# Nitrogen-14 NQR Multiple-Pulse Spin-locking in the Axial Electric Field Gradient *

G. B. Furman

Department of Theoretical Physics, Perm University, 614600 Perm, Russia

Z. Naturforsch. **49a,** 97–102 (1994); received September 4, 1993

The behavior of a nuclear spin-1 system with the Hamiltonian including: a) the interaction of the electric quadrupole moment of nuclei with the axial gradient of the crystal electric field; b) a homonuclear and heteronuclear dipole-dipole coupling; and c) the interaction with a multiple pulse radiofrequency field of arbitrary orientation was considered. The effective Hamiltonian is constructed by using the Floquet theory. The secular parts of the homonuclear and heteronuclear dipole-dipole interaction was found and the quasi-equilibrium magnetization was calculated.

*Key words:* NQR; Multiple-pulse spin-locking; Nitrogen-14.

## 1. Introduction

To obtain the high resolution NMR or NQR spectra and to study slow molecular motions in solids, various experimental techniques have been developed, many of which utilize multiple-pulse radio-frequency (r.f.) fields [1, 2]. Various theoretical methods have been used to explain the behavior of a nuclear spin under multiple-pulse irradiation.

Recently, the multiple-pulse irradiation has been applied to a polycrystalline sample containing spin-1 nuclei in the axial electric field gradient (EFG) to observe the long time evolution of the spin system [3]. But the multiple-pulse spin-locking state was not observed in the experiment, which is rather surprising.

To explain this situation, we generalize in the present paper, the earlier theoretical consideration [4] to the case of the spin $I=1$ system in an axially symmetric EFG.

## 2. Hamiltonian of the System

Let us consider a crystalline sample containing spin-1 nuclei and irradiated by the multiple-pulse spin-locking sequence [1–3]. The total Hamiltonian of the spin system at times $t \ll T_1$ (the spin lattice relaxation time) is given by

$$\mathscr{H}(t)=\mathscr{H}_Q+\mathscr{H}_{dd}+\mathscr{H}_{\text{r.f.}}(t), \tag{1}$$

where

$$\mathscr{H}_Q=\sum_j \frac{eQq}{4}\left(3 I_z^{j2}-\boldsymbol{I}^2\right) \tag{2}$$

represents in the quadrupole principal axes frame the interaction of the $I$-spins quadrupole moment with the axially symmetric EFG, and the sum is over all spins of an $I$ species.

$$\mathscr{H}_{dd}=\mathscr{H}_{SS}+\mathscr{H}_{II}+\mathscr{H}_{IS} \tag{3}$$

is the dipole-dipole interaction between $S-S$, $I-I$, and $I-S$ spins. $\mathscr{H}_{\text{r.f.}}(t)$ defines the interaction between only $I$ spins and the multiple-pulse r.f. magnetic field

$$\mathscr{H}_{\text{r.f.}}(t)=\sum_j \omega_1(t)\, a\cdot I^j \cos(\omega t+\phi), \tag{4}$$

where $\phi=0$ and $\omega_1(t)=\alpha_0\,\delta(t)$ for the preparatory pulse and $\phi=\pi/2$ and $\omega_1(t)=\alpha\sum_{\varkappa=0}^{\infty}\delta(t-(\varkappa+\frac{1}{2})t_c)$ for the remaining pulses, $\alpha=\gamma H_1 t_w$, $H_1$ and $t_w$ are amplitude and pulse duration of the r.f. pulses. $\boldsymbol{a}=\{\cos\phi_L \sin\theta_L, \sin\phi_L \sin\theta_L, \cos\theta_L\}$ is the unit vector directed along the r.f. coil axis. Henceforth the units of $\gamma$, the gyromagnetic ratio, and $eQq/4$, the quadrupole coupling constant, are defined so that $\hbar=1$, and energy is expressed in *radians/sec*.

Using the projection operators $e^j_{mn}$ for the spins $I$ and $p^j_{\mu\eta}$ for spins $S=1/2$ defined by their matrix elements $<m|e^j_{m'n'}|n>=\delta_{mm'}\,\delta_{nn'}$ and $<\mu|p^j_{\mu'\eta'}|\eta>=\delta_{\mu\mu'}\,\delta_{\eta\eta'}$ with $m, n=0, \pm 1$ and $\mu, \eta=\pm\frac{1}{2}$ and commutator correlation $[e^j_{mn}, p^k_{\mu\eta}]=0$, the following expres-

* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

Reprint requests to Dr. G.B. Furman, Department of Theoretical Physics, Perm University, Perm 614600, Russia.

0932-0784 / 94 / 0100-0097 $ 01.30/0. – Please order a reprint rather than making your own copy.

sions of all operators included in $\mathscr{H}(t)$ may be obtained:

$$\mathscr{H}_Q = \frac{\omega_0}{3} \sum_j (e^j_{11} - 2e^j_{00} + e^j_{\bar{1}\bar{1}}), \quad \bar{1} \equiv -1, \tag{5}$$

$$\mathscr{H}_{SS} = \sum_{jk} \sum_{\mu\eta\mu'\eta'} \mathscr{D}^{jk}_{\mu\eta\mu'\eta'} p^j_{\mu\eta} p^k_{\mu'\eta'}, \tag{6}$$

$$\begin{aligned}\mathscr{H}_{II} = \sum_{jk} \gamma^2 r_{jk}^{-3} \{ & A_{jk}(e^j_{11} - e^j_{\bar{1}\bar{1}})(e^k_{11} - e^k_{\bar{1}\bar{1}}) \\ & + 2B_{jk}[(e^j_{10} + e^j_{0\bar{1}})(e^k_{01} + e^k_{\bar{1}0}) \\ & \quad + (e^j_{01} + e^j_{\bar{1}0})(e^k_{10} + e^k_{\bar{1}0})] \\ & + \sqrt{2}\, C_{jk}[(e^j_{11} - e^j_{\bar{1}\bar{1}})(e^k_{10} + e^k_{0\bar{1}}) \\ & \quad + (e^j_{10} + e^j_{0\bar{1}})(e^k_{11} - e^k_{\bar{1}\bar{1}})] \\ & + \sqrt{2}\, D_{jk}[(e^j_{11} - e^j_{\bar{1}\bar{1}})(e^k_{10} + e^k_{\bar{1}0}) \\ & \quad + (e^j_{01} + e^j_{\bar{1}0})(e^k_{11} - e^k_{\bar{1}\bar{1}})] \\ & + 2E_{jk}(e^j_{10} + e^j_{0\bar{1}})(e^k_{10} + e^k_{0\bar{1}}) \\ & \quad + 2F_{jk}(e^j_{01} + e^j_{\bar{1}0})(e^k_{01} + e^k_{\bar{1}0})\},\end{aligned} \tag{7}$$

$$\begin{aligned}\mathscr{H}_{IS} = \sum_{jk} \gamma_I \gamma_S r_{jk}^{-3} \{ & \tfrac{1}{2} A^{IS}_{jk}(e^j_{11} - e^j_{\bar{1}\bar{1}})(p^k_{\frac{1}{2}\frac{1}{2}} - p^k_{-\frac{1}{2}-\frac{1}{2}}) \\ & + \sqrt{2}\, B^{IS}_{jk}[(e^j_{10} + e^j_{0\bar{1}})\, p^k_{-\frac{1}{2}\frac{1}{2}} + (e^j_{01} + e^j_{\bar{1}0})\, p^k_{\frac{1}{2}-\frac{1}{2}}] \\ & + C^{IS}_{jk}[(e^j_{11} - e^j_{\bar{1}\bar{1}})\, p^k_{\frac{1}{2}-\frac{1}{2}} \\ & \quad + \sqrt{2}(e^j_{10} + e^j_{0\bar{1}})(p^k_{\frac{1}{2}\frac{1}{2}} - p^k_{-\frac{1}{2}-\frac{1}{2}})] \\ & + 2D^{IS}_{jk}[(e^j_{11} - e^j_{\bar{1}\bar{1}})\, p^k_{-\frac{1}{2}\frac{1}{2}} \\ & \quad + \sqrt{2}(e^j_{01} + e^j_{\bar{1}0})(p^k_{\frac{1}{2}\frac{1}{2}} - p^k_{-\frac{1}{2}-\frac{1}{2}})] \\ & + \sqrt{2}\, E^{IS}_{jk}(e^j_{10} + e^j_{0\bar{1}})\, p^k_{\frac{1}{2}-\frac{1}{2}} \\ & \quad + \sqrt{2}\, F^{IS}_{jk}(e^j_{01} + e^j_{\bar{1}0})\, p^k_{-\frac{1}{2}\frac{1}{2}}\},\end{aligned} \tag{8}$$

$$\begin{aligned}\mathscr{H}_{\text{r.f.}}(t) = \sqrt{2}\,\omega_1(t) \sin\theta_L \sum_j \{ & (e^j_{10} + e^j_{0\bar{1}})\, e^{-i\phi_L} \\ & + (e^j_{01} + e^j_{\bar{1}0})\, e^{i\phi_L} \\ & + \sqrt{2} \cos\theta_L (e^j_{11} - e^j_{\bar{1}\bar{1}})\} \cos(\omega t + \phi),\end{aligned} \tag{9}$$

where $\omega_0$ is the NQR frequency, $\mathscr{D}^{jk}_{\mu\eta\mu'\eta'}$ are the matrix elements of the dipole-dipole Hamiltonian $\mathscr{H}_{SS}$,

$$\begin{aligned} A_{jk} &= 1 - 3\cos^2\theta_{jk}, \\ B_{jk} &= -\tfrac{1}{4}(1 - 3\cos^2\theta_{jk}), \\ C_{jk} &= D^*_{jk} = -\tfrac{3}{4}\sin 2\theta_{jk}\, e^{-i\phi_{jk}}, \\ E_{jk} &= F^*_{jk} = -\tfrac{3}{4}\sin^2\theta_{jk}\, e^{-i2\phi_{jk}}, \end{aligned} \tag{10}$$

$\theta_{jk}$ and $\phi_{jk}$ are spherical coordinates of the distance $\boldsymbol{r}_{jk}$ connecting $j$ and $k$ spins.

The dynamics of the spin system will be handled by the von Neumann equation

$$i\frac{\mathrm{d}\varrho(t)}{\mathrm{d}t} = [\mathscr{H}(t), \varrho(t)]. \tag{11}$$

To solve (11) it proves profitable to carry out the unitary transformation of all operators used by means of the operator $Q(t) = \exp(i\mathscr{A}t)$ with

$$\mathscr{A} = \frac{\omega}{3} \sum_j (e^j_{11} - 2e^j_{00} + e^j_{\bar{1}\bar{1}}). \tag{12}$$

Inserting $\varrho(t) = Q^+(t)\,\tilde{\varrho}(t)\,Q(t)$ into (11) and omiting the terms which oscillate rapidly with frequencies $\omega$ and $2\omega$ we obtain

$$i\frac{\mathrm{d}\tilde{\varrho}(t)}{\mathrm{d}t} = [\tilde{\mathscr{H}}(t), \tilde{\varrho}(t)], \tag{13}$$

where

$$\tilde{\mathscr{H}}(t) = \mathscr{H}_\Delta + \tilde{\mathscr{H}}_{dd} + \tilde{\mathscr{H}}_{\text{r.f.}}(t), \tag{14}$$

$$\mathscr{H}_\Delta = \frac{\Delta}{3} \sum_j (e^j_{11} - 2e^j_{00} + e^j_{\bar{1}\bar{1}}), \quad \Delta = \omega_0 - \omega. \tag{15}$$

$$\tilde{\mathscr{H}}_{dd} = \mathscr{H}_{SS} + \tilde{\mathscr{H}}_{IS} + \tilde{\mathscr{H}}_{II}, \tag{16}$$

$$\begin{aligned}\tilde{\mathscr{H}}^{\text{sec}}_{II} = \sum_{jk} \gamma^2 r_{jk}^{-3} \{ & A_{jk}(e^j_{11} - e^j_{\bar{1}\bar{1}})(e^k_{11} - e^k_{\bar{1}\bar{1}}) \\ & + 2B_{jk}(e^j_{10} e^k_{01} + e^j_{01} e^k_{10} \\ & + e^j_{0\bar{1}} e^k_{\bar{1}0} + e^j_{\bar{1}0} e^k_{0\bar{1}}) \\ & + 2E_{jk}(e^j_{10} e^k_{0\bar{1}} + e^j_{0\bar{1}} e^k_{10}) \\ & + 2F_{jk}(e^j_{01} e^k_{\bar{1}0} e^k_{01} + e^j_{\bar{1}0} e^k_{01})\},\end{aligned} \tag{17}$$

$$\begin{aligned}\tilde{\mathscr{H}}^{\text{sec}}_{IS} = \sum_{jk} \gamma_I \gamma_S r_{jk}^{-3} (e^j_{11} - e^j_{\bar{1}\bar{1}}) \{ & \tfrac{1}{2} A^{IS}_{jk}(p^k_{\frac{1}{2}\frac{1}{2}} - p^k_{-\frac{1}{2}-\frac{1}{2}}) \\ & + C^{IS}_{jk}\, p^k_{\frac{1}{2}-\frac{1}{2}} + D^{IS}_{jk}\, p^k_{-\frac{1}{2}\frac{1}{2}}\},\end{aligned} \tag{18}$$

$$\begin{aligned}\tilde{\mathscr{H}}_{\text{r.f.}}(t) = \sqrt{2}\,\alpha_0 \sin\theta_L \sum_j [ & e^{-i\phi_L}(e^j_{10} + e^j_{0\bar{1}}) \\ & + e^{i\phi_L}(e^j_{01} + e^j_{\bar{1}0})] \quad \text{for the first pulse,}\end{aligned} \tag{19}$$

$$\begin{aligned}\tilde{\mathscr{H}}_{\text{r.f.}}(t) = i\sqrt{2}\,\omega_1(t) \sin\theta_L \sum_j [ & e^{i\phi_L}(e^j_{01} + e^j_{\bar{1}0}) \\ & + e^{-i\phi_L}(e^j_{0\bar{1}} - e^j_{10})] \quad \text{for other pulses.}\end{aligned} \tag{20}$$

The operators $\tilde{\mathscr{H}}^{\text{sec}}_{II}$ and $\tilde{\mathscr{H}}^{\text{sec}}_{IS}$ represent the secular parts of the homonuclear and heteronuclear dipole-dipole interaction Hamiltonians, respectively,

$$[\mathscr{H}_Q, \tilde{\mathscr{H}}^{\text{sec}}_{II}] = [\mathscr{H}_Q, \tilde{\mathscr{H}}^{\text{sec}}_{IS}] = 0. \tag{21}$$

## 3. Effective Hamiltonian

The spin system is assumed to be at equilibrium before the preparatory pulse. The action of the periodic r.f. field pulses on a spin system consists of the preparatory pulse taking the spin system out of equilibrium and the multiple-pulse sequence. The state operator $\varrho_+(0)$, immediately after the end of the action of the preparatory pulse forms the initial condition for (13) [5] which describes the evolution of the spin system under the influence of the multiple-pulse periodic action.

Equation (13) has the formal solution

$$\tilde{\varrho}(t) = U(t)\,\varrho_+(0)\,U^+(t), \tag{22}$$

where $U(t)$ is the solution of the equation

$$i\frac{\mathrm{d}U(t)}{\mathrm{d}t} = \tilde{\mathscr{H}}(t)\,U(t) \tag{23}$$

with the initial condition

$$U(0) = 1. \tag{24}$$

The periodicity of $\tilde{\mathscr{H}}(t)$ allows us to write the evolution operator $U(t)$ in Floquet form [6] as

$$U(t) = P(t)\,e^{-itH}, \tag{25}$$

where $P(t)$ has the same periodicity as $\tilde{\mathscr{H}}(t)$ and $H$ is the time-independent effective Hamiltonian.

In the multiple-pulse experiments one usually chooses $t_c$ in such a manner that $\varepsilon = \|\tilde{\mathscr{H}}_{dd}\|\,t_c \ll 1$ (here $\|\tilde{\mathscr{H}}_{dd}\|$ is the norm of the operator $\tilde{\mathscr{H}}_{dd}$), so we can expand the solution (22) of (13) in a series as powers of $\varepsilon$. From (23) we have for zeroth approximation

$$i\frac{\mathrm{d}U_0(t)}{\mathrm{d}t} = \tilde{\mathscr{H}}_0(t)\,U_0(t), \tag{26}$$

where $\tilde{\mathscr{H}}_0(t) = \mathscr{H}_\Delta + \tilde{\mathscr{H}}_{\text{r.f.}}(t)$ and

$$U_0(t) = P_0(t)\,e^{-itH^{(0)}}. \tag{27}$$

The operator $P_0(t)$ is the solution of the equation

$$i\frac{\mathrm{d}P_0(t)}{\mathrm{d}t} = \{\mathscr{H}_\Delta + \tilde{\mathscr{H}}_{\text{r.f.}}(t)\}\,P_0(t) - P_0(t)\,H^{(0)} \tag{28}$$

with the initial condition

$$P_0(0) = 1, \tag{29}$$

where $H^{(0)}$ is given by

$$\begin{aligned} H^{(0)} &= \frac{i}{t_c}\ln U_0(t_c) \\ &= \frac{i}{t_c}\ln\{T\exp[-i\int_0^{t_c}\mathrm{d}t\,(\mathscr{H}_\Delta + \tilde{\mathscr{H}}_{\text{r.f.}}(t))]\}; \end{aligned} \tag{30}$$

here $T$ is the Dyson time-ordering operator.

During the time $t_c$ of the period, $U_0(t_c)$ can be represented as

$$\begin{aligned} U_0(t_c) &= \exp\left[-i\frac{\Delta t_c}{6}\sum_j (e^j_{11} - 2e^j_{00} + e^j_{\bar{1}\bar{1}})\right] \\ &\cdot \exp\left\{-\frac{\lambda}{2\sqrt{2}},\sum_j [(e^j_{01} - e^j_{10})\,e^{i\phi_L} + (e^j_{0\bar{1}} - e^j_{\bar{1}0})\,e^{-i\phi_L}]\right\} \\ &\cdot \exp\left[-i\frac{\Delta t_c}{6}\sum_j (e^j_{11} - 2e^j_{00} + e^j_{\bar{1}\bar{1}})\right] \\ &= \sum_j \left\{\frac{1}{2}\left(\cos\frac{\lambda}{2} + 1\right)e^{-i2\beta}(e^j_{11} - e_{\bar{1}\bar{1}}) \right. \\ &+ \frac{1}{\sqrt{2}}\sin\frac{\lambda}{2}\,e^{i\beta}[e^{-i\phi_L}(e^j_{0\bar{1}} - e^j_{\bar{1}0}) \\ &+ e^{i\phi_L}(e^j_{01} - e^j_{10})] + \cos\frac{\lambda}{2}\,e^{i4\beta}\,e^j_{00} \\ &\left. + \frac{1}{2}\left(\cos\frac{\lambda}{2} - 1\right)e^{-i2\beta}(e^{i2\phi_L}e^j_{11} + e^{-i2\phi_L}e^j_{\bar{1}\bar{1}})\right\}, \end{aligned} \tag{31}$$

where $\lambda = \alpha\sin\theta_L$ and $\beta = \Delta t_c/6$. Diagonalization of the operator (31) gives the effective Hamiltonian in zeroth approximation

$$H^{(0)} = \frac{1}{t_c}\sum_j [(\xi - \beta)\,e^j_{11} - 2\beta\,e^j_{00} - (\xi + \beta)\,e^j_{\bar{1}\bar{1}}] \tag{32}$$

with

$$\cos\xi = \cos\frac{\lambda}{2}\cos 3\beta. \tag{33}$$

For the sake of simplicity we consider a case when $\Delta = 0$, so (32) takes the form

$$H^{(0)} = \frac{\xi}{t_c}\sum_j (e^j_{11} - e^j_{\bar{1}\bar{1}}). \tag{34}$$

The spin operators will be considered in a basis in which the Hamiltonian $H^{(0)}$ is diagonal, and it is convenient to expand the operators $\tilde{\mathscr{H}}^{\text{sec}}_{II}$ and $\tilde{\mathscr{H}}^{\text{sec}}_{IS}$ (see Appendix) as follows:

$$\tilde{\mathscr{H}}^{\text{sec}}_{II} = \sum_l \mathscr{H}^l_{II}, \quad l = 0, \pm 1/2, \pm 1, \pm 3/2, \pm 2 \tag{35}$$

and

$$\tilde{\mathscr{H}}^{\text{sec}}_{IS} = \sum_l \mathscr{H}^l_{IS}, \quad l = \pm 1/2. \tag{36}$$

Using the unitary transformation

$$U^*(t) = P_0^+(t)\,U(t), \tag{37}$$

(13) may be rewritten as

$$i\frac{\mathrm{d}U^*(t)}{\mathrm{d}t}=\{H^{(0)}+\tilde{\mathscr{H}}^*_{dd}(t)\}\,U^*(t) \tag{38}$$

with the initial condition

$$U^*(0)=1, \tag{39}$$

where

$$\tilde{\mathscr{H}}^*_{dd}(t)=\mathscr{H}_{SS}+\sum_{n=-\infty}^{\infty}\left(\sum_{l=-1/2}^{1/2}c_l^n\,\mathscr{H}^l_{IS}\,e^{-i\frac{2\pi n i}{t_c}}+\sum_{l=-2}^{2}b_l^n\,\mathscr{H}^l_{II}\,e^{-i\frac{2\pi n i}{t_c}}\right), \tag{40}$$

$$\chi_l^n=\frac{(-1)^n\sin\theta_l}{n\pi+\theta_l}\quad\text{for}\quad \chi=c,b,\ \ \theta_l=l\xi/2. \tag{41}$$

The operators $\mathscr{H}^l_{II}$ and $\mathscr{H}^l_{IS}$ satisfy the commutation rules

$$[H^{(0)},\mathscr{H}^l_k]=-\frac{\theta_l}{t_c}\mathscr{H}^l_k\quad\text{for}\quad k=II\ \text{ and }\ IS. \tag{42}$$

Unitary transformation

$$U_1(t)=[1+C(t)]^+\,U^*(t) \tag{43}$$

of (38) gives

$$i\frac{\mathrm{d}U_1(t)}{\mathrm{d}t}=\{H_{\mathrm{eff}}+V(t)\}\,U_1(t), \tag{44}$$

where the effective Hamiltonian with accuracy to $\varepsilon$ is

$$H_{\mathrm{eff}}=H^{(0)}+H^{(1)}; \tag{45}$$

here

$$H^{(1)}=\mathscr{H}_{SS}+\mathscr{H}^0_{II}+\sum_{l=-1/2}^{1/2}\theta_l\cot\theta_l\,\mathscr{H}^l_{IS}+\sum_{l=-2}^{2}\theta_l\cot\theta_l\,\mathscr{H}^l_{II}, \tag{46}$$

and the operator $C(t)$ is the solution of the equation

$$i\frac{\mathrm{d}C(t)}{\mathrm{d}t}=[H^{(0)},C(t)]-H^{(1)}+\tilde{\mathscr{H}}^*_{dd}(t) \tag{47}$$

with the initial condition

$$C(0)=0. \tag{48}$$

## 4. Quasi-Equilibrium Magnetization

Now the order of the time-dependent part of the right-hand side of (44) is proportional to $\varepsilon^2$ and sufficiently smaller than the order of interactions inserted in $H_{\mathrm{eff}}$, and may be taken into account by means of perturbation theory [7]. So one may assume that during the time $\sim T_2$ the spin system will reach a quasi-equilibrium state [7, 8] with state operator

$$\varrho_{\mathrm{eq}}=1-\beta_{\mathrm{eq}}H_{\mathrm{eff}}. \tag{49}$$

For the times $\sim T_2$ we may also neglect the absorption of r.f. field energy by the spin system and use the law of energy conservation [8]:

$$Sp(\varrho_+(0)\,H_{\mathrm{eff}})=Sp(\varrho_{\mathrm{eq}}\,H_{\mathrm{eff}}), \tag{50}$$

which gives

$$\frac{M_{\mathrm{eq}}}{M_0}=\left\{1+2\left[\frac{Sp(\mathscr{H}^0_{II})^2}{2Sp(H^{(0)})^2}+(\theta_{1/2}\cot\theta_{1/2})^2\frac{Sp(\mathscr{H}^{1/2}_{IS}H^{-1/2}_{IS})}{Sp(H^{(0)})^2}+\sum_{l=1/2}^{2}(\theta_l\cot\theta_l)^2\frac{Sp(\mathscr{H}^l_{II}H^{-l}_{II})}{Sp(H^{(0)})^2}\right]+\frac{Sp(\mathscr{H}_{SS})^2}{Sp(H^{(0)})^2}\right\}^{-1}, \tag{51}$$

where $M_{\mathrm{eq}}$ is the quasi-equilibrium magnetization in the $\boldsymbol{a}$ axis direction and $M_0$ is the magnetization immediately after the first pulse. The expression (50) shows that the observed quasi-equilibrium magnetization is not zero but decreases, which means that for the times $\sim T_2(\sim 1/\|\mathscr{H}_{dd}\|)$ there is an energy exchange between $I$-spin effective Zeeman and dipole-dipole reservoirs of the $I$- and $S$-spin systems [9]. The destruction of the $I$-spin magnetization may be considerable if $Sp\,\mathscr{H}^2_{SS}/Sp(H^{(0)})^2\gg 1$.

Further evolution of the spin system leads to the decrease of the magnetization under the influence of the time-dependent perturbation $V(t)$.

## 5. Conclusion

The effective Hamiltonian (3) is similar to one which describes the NQR Zeeman effect.

The degeneracy of the energy spectrum is removed but the spin-spin coupling with surrounding neighbors is not quenched [10]. The last circumstance may lead to shortening of the spin echo decay time [11, 12], $T_2$, which means that the spin-locking effect cannot be detected. But there exists the method of continuous wave non-resonant irradiation of the nuclear spin during the multiple-pulse experiment [13], making it possible to overcome these difficulties.

## Appendix

The secular part of the homonuclear dipole-dipole Hamiltonian $\tilde{\mathscr{H}}_{II}^{\text{sec}}$ can be expanded in secular part relative to the operator (34), $H^{(0)}$, as

$$\begin{aligned}\mathscr{H}_{II}^{0} = \sum_{ik} \gamma^2 r_{jk}^{-3} \{ & -\tfrac{1}{4}(1-3\cos\theta_{jk})[2(e^j_{01}-e^j_{\bar{1}0})(e^k_{0\bar{1}}-e^k_{10}) + 2(e^j_{0\bar{1}}-e^j_{10})(e^k_{01}-e^k_{\bar{1}0}) \\ & + (e^j_{11}-e^j_{\bar{1}\bar{1}})(e^k_{11}-e^k_{\bar{1}\bar{1}}) + e^j_{\bar{1}1}e^k_{1\bar{1}} + e^j_{1\bar{1}}e^k_{\bar{1}1} + e^j_{01}e^k_{\bar{1}0} + e^j_{0\bar{1}}e^k_{\bar{1}0} + e^j_{10}e^k_{01} + e^j_{\bar{1}0}e^k_{0\bar{1}}] \\ & - \tfrac{3}{4}\sin^2\theta_{jk}\cos 2(\phi_{jk}-\phi_L)[(e^j_{11}-e^j_{\bar{1}\bar{1}})(e^k_{11}-e^k_{\bar{1}\bar{1}}) + e^j_{\bar{1}1}e^k_{1\bar{1}} + e^j_{1\bar{1}}e^k_{\bar{1}1} - e^j_{01}e^k_{10} \\ & - e^j_{0\bar{1}}e^k_{\bar{1}0} - e^j_{10}e^k_{01} - e^j_{\bar{1}0}e^k_{0\bar{1}}]\}\end{aligned} \tag{52}$$

and nonsecular parts

$$\begin{aligned}\mathscr{H}_{II}^{1/2} = -\frac{3}{4\sqrt{2}} e^{-i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \sin^2\theta_{jk} \sin 2(\phi_{jk}-\phi_L)[ & (e^j_{11}-e^j_{\bar{1}\bar{1}})(e^k_{0\bar{1}}-e^k_{10}) \\ & + (e^j_{0\bar{1}}-e^j_{10})(e^k_{11}-e^k_{\bar{1}\bar{1}}) - e^j_{1\bar{1}}(e^k_{01}+e^k_{\bar{1}0}) - (e^j_{01}+e^j_{\bar{1}0})e^k_{1\bar{1}}],\end{aligned} \tag{53}$$

$$\begin{aligned}\mathscr{H}_{II}^{-1/2} = -\frac{3}{4\sqrt{2}} e^{-i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \sin^2\theta_{jk} \sin 2(\phi_{jk}-\phi_L)[ & (e^j_{11}-e^j_{\bar{1}\bar{1}})(e^k_{01}-e^k_{\bar{1}0}) \\ & + (e^j_{01}-e^j_{\bar{1}0})(e^k_{11}-e^k_{\bar{1}\bar{1}}) - e^j_{\bar{1}1}(e^k_{10}+e^k_{0\bar{1}}) - (e^j_{10}+e^j_{0\bar{1}})e^k_{\bar{1}1}],\end{aligned} \tag{54}$$

$$\begin{aligned}\mathscr{H}_{II}^{1} = \tfrac{1}{2} e^{-2i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \{ & (1-3\cos\theta_{jk})[(e^j_{01}-e^j_{\bar{1}0})(e^k_{0\bar{1}}-e^k_{10}) - \tfrac{1}{2}(e^j_{0\bar{1}}e^k_{10}+e^j_{10}e^k_{0\bar{1}})] \\ & - \tfrac{3}{2}\sin^2\theta_{jk}\cos 2(\phi_{jk}-\phi_L)(e^j_{10}e^k_{0\bar{1}}+e^j_{0\bar{1}}e^k_{10})\},\end{aligned} \tag{55}$$

$$\begin{aligned}\mathscr{H}_{II}^{-1} = \tfrac{1}{2} e^{-2i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \{ & (1-3\cos\theta_{jk})[(e^j_{01}-e^j_{\bar{1}0})(e^k_{\bar{1}0}-e^k_{01}) + \tfrac{1}{2}(e^j_{01}e^k_{\bar{1}0}+e^j_{\bar{1}0}e^k_{01})] \\ & - \tfrac{3}{2}\sin^2\theta_{jk}\cos 2(\phi_{jk}-\phi_L)(e^j_{01}e^k_{\bar{1}0}+e^j_{\bar{1}0}e^k_{01})\},\end{aligned} \tag{56}$$

$$\mathscr{H}_{II}^{3/2} = -\frac{3}{4\sqrt{2}} e^{-3i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \sin^2\theta_{jk} \sin^2(\phi_{jk}-\phi_L)[(e^j_{10}+e^j_{0\bar{1}})e^k_{1\bar{1}} + e^j_{1\bar{1}}(e^k_{0\bar{1}}+e^k_{10})], \tag{57}$$

$$\mathscr{H}_{II}^{-3/2} = -\frac{3}{4\sqrt{2}} e^{3i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \sin^2\theta_{jk} \sin^2(\phi_{jk}-\phi_L)[(e^j_{\bar{1}0}+e^j_{01})e^k_{\bar{1}1} + e^j_{\bar{1}1}(e^k_{\bar{1}0}+e^k_{01})], \tag{58}$$

$$\mathscr{H}_{II}^{2} = \tfrac{3}{4} e^{-4i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \sin^2\theta_{jk} \cos 2(\phi_{jk}-\phi_L)\, e^j_{1\bar{1}} e^k_{1\bar{1}}, \tag{59}$$

$$\mathscr{H}_{II}^{-2} = \tfrac{3}{4} e^{4i\phi_L} \sum_{ik} \gamma^2 r_{jk}^{-3} \sin^2\theta_{jk} \cos 2(\phi_{jk}-\phi_L)\, e^j_{\bar{1}1} e^k_{\bar{1}1}. \tag{60}$$

The heteronuclear dipole-dipole Hamiltonian $\tilde{\mathscr{H}}_{II}^{\text{sec}}$ has only the non-secular parts relative to the operator (34) $H^{(0)}$:

$$\begin{aligned}\mathscr{H}_{IS}^{1/2} = \frac{i}{\sqrt{2}} e^{-i\phi_L} \sum_{ik} \gamma_I \gamma_S r_{jk}^{-3} (e^j_{10}-e^j_{0\bar{1}})[ & (1-3\cos^2\theta_{jk})(p^k_{\frac{1}{2}\frac{1}{2}} - p^k_{-\frac{1}{2}-\frac{1}{2}}) \\ & - \tfrac{3}{2}\sin 2\theta_{jk}(e^{-i\phi_{jk}} p^k_{-\frac{1}{2}\frac{1}{2}} + e^{i\phi_{jk}} p^k_{\frac{1}{2}-\frac{1}{2}})]\end{aligned} \tag{61}$$

$$\begin{aligned}\mathscr{H}_{IS}^{-1/2} = \frac{i}{\sqrt{2}} e^{i\phi_L} \sum_{ik} \gamma_I \gamma_S r_{jk}^{-3} (e^j_{\bar{1}0}-e^j_{01})[ & (1-3\cos^2\theta_{jk})(p^k_{\frac{1}{2}\frac{1}{2}} - p^k_{-\frac{1}{2}-\frac{1}{2}}) \\ & - \tfrac{3}{2}\sin 2\theta_{jk}(e^{-i\phi_{jk}} p^k_{-\frac{1}{2}\frac{1}{2}} + e^{i\phi_{jk}} p^k_{\frac{1}{2}-\frac{1}{2}})].\end{aligned} \tag{62}$$

[1] a) U. Haeberlen, High Resolution NMR in Solids, Academic, New York 1976.
b) R. A. Marino and S. M. Klainer, J. Chem. Phys. **67,** 3388 (1977).
[2] a) M. Mehring, High Resolution NMR in Solids, 2nd edn. Springer-Verlag, Heidelberg 1983.
b) S. M. Klainer, T. Hershfeld, and R. A. Marino, in: "Fourier, Hadamard, and Hilbert Transforms in Chemistry", ed. A. G. Marshall (Plenum, New York 1982).
[3] D. Ya. Osokin, V. L. Ermakov, R. H. Kurbanov, and V. A. Shagalov, Z. Naturforsch. **47a,** 439 (1992).
[4] N. E. Ainbinder and G. B. Furman, Sov. Phys. JETP **58,** 575 (1983).
[5] J. C. Pratt and W. Watton, J. Chem. Soc., Faraday Trans. 2, **83,** 2261 (1987).
[6] M. M. Maricq, Phys. Rev. B **25,** 6622 (1982).
[7] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Clarendon Press, Oxford 1970.
[8] Yu. N. Ivanov, B. N. Provotorov, and E. B. Feldman, Sov. Phys. JETP **48,** 930 (1978).
[9] D. A. McArthur, E. L. Hahn, and R. E. Walstedt, Phys. Rev. **188,** 609 (1969).
[10] G. W. Leppelmeir and E. L. Hahn, Phys. Rev. **141,** 724 (1966).
[11] G. W. Leppelmeir and E. L. Hahn, Phys. Rev. **142,** 179 (1966).
[12] G. E. Kibrik and A. Yu. Poljakov, Abstracts 26th Congress AMPERE on NMR, Athens, Greece, 1992, p. 601.
[13] Y. L. Zhuang and R. A. Marino, Z. Naturforsch. **45a,** 587 (1990).