{2} A_{m_0}^2 \right) q_{m_0+1, m_0}^j q_{m_0, m_0+1}^i \\ &+ \left(1 - \frac{1}{2} A_{m_0}^2 \right) (q_{m_0+1, m_0+1}^i - q_{m_0, m_0}^i) (q_{m_0+1, m_0+1}^j - q_{m_0, m_0}^j) \\ &+ \frac{1}{2} A_{m_0-1}^2 (q_{m_0, m_0-1}^i - q_{m_0-1, m_0}^i + q_{m_0+1, m_0-1}^j - q_{m_0-1, m_0+1}^j) \\ &\left. + \frac{1}{2} A_{m_0+1}^2 (q_{m_0+1, m_0+2}^i - q_{m_0+2, m_0+1}^i + q_{m_0+2, m_0+1}^j - q_{m_0+1, m_0+2}^j) \right\} \quad (21) \end{aligned}$$

(it does not depend on the direction (φ) of the field in the pulse). The nonsecular operators $\mathcal{P}^{(\varphi)} = \mathcal{P}_{ij}^{(\varphi)} + \mathcal{P}_{ji}^{(\varphi)}$ and $\mathcal{Q}^{(\varphi)}$ are of the form

$$\begin{aligned} \mathcal{P}_{ij}^{(\varphi)} &= \frac{i}{2} \sum_{i>j} B_{ij} \left\{ \left[\sum_m m q_{mm}^i - \frac{1}{2} (q_{m_0+1, m_0+1}^i - q_{m_0, m_0}^i) \right] \right. \\ &\times (e^{-i\varphi} q_{m_0+1, m_0}^j - e^{i\varphi} q_{m_0, m_0-1}^j) + \frac{1}{4} A_{m_0+1}^2 (e^{i\varphi} q_{m_0+2, m_0+1}^j q_{m_0, m_0+2}^i - e^{-i\varphi} q_{m_0+2, m_0}^j q_{m_0+1, m_0+2}^i) \\ &\left. + \frac{1}{4} A_{m_0-1}^2 (e^{i\varphi} q_{m_0-1, m_0+1}^j q_{m_0, m_0-1}^i - e^{-i\varphi} q_{m_0-1, m_0}^j q_{m_0+1, m_0-1}^i) \right\}, \quad (22) \end{aligned}$$

$$\mathcal{Q}^{(\varphi)} = - \sum_{i>j} \frac{1}{4} B_{ij} \left(1 + \frac{1}{2} A_{m_0}^2 \right) (e^{2i\varphi} q_{m_0, m_0+1}^i q_{m_0+1, m_0}^j + e^{-2i\varphi} q_{m_0+1, m_0}^i q_{m_0, m_0+1}^j). \quad (23)$$

We introduce the following notation for certain concrete orientations of the magnetic field of the pulse

$$\begin{aligned} \varphi=0: \quad P_{n_0}^{m_0} &= P_x^{m_0} = \exp\left(-i \frac{\pi}{2} I_x^{m_0}\right), \quad \mathcal{H}_d^{(\varphi)} = \mathcal{H}_d^{(-y)} = \mathcal{H}_d + \mathcal{P}_y + \mathcal{Q}_{zy}, \\ \varphi=\frac{\pi}{2}: \quad P_{n_0}^{m_0} &= P_y^{m_0} = \exp\left(-i \frac{\pi}{2} I_y^{m_0}\right), \quad \mathcal{H}_d^{(\varphi)} = \mathcal{H}_d^{(xz)} = \mathcal{H}_d + \mathcal{P}_x + \mathcal{Q}_{zx}, \end{aligned} \quad (24)$$

$$\varphi=\pi: \quad P_{n_0}^{m_0} = P_{-x}^{m_0} = \exp\left(i \frac{\pi}{2} I_x^{m_0}\right), \quad \mathcal{H}_d^{(\varphi)} = \mathcal{H}_d^{(y)} = \mathcal{H}_d + \mathcal{P}_y + \mathcal{Q}_{zy}.$$

$$\varphi=3\pi/2: \quad P_{n_0}^{m_0} = P_{-y}^{m_0} = \exp\left(i \frac{\pi}{2} I_y^{m_0}\right), \quad \mathcal{H}_d^{(\varphi)} = \mathcal{H}_d^{(-xz)} = \mathcal{H}_d + \mathcal{P}_{-x} + \mathcal{Q}_{zx}.$$

The meaning of this notation becomes understandable if it is recognized that in the particular case $K=1/2$, we have, e.g.,

$$\mathcal{H}_d^{(xz)} = \sum_{i>j} B_{ij} (3I_x^i I_x^j - \mathbf{I}^i \cdot \mathbf{I}^j). \quad (25)$$

The operators (24) have the following properties:

$$\mathcal{P}_x = -\mathcal{P}_{-x}, \quad \mathcal{P}_y = -\mathcal{P}_{-y}, \quad \mathcal{Q}_{zx} = -\mathcal{Q}_{zy}, \quad (26)$$

$$[\mathcal{P}_x, I_x^{m_0}] = 0, \quad [\mathcal{H}_d^{(\pm x)}, I_x^{m_0}] = 0, \quad (27)$$

which follow from relations (21)–(23)

3. ANALYSIS OF PULSE SEQUENCES THAT LEAD TO HIGH-RESOLUTION NMR

We proceed now to an analysis of concrete sequences. Since we are considering a case when all the pulses making up the cycle are applied at only one of the resonant frequencies of the system, ω_{m_0} , we shall henceforth omit the subscript m_0 . We assume that the initial state of the system is the polarization of the resonant spins along the x axis (e.g., after the $P_y^{m_0}$ pulse).

1) *Multiple 90-degree pulses:* ($\tau - P_x - 2\alpha\tau - P_x - 2\tau - P_x - 2\alpha\tau - P_x - \tau$)_n. Described in many articles,^[1-3] this method is based on the fact that although $\bar{\mathcal{H}} \neq 0$, the operator $\bar{\mathcal{H}}$ commutes with the initial state of the density matrix for $\alpha=1$, thus indicating the absence of damping.

In the case of a nonequidistant spectrum, the Hamiltonian $\bar{\mathcal{H}}$ obtained for this sequence is equal to

$$\bar{\mathcal{H}} = \frac{1}{1+\alpha} (\mathcal{H}_d^{(x)} + \alpha \mathcal{H}_d + \alpha \mathcal{Q}_{zx}). \quad (28)$$

It is easy to verify that it does not have the indicated property. Therefore damping of the magnetization will be observed in the system at the frequency ω_{m_0} . This damping is determined by the operator $\bar{\mathcal{H}}$ and can be characterized by the second moment $\bar{M}_2(\alpha)$. It has turned out that the minimal value of $\bar{M}_2(\alpha)$, which takes place at $\alpha = 1 + (C+D)/2B$, is equal to

$$\bar{M}_2 = \frac{B(C+D)}{(4B+C+D)(B+C+D)} M_2. \quad (29)$$

For the case $I=1/2$, where $C=D=0$, we have $\bar{M}_2=0$ in full accord with the calculations for an equidistant spectrum. For $I>1/2$, the second moment \bar{M}_2 is approximately²⁾ 10–15% of M_2 . Generally speaking this result is by itself not bad, but it will be shown later that a much larger narrowing can be obtained with the aid of other sequences.

2) *Phase-alternating 90-degree pulses:* ($\tau - P_x - 2\alpha\tau - P_x - \tau$)_n. This method is a modification of the first,

and for equidistant spin spectra the effective Hamiltonian $\bar{\mathcal{H}}$ is the same in both cases.

For the non-equidistant spectrum we have

$$\bar{\mathcal{H}} = \frac{1}{1+\alpha} (\mathcal{H}_d^{(1)} + \alpha \mathcal{H}_d' + \alpha \mathcal{P}_y + \alpha Q_{\pm y}). \quad (30)$$

The second moment is minimal at $\alpha = 1$ and is described by the formula

$$\bar{M}_2 = \frac{C+D}{2(B+C+D)} M_2, \quad (31)$$

which shows that \bar{M}_2 is of the order of $\sim 30\%$ of M_2 .

3) *Four-pulse cycle*: $(\tau - P_x - \alpha\tau - P_x - \tau - P_y - \alpha\tau - P_y)_n$. Four-pulse cycles with $\alpha = 2$ (WHH cycles) yield $\bar{\mathcal{H}} = 0$ in the case of equidistant spectra. In our case

$$\bar{\mathcal{H}} = \frac{1}{1+\alpha} \left(\mathcal{H}_d^{(1)} + \alpha \mathcal{H}_d' + \frac{\alpha}{2} \mathcal{P}_y + \frac{\alpha}{2} \mathcal{P}_z \right). \quad (32)$$

The minimum of the second moment \bar{M}_2 takes place at

$$\alpha = 2 + 2(C+D)/(3B+C+D). \quad (33)$$

Under this condition

$$\bar{M}_2 = \frac{(C+D)(2B+C+D)}{(9B+5C+5D)(B+C+D)} M_2, \quad (34)$$

which is approximately 15% of M_2 .

4) *Pulsed analog of the Lee-Goldberg experiment*: $(\tau - P_{111} - \frac{1}{2}\alpha\tau - P_{111} - \frac{1}{2}\alpha\tau - P_{111})_n$. In this experiment pulses that rotate the magnetization by 120° around the (111) direction are applied to the system at equal time intervals ($\alpha = 2$). This rotation is described, in the case of equidistant spectra, by the operator

$$P_{111} = \exp \left[-\frac{2i\pi}{3\sqrt{3}} (I_x + I_y + I_z) \right], \quad (35)$$

which can be represented in the form of two 90-degree rotations, namely

$$P_{111} = \exp \left(-i \frac{\pi}{2} I_x \right) \exp \left(-i \frac{\pi}{2} I_y \right) = P_x P_y. \quad (36)$$

It can be shown by direct calculation that in our case there is an analogous relation $P_{111}^{m_0} = P_x^{m_0} P_y^{m_0}$ and that

$$P_{111}^{m_0} \mathcal{H}_d^{(1)} (P_{111}^{m_0})^{-1} = \mathcal{H}_d^{(1)}, \quad P_{111}^{m_0} P_{111}^{m_0} \mathcal{H}_d^{(1)} (P_{111}^{m_0} P_{111}^{m_0})^{-1} = \mathcal{H}_d^{(y)}. \quad (37)$$

The effective Hamiltonian and the optimal values of α are determined by formulas that coincide exactly with formulas (32)–(34) of the preceding item.

5) *Other analogs of the Lee-Goldberg experiment*. Another analog of the Lee-Goldberg experiment^[5] is the sequence $(\tau - P_y - \alpha\tau - P_y - P_x - \alpha\tau - P_x - \tau)_n$. The effective Hamiltonian is determined here, too, by formula (32), i.e., in this case \bar{M}_2 is of the order of 15% of M_2 . The same properties is possessed by the Mansfield sequence^[8]

$$\left(\tau - P_x P_y - \frac{\alpha}{2} \tau - P_y - \alpha\tau - P_y - \frac{\alpha}{2} \tau - P_x P_x - \tau \right)_n.$$

6) *Eight-pulse cycle*: $(\tau - P_x - \alpha\tau - P_x - \tau - P_y - \alpha\tau - P_y - \tau - P_x - \alpha\tau - P_x - \tau - P_y - \alpha\tau - P_y)_n$. Known as the HW cycle^[7] for $\alpha = 2$, it yields $\bar{\mathcal{H}} = 0$ in the case of equidistant spectra. In our case, owing to relations (26), all the nonsecular parts cancel each other and the system is described by the Hamiltonian

$$\bar{\mathcal{H}} = \frac{1}{1+\alpha} (\mathcal{H}_d^{(1)} + \mathcal{H}_d'). \quad (38)$$

This Hamiltonian was investigated by us earlier in^[14]. The values of α for which \bar{M}_2 is determined by the formula

$$\alpha = 2 + 4(C+D)/3B, \quad (39)$$

and the second moment itself is in this case equal to

$$\bar{M}_2 = \frac{B(C+D)}{(9B+4C+4D)(B+C+D)} M_2. \quad (40)$$

The optimal values of α and the corresponding values of the ratio \bar{M}_2/M_2 for any spin and arbitrary transition are given in the tables of^[14]. It is seen from them that \bar{M}_2 amounts to 3.5–4% of M_2 . This example shows the importance that elimination of all the nonsecular parts from the effective Hamiltonian acquires in the case of nonequidistant spectra.

The generalized HW cycle is not the only example of sequences having such properties and leading consequently to so noticeable a narrowing of the resonance lines. By modifying some of the cycles described by us we can obtain also sequences whose effective Hamiltonian is described by formula (38).

Consider, for example, the cycle (Fig. 2a), two half-cycles of which are pulse analogs of the Lee-Goldberg experiment. The action of the pulses of the second sub-cycle is equivalent to rotation of the magnetization by 120° around the (111) axis

$$P_y P_x = \exp \left[-\frac{2i\pi}{3\sqrt{3}} (I_x + I_y - I_z) \right] = P_{111}. \quad (41)$$

Another example may be the cycle of Fig. 2b. Here τ_0 lies in the interval $\tau \geq \tau_0 \geq 0$. In both cases, the effective Hamiltonian does not contain any nonsecular parts and is described by formula (38).

We consider as even more interesting the case of Fig. 2c. The effective Hamiltonian is described in this case by the formula

$$\bar{\mathcal{H}}' = \frac{1}{1+\alpha} (\mathcal{H}_d^{(1)} + \alpha \mathcal{H}_d' + \alpha \mathcal{P}_x) = \bar{\mathcal{H}} + \frac{\alpha}{1+\alpha} \mathcal{P}_x. \quad (42)$$

However, by virtue of the property (27) we have

$$[\bar{\mathcal{H}}', I_x^{m_0}] = [\bar{\mathcal{H}}, I_x^{m_0}], \quad (43)$$

and therefore the second moment due to $\bar{\mathcal{H}}'$, and the optimal values of α , are also determined by formulas (39) and (40).

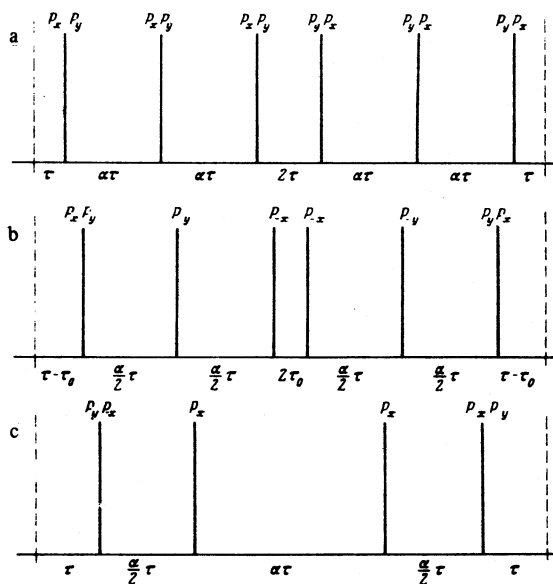


FIG. 2.

We note also that a system acted upon by a cycle of the type

$$(\tau - P_x - \frac{1}{2}\alpha\tau - P_y - \alpha\tau - P_y - \frac{1}{2}\alpha\tau - P_x - 2\tau - P_x - \frac{1}{2}\alpha\tau - P_y - \alpha\tau - P_y - \frac{1}{2}\alpha\tau - P_x - \tau)_n,$$

which is known for $\alpha = 2$ as REV-8,^[16] is also described by the Hamiltonian (42). In addition, the compensation cycles introduced by Mansfield,^[17,18] which consist of aggregates of sequences described by us earlier, can lead to the Hamiltonian (42).

We have thus shown that there exist pulse sequences with the aid of which the second moment, which determines the effective width of the resonance line, can be decreased by a factor 25-30, depending on the magnitude of the spin and on the position of the simple line in the nonequivalent spin spectrum. Since it follows from a direct observation of the NMR signal in a rotating coordinate frame, recently carried out by Mefed and Atsarkin,^[19] that the line has a near-Lorentz shape, there are some grounds for assuming that the effective width of the resonance line will be proportional not to $\bar{M}_2^{1/2}$, but directly to \bar{M}_2 .

APPENDIX

Besides the suppression of the spin-spin width of the resonance lines, the considered aggregates of the RF pulses exert a collateral effect by acting also on weak interactions, whose study in principle becomes possible after the elimination of the spin-spin width. Using as an example the operator

$$\mathcal{H}_0 = \hbar \sum_k \delta_k I_k^z, \quad (\text{A. 1})$$

which is responsible for the chemical shift, we shall show that this collateral action is not strong enough to prevent observation of this interaction (δ_k is the frequency shift of the k -th nucleus from the value ω_0 of the free spin).

The only part of the operator (A. 1) that contributes to the shape of an individual line of a nonequidistant spectrum is

$$\mathcal{H}_0^{(k)}(m_0) = \frac{\hbar}{2} \sum_k \delta_k (q_{m_0+1, m_0+1}^k - q_{m_0, m_0}^k) = \hbar \sum_k \delta_k I_z^{(m_0)} \quad (\text{A. 2})$$

and is connected with resonant transitions at the frequency ω_0 .

The action of various pulse sequences on the spin system in the presence of a chemical shift can be described by introducing into the effective Hamiltonian (19) a term

$$\bar{\mathcal{H}}_0 = \frac{1}{T} \sum_{k=1}^n \mathcal{H}_0^{(k)}(m_0) \tau_k, \quad (\text{A. 3})$$

which is responsible for the effective chemical shift ($\mathcal{H}_0^{(k)}(m_0)$) is defined in analogy with \mathcal{H}_0^k (see Eq. (16)).

For concrete pulse sequences, the magnitude of the chemical shift $\bar{\mathcal{H}}_0$ is, naturally, different. Since the largest narrowing of the resonance lines is caused by sequences with effective Hamiltonians (38) and (42), we consider the change of the chemical shift in only these two cases.

In the first case

$$\bar{\mathcal{H}}_0 = \frac{1}{1+\alpha} \mathcal{H}_0^{(k)}(m_0). \quad (\text{A. 4})$$

If we recognize that the optimal values are $\alpha > 4$, we can conclude that the chemical shift is suppressed no less than the spin-spin width. Such RF pulse sequences therefore offer no gain in the elimination of the spin-spin width for the purpose of studying the chemical shift.

In the second case we have a favorable situation. The effective Hamiltonian corresponding to the chemical shift is described by the expression

$$\bar{\mathcal{H}}_0 = \frac{1}{1+\alpha} \left[\mathcal{H}_0^{(k)}(m_0) + \frac{\alpha}{2} \mathcal{H}_0^{(k)}(m_0) \right], \quad (\text{A. 5})$$

$$\mathcal{H}_0^{(k)}(m_0) = \hbar \sum_k \delta_k I_z^{(m_0)}.$$

If we change over to a system rotated about the y axis through an angle $\theta = \tan^{-1}(\alpha/2)$, then the Hamiltonian $\bar{\mathcal{H}}_0'$ takes the form

$$\bar{\mathcal{H}}_0' = \frac{(1+\alpha^2/4)^{1/2}}{1+\alpha} \mathcal{H}_0^{(k)}(m_0). \quad (\text{A. 6})$$

It follows from this formula that the chemical-shift constant δ at optimal values of α is approximately smaller by a factor $\sqrt{5}$ than prior to the application of the pulse sequence. This example shows that by using appropriate pulse sequences it is possible to attain a noticeable gain in the resolution of the chemical shift.

¹⁾It must be noted that here, in contrast to the equidistant case, weak shifts of the NMR frequency will appear against the background of an appreciable quadrupole splitting. The study of

these weak shifts entails therefore an analysis of the deviations of the splittings from the quadrupole regularities.

²At $I > \frac{1}{2}$ a transition to the case of the equidistant spectrum is impossible, since we have considered above an excitation which is not realizable in an equidistant spectrum, of only one transition.

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Investigation of the parametric mechanism of spin-echo formation and the dynamics of spin motion in systems with a dynamic frequency shift

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The formation of a nuclear spin-echo signal from a resonance radio-frequency pulse and a parametric-pumping pulse at double the frequency has been investigated experimentally in a system of Mn^{55} nuclei in $MnCO_3$ and $CsMnF_3$ in the case of arbitrary pulse duration and shape. Echo signals have been obtained from more complex sequences of resonance and parametric pulses. The time dependence of the oscillation amplitude of the parametrically excited nuclear spin system has been directly observed. A technique has been developed for measuring the frequency distribution of the radio-frequency radiation of a spin system excited by a resonance radio-frequency pulse. The frequency distribution of the radio-frequency radiation has been investigated in systems with a dynamic frequency shift under conditions of frequency-modulated echo formation. A theory of parametric echo formation is developed, and a theoretical interpretation of the experimental results is presented.

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1. INTRODUCTION

The known pulse techniques for investigating spin systems with inhomogeneous broadening of the resonance line consist in the excitation of these systems by a sequence of radio-frequency (RF) pulses that act in resonant fashion. There exist two mechanisms for spin-echo signal formation in such experiments: the phase mechanism (the Hahn echo)^[1] and the frequency-modulation mechanism (the FM echo).^[2-5]

Recently, a number of experiments on the investigation of the so-called "enhanced" echo in ferrites have been performed.^[6,7] It has been shown^[8] that in this case the spin echo is formed on a system of quasistationary spin waves in an inhomogeneous external magnetic field. The RF pulses excite this system parametrically. There exist, however, systems on which the pulses can act both resonantly and parametrically. To

them, from among spin systems, pertain in particular, the system of Mn^{55} nuclei in antiferromagnets with the "easy-plane" type of anisotropy ($MnCO_3$ and $CsMnF_3$). In these substances the antiferromagnetic resonance frequency turns out to be so low that there arise mixed nuclear-electronic oscillations. In this case the frequency, ν_n (below it will be called the nuclear frequency), of the quasinuclear branch of the magnetic resonance shifts from the value $\nu_{n0} = \gamma H_{hf}$ by an amount, ν_{DFS} , called the dynamic frequency shift (DFS). (H_{hf} is the strength of the hyperfine field at the nuclei.) As will be shown in the Appendix, in the case of the oscillations of the quasinuclear branch the component of the resultant magnetic moment of the sample along the direction of the external magnetic field lying in the easy plane of the sample oscillates at the frequency $2\nu_n$. In view of this, a RF field of frequency $2\nu_n$ directed along the magnetic field acts parametrically on this oscillation mode.