the boundary conditions, by the external fields, and by other factors.

3) It should be noted that the expressions for $\delta\eta$ and $\delta\tau$ contain as a factor the Ginzburg coefficient $\tilde{G}i = T^2A_3^2/A_1A_2^3$ for the functional (26). The value of $\tilde{G}i$ can be obtained by matching (27) to (2) in the region $\tau\sim$ Gi. It is easy to verify that the $\tilde{G}i\sim 1$.

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Thermodynamic effects in multipulse NMR spectroscopy in solids

B. N. Provotorov and É. B. Fel'dman

Division of Institute of Chemical Physics, USSR Academy of Sciences

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We consider the behavior of multispin systems in solids under the influence of multipulse trains. An important role is played here by the small fraction of the spins whose interaction is not averaged out by the external actions because these spins are in local fields $\omega_{\rm loc}\sim 2\pi/t_c$, where t_c is the period of the external actions. It is shown that these nonaveraged interactions play an important role in the absorption of energy from the external fields by the spin system. A method of canonical transformations is developed to study the dynamics of spin systems in arbitrary multipulse experiments. The behavior of spin systems acted upon by pulse trains that average out the dipole-dipole interaction is investigated. The nature of the damping of the longitudinal component of the magnetization in the pulse trains WHH-4 [J. S. Waugh, L. M. Huber, and U. Haeberlen, Phys. Rev. Lett. **20**, 180 (1968)] and HW-8 [U. Haeberlen and J. S. Waugh, Phys. Rev. **175**, 453 (1968)] is investigated. Solution of the equation for the spin-system density matrix yields the damping time of the transverse magnetization component as a function of the period of the pulse train and of the detuning of the RF-pulse carrier frequency from the spin Larmor-precession frequency. New pulse trains that average out dipole-dipole interactions between spin nuclei are considered.

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Recently reported multipulse NMR methods[1-3] have improved of the resolution in the spectra by a factor of several hundred, thus substantially extending the possibilities of investigating the structure of matter and dynamic processes in solids. The resolution was improved by using intense radio-frequency pulsed fields. Unlike in ordinary spectroscopy however, the fields were used not to register the absorption lines, but for dynamic averaging of the dipole-dipole interactions responsible for the broadening of the NMR spectral lines in solids. By using periodic trains of intense RF pulses (with periods t_c) it became possible to organize rapid transitions (within a time $\sim t_c$) between Zeeman levels of dipole-coupled nuclei. As a result the anisotropic dipole interactions become oscillatory with frequencies that are multiples of $2\pi/t_c$ and exceed greatly the characteristic frequency $\omega_{\rm loc}$ of the dipole-dipole interaction.

It is well known from classical mechanics[4] that similar rapidly oscillating interactions exert on a system the same action as a suitably constructed[4] time-independent effective interaction. Unlike in mechanics, in multipulse NMR spectroscopy of solids it is necessary to deal with systems having macroscopically large numbers of degrees of freedom, i.e., with thermodynamic systems. This circumstance greatly complicates the theoretical analysis of the multipulse problem, and as a result we have for it to this day no theory based on a solution of the corresponding equation for the density matrix.

In the present paper we attempt to develop such a theory for pulse trains that average out the dipole-dipole interactions, and to apply this theory to a number of hiterto unexplained experimental data. Such a theory of course, should include the well known and experimentally confirmed results of the average-Hamiltonian theory.[2]

In the average-Hamiltonian theory (the first theory of multipulse experiments) there was considered and approximately solved the problem of construction of an effective Hamiltonian for pulse trains in which the so-called cyclicity condition is satisfied.[2] Unlike in the book of Landau and Lifshitz,[4] where the effective Hamiltonian was obtained in mechanical problems with a small number of particles, Haeberlen and Waugh[2] have succeeded in constructing an effective Hamiltonian for multispin thermodynamic systems (up to third order in the small parameter $\varepsilon = t_c\omega_{loc}$). Pulse trains were proposed and experimentally investigated[1-3] which made it possible to obtain an effective-Hamiltonian characteristic frequency ω_{loc}^{eff} several times smaller than ω_{loc}, and this led to the already mentioned narrowing of the observed lines and to the increase of the resolution in the spectrum.

The explanation of the observed line narrowing was the major success of the average-Hamiltonian theory. At the same time it must be emphasized that in this theory spin systems situated in external alternating pulse fields are described by time-independent Hamiltonians. When this circumstance is taken into account, it is possible to draw a simple and important conclusion. In fact, since the system is now described by a time-independent Hamiltonian, it follows that within times $t \sim 1/\omega_{loc}^{eff} \gg 1/\omega_{loc}^{eff}$ there is established in it an equilibrium of the type $1+\alpha\hat{H}_{eff}$ ($\hat{H}_{eff}$ is the effective Hamiltonian and α is the reciprocal spin-system temperature), after which the properties of the system should no longer depend on the time. This obvious conclusion of the average-Hamiltonian theory contradicts greatly the experimental data,[5-7] which revealed, besides the processes that take place within times $1/\omega_{loc}^{eff}$, also processes with characteristic times frequently longer by several orders than $1/\omega_{loc}$.

The presence of these slow processes, which cannot be fitted in the average-Hamiltonian theory, is not surprising. The point is that fluctuating dipole fields, which result from the modulation of the dipole-dipole interaction by the pulse train play a double role. On the one hand, they lead to dephasing of the nuclear spins, and on the other they are responsible for processes involving absorption of the external-field energy by the spin system and for the associated heating of the system. The average-Hamiltonian theory, in which a real system with a dipole-dipole interaction that fluctuates rapidly under the influence of the pulse train is replaced by an equivalent model system described by a time-dependent average Hamiltonian, considers only the spin-dephasing processes, and neglects the heating of the system by nonconservative effects. It is reasonable to assume that the considered system can be regarded as conservative one only over times $t \sim 1/\omega_{loc}^{eff}$, while at times $t \gg 1/\omega_{loc}^{eff}$ nonconservative effects are important. This conclusion is confirmed in the present paper by solving the corresponding equation for the density matrix. We note that the indicated investigations were already performed earlier[8,9] by the method of canonical transformations for a very simple pulse train in which the dipole interactions were only partially averaged.

In the present paper the method of canonical transformations of the equation for the density matrix was further developed and can now be applied to arbitrary periodic pulsed sequences, and the RF-pulse carrier frequency can differ from the spin Larmor-precession frequency. The cyclicity property of the pulse train,[2] which is important in the average-Hamiltonian theory,[2] is not used here. The gist of the developed method of canonical transformations consists in a transition, with their aid, to a new representation in which each rapidly oscillating harmonic of the initial Hamiltonian is replaced in a new Hamiltonian by a harmonic of lower amplitude and of the same frequency and by a time-independent contribution to a time-independent effective Hamiltonian. These lower-amplitude harmonics can be easily taken into account by thermodynamic perturbation theory and lead to conservative effects, whereas the time-independent contributions coincide with the results of Haeberlen and Waugh[2] in the first nonvanishing order in the small parameter $\varepsilon = t_c\omega_{loc}$. We note also of the work of Buishvili and Menabde,[10,11] who generalized the averaging method of Refs. 12 and 13 to include multiparticle problems. This method makes it possible to take correct account of the dephasing of the nuclear spins in all orders in the parameter ε, but just as the average-Hamiltonian theory,[2] it neglects nonconservative effects.

1. THE METHOD OF CANONICAL TRANSFORMATIONS IN MULTIPULSE PROBLEMS

We consider a system of nuclear spins ($s=\frac{1}{2}$) acted upon by a sequence consisting of periodic (with period t_c) sets of k pulses separated by time intervals t_p ($p=1,2,\ldots,k$). The RF carrier frequency of the pulses can differ from the spin Larmor-precession frequency by an amount Δ. In a rotating coordinate system (RCS), the equation for the density matrix $\rho(t)$ of the spin system takes the form ($\hbar=1$)

$$i\frac{d\rho}{dt}=\left[-\hat{f}(t)+\Delta\hat{S}_z+\hat{H}_d^z, \rho(t)\right], \tag{1}$$

with

$$\hat{f}(t)=\sum_{n=0}^{\infty}\sum_{p=1}^{k}\varphi_p\delta\left(t-\sum_{j=1}^{p}t_j-nt_c\right)(\mathbf{n}_p\hat{\mathbf{S}}), \tag{2}$$

where φ_p is the angle through which the pth pulse rotates the spins about the axis directed along $\mathbf{n}_p$ ($p=1,2,\ldots,k$); $\delta(t)$ is the Dirac delta function, and $\hat{H}_d^z$ is the secular (relative to the z axis) part of the dipole-dipole interaction.

We introduce an effective field ω_e that characterizes the external action on the system during the period t_c:

$$\exp[-i\omega_e t_c(\mathbf{n}_e\hat{\mathbf{S}})]=\exp\left[-i\Delta\left(t_c-\sum_{p=1}^{k}t_p\right)\hat{S}_z\right]\hat{P}_{\varphi_k\mathbf{n}_k}\ldots \quad (3)$$

where $\hat{P}_{\varphi_i n_i}$ is the operator of rotation through the angle φ_i about the axis $\mathbf{n}_i$ $(i=1,2,\ldots,k)$, and $\mathbf{n}_e$ is the direction of the effective field. Changing to the interaction representation with respect to the momenta and the detuning, i.e., making the substitutions

$$\rho(t)=\hat{L}(t)\bar{\rho}(t)\hat{L}^{-1}(t), \quad (4)$$

$$\hat{L}(t)=T\exp\left\{-i\int_0^t[\hat{f}(t')+\Delta\hat{S}_z)dt'\right\}, \quad (5)$$

where the symbol T denotes chronological ordering of the product, and introducing the dimensionless time $\bar{T}=t/t_c$, we find that the density matrix $\bar{\rho}(\bar{t})$ satisfies the equation

$$i\frac{d\bar{\rho}(\bar{t})}{d\bar{t}}=\varepsilon\left[\sum_{m=-2}^{2}\chi_m(\bar{t})\exp(-im\theta\bar{t})\hat{V}_d{}^m,\bar{\rho}(\bar{t})\right]; \quad (6)$$

$$\varepsilon=t_c\omega_{\text{loc}},\quad \theta=\omega_e t_c,\quad \hat{V}_d{}^m=\hat{H}_d{}^m/\omega_{\text{loc}}\quad (m=0,\pm1,\pm2),$$

in which $\hat{H}_d^m$ $(m=0,\pm1,\pm2)$ are the secular and nonsecular parts of the dipole-dipole interaction relative to the $\mathbf{n}_e$ axis and satisfy the commutation relations

$$[\hat{S}_{n_e},\hat{H}_d{}^m]=m\hat{H}_d{}^m\quad (m=0,\pm1,\pm2),\quad \hat{S}_{n_e}=\mathbf{n}_e\hat{\mathbf{S}}, \quad (7)$$

while $\chi_m(\bar{t})$ are periodic functions of the time with unity period $(\chi_{-m}=\chi_m^*,\ m=0,\pm1,\pm2)$. We shall omit hereafter the bars denoting the dimensionless time.

In multipulse experiments the tendency is to create conditions in which $2\pi/t_c\gg\omega_{\text{loc}}$. It is precisely under this condition that it is possible in a number of cases to weaken effectively the dipole-dipole interaction of the spins.[2] Assuming hereafter that $\varepsilon\ll1$, we subject (6) to a cononical transformation that makes it possible to separate the slowly varying (with characteristic frequencies much lower than $2\pi/t_c$) part $\bar{\rho}_s(t)$ of the density matrix $\bar{\rho}(t)$:

$$\bar{\rho}(t)=\hat{F}^+(t)\bar{\rho}_s(t)\hat{F}(t), \quad (8)$$

$$\hat{F}(t)=\exp\left(i\sum_{n=1}^{\infty}\varepsilon^n\hat{U}_n(t)\right), \quad (9)$$

where the Hermitian operators $\hat{U}_n(t)$ are determined from the condition that the equation for $\bar{\rho}_s(t)$ has no rapidly oscillating (with frequencies $2\pi m/t_c$, $m=\pm1,\pm2,\ldots$) terms of the order of ε^n $(n\,1,2,\ldots)$.

Expanding $\hat{F}(t)$ in powers of ε and recognizing that the slowly varying part of $\bar{\rho}(t)$ is included in $\bar{\rho}_s(t)$, we easily find that the operators $\hat{U}_n(t)$ must not contain slowly varying parts. With the aid of (8) we obtain an equation for the density matrix $\rho_s(t)$:

$$i\frac{d\bar{\rho}_s(t)}{dt}=\left[\varepsilon\sum_{m=-2}^{2}\chi_m(t)e^{-im\theta t}\hat{F}(t)\hat{V}_d{}^m\hat{F}^+(t)+i\frac{d\hat{F}}{dt}\hat{F}^+(t),\bar{\rho}_s(t)\right]. \quad (10)$$

To determine $\hat{U}_1(t)$ at $\theta\lesssim\varepsilon$ $(\omega_e\lesssim\omega_{\text{loc}})$, we obtain the equation

$$\frac{d\hat{U}_1}{dt}=\sum_{m=-2}^{2}\{\chi_m(t)-\chi_m{}^0\}e^{-im\theta t}\hat{V}_d{}^m. \quad (11)$$

where α_m^0 is the function $\alpha_m(t)$ $(m=0,\pm1,\pm2)$ averaged over the period.

The solution of (11) can be written in the form

$$\hat{U}_1(t)=\sum_{m=-2}^{2}g_m(t)\hat{V}_d{}^m, \quad (12)$$

$$g_m(t)=\int_0^t\{\chi_m(t')-\chi_m{}^0\}e^{-im\theta t'}dt'-\frac{1}{i}\sum_{n\neq0}\frac{\chi_m{}^n}{|m|\theta+2\pi n}, \quad (13)$$

where χ_m^n is the Fourier coefficient of the function $\chi_m(t)$ $(m=0,\pm1,\pm2)$. We then obtain a Hamiltonian that describes the change of the density matrix $\bar{\rho}_s(t)$, accurate to terms $\sim\varepsilon^2$:

$$\hat{V}_{\text{eff}}^{(1)}=\sum_{m=-2}^{2}\chi_m{}^0e^{-im\theta t}\hat{V}_d{}^m. \quad (14)$$

If now $\theta\gg\varepsilon$ $(\omega_e\gg\omega_{\text{loc}})$, then it is necessary to leave out of (14) the time-dependent terms, omit from (13) at $m\neq0$ the subtraction of the zeroth harmonics, and carry out the summation over all n.

We obtain similarly the corrections to V_{eff} due to the terms $\sim\varepsilon^2$ $(\hat{V}_{\text{eff}}^{(2)})$ and to the terms $\sim\varepsilon^3$ $(\hat{V}_{\text{eff}}^{(3)})$. At $\theta\lesssim\varepsilon$, the Hamiltonian $\hat{V}_{\text{eff}}^{(2)}$ takes the form

$$\hat{V}_{\text{eff}}^{(2)}=\sum_{m=-1}^{2}\sum_{n=-2}^{m-1}s_{m,n}^0[\hat{V}_d{}^m,\hat{V}_d{}^n]e^{-i\theta(m+n)t}, \quad (15)$$

where $s_{m,n}^0$ is the average, over the period, of the function

$$s_{m,n}(t)={}^1/{}_2i\{g_m(t)(\chi_n(t)+\chi_n{}^0)e^{im\theta t}$$
$$-g_n(t)(\chi_m(t)+\chi_m{}^0)e^{in\theta t}\}\quad (m,\ n=0,\ \pm1,\ \pm2,\ m>n). \quad (16)$$

At $\theta\gg\varepsilon$ it is necessary, just as before, to leave out the oscillatory terms in (15), and replace $\chi_n(t)+\chi_n^0$ $(n=\pm1,\pm2)$ in (16) by $\chi_n(t)$.

Specially noteworthy is the case $\theta\approx2\pi/3$, for which we easily find that

$$\hat{V}_{\text{eff}}^{(2)}=\sum_{m=1}^{2}s_{m,-m}^0[\hat{V}_d{}^m,\hat{V}_d{}^{-m}]+s_{2,1}^{-1}e^{i(2\pi-3\theta)t}[\hat{V}_d{}^2,\hat{V}_d{}^1]+\text{H.c.}, \quad (17)$$

where $s_{2,1}^{-1}$ is the Fourier coefficient of the harmonic $\exp(2\pi it)$ of the function $s_{2,1}(t)$.

We now write out the correction that must be added to the Hamiltonian to account for the change produced in the density matrix $\bar{\rho}_s(t)$ by the terms $\sim\varepsilon^3$ at $\theta\lesssim\varepsilon$:

$$\hat{V}_{\text{eff}}^{(3)}=\sum_{i=-4}^{4}\hat{R}_s^{(i)}(t), \quad (18)$$

where $\hat{R}_s^{(i)}(t)$ represents the contribution made to $\hat{V}_{\text{eff}}^{(3)}$ by the terms that change the orientation of the spins i $(i=0,1,2,3,4)$, with

$$\hat{R}_s^{(0)}=\sum_{m=1}^{2}\sum_{n=0}^{2-m}u_{m,n}^0[\hat{V}_d{}^m,[\hat{V}_d{}^n,\hat{V}_d{}^{-(m+n)}]]+\text{H.c.}, \quad (19)$$

$$\hat{R}_s^{(4)}(t)=\sum_{m=1}^{2}v_m{}^{4}(t)[\hat{V}_d{}^m,[\hat{V}_d{}^{4-2m},\hat{V}_d{}^m]]+\text{H.c.}, \quad (20)$$

where $u_{m,n}^0$ are the zeroth harmonics of the periodic functions $u_{m,0}(t)$ $(m=1,2)$ and $u_{1,1}(t)$:

$$u_{m,0}(t)=\frac{1}{2}i\{s_{m,-m}(t)-\overset{0}{s}_{m,-m}\}g_0(t)-\frac{1}{2}i\{\dot{s}_{m,0}(t)-\dot{s}_{m,0}\}e^{im\theta t}g_m(t)$$

$$-\frac{1}{2}ib_{m,-m}(t)(\chi_0(t)+\chi_0^0)-\frac{1}{2}i\dot{b}_{m,0}(t)(\chi_m(t)+\chi_m^0)e^{-im\theta t}$$

$$+\frac{1}{6}g_0(t)\{(2\chi_m(t)+\chi_m^0)e^{-i\theta mt}g_m^*(t)-(2\chi_{-m}(t)+\chi_{-m}^0)e^{i\theta mt}g_m(t)\}$$

$$-\frac{1}{6}g_m(t)\{(2\chi_{-m}(t)+\chi_{-m}^0)e^{i\theta mt}g_0(t)-(2\chi_0(t)+\chi_0^0)g_m^*(t)\}\quad (m=1,2);\tag{21}$$

$$u_{1,1}(t)=\frac{1}{2}i\{\dot{s}_{2,-1}(t)-(\overset{0}{s}_{2,-1})^*e^{i\theta t}g_1(t)-\frac{1}{2}ib_{2,-1}(t)(\chi_1(t)+\chi_1^0)e^{-i\theta t}$$

$$+\frac{1}{6}g_1(t)\{(2\chi_1(t)+\chi_1^0)e^{-i\theta t}g_2^*(t)-(2\chi_{-2}(t)+\chi_{-2}^0)e^{2i\theta t}g_1(t)\}.\tag{22}$$

In formula (20), $v_m^s(t)$ $(m=1,2)$ are the slowly varying parts of the functions

$$v_m(t)=(-1)^m\frac{i}{2}\{(s_{2,2-m}(t)-\overset{0}{s}_{2,2-m})e^{-i(4-m)\theta t}$$

$$+b_{2,2-m}(t)(\chi_m(t)+\chi_m^0)e^{-i\theta mt}\}+(-1)^{m+1}\frac{g_m(t)}{6}\{(2\chi_2(t)$$

$$+\chi_2^0)g_{2-m}(t)-(2\chi_{2-m}(t)+\overset{0}{\chi}_{2-m})g_2(t)\}\quad (m=1,2).\tag{23}$$

In formulas (21)–(23)[1)]

$$b_{m,k}(t)=\int_0^t[s_{m,k}(t')-\overset{0}{s}_{m,k}]e^{-i(m+k)\theta t'}dt'-\frac{1}{i}\sum_{n\neq 0}\frac{\overset{n}{s}_{m,k}}{|m+k|\theta+2\pi n}\tag{24}$$

$$(m,\ k=0,\ \pm1,\ \pm2,\ m>k).$$

In the case $\theta\gg\varepsilon$ it is necessary to leave out of (21)–(24) χ_m^0 at $m\neq 0$ and $s_{m,k}^0$ at $k=-m$, extended the summation in (24) over all n, and leave out of (18) the oscillatory terms.

Special consideration must be given to the case $\theta\approx\pi/2$, when $\hat{V}_{\rm eff}^{(3)}$ takes the form

$$\hat{V}_{\rm eff}^{(3)}=\hat{R}_s^{(0)}+\sum_{k=1}^{2}\bar{v}_k^{-1}e^{2i(\pi-2\theta)t}[\hat{V}_d^k,[\hat{V}_d^{4-2k},\hat{V}_d^k]]+\text{H.c.},\tag{25}$$

where $\bar{v}_k^{-1}$ $(k=1,2)$ are the Fourier coefficients of the harmonic $\exp(2\pi it)$ of the periodic functions

$$\bar{v}_k(t)=v_k(t)e^{ik\theta t}\quad (k=1,\ 2).\tag{26}$$

Thus, up to three orders in the parameter ε we have obtained an effective Hamiltonian that describes the time evolution of the density matrix $\bar{\rho}_s(t)$.

The amplitude of the oscillating terms that did not enter in the effective Hamiltonian is of the order ε^4 and it might seem at first glance that these terms exert no substantial influence on the behavior of the spin system. This is precisely the case in mechanics problems with few particles,[12,13] where it was rigorously proved[12] that over sufficiently long times the solution of the system of equations with the effective Hamiltonian is close to the solution of the problem with an initial rapidly oscillating Hamiltonian. Here, however, we consider a spin system with a macroscopically large number of degrees of freedom, i.e., a thermodynamic system. Just as in saturation theory,[14] a quasi-equilibrium determined at $\theta\gg\varepsilon$ by a two-temperature density matrix is established in a spin system over times determined by secular interactions in the effective Hamiltonian.[8,9] The role of the oscillating nonsecular terms consists here, first, in the fact that they contribute to the effective Hamiltonian calculated above, and second, that they are responsible for the multispin absorption, which leads to heating of the spins, of the external-field energy by the system.[9]

In Goldman's book,[15] in the study of continuous spin locking, it is shown that a decrease of the amplitude of the nonsecular terms of the dipole-dipole interaction via canonical transformations does not lead to a change of the rate of equalization of the Zeeman and dipole temperatures compared with the mixing rate ensured by the initial nonsecular dipole interactions. Thus, the canonical transformations make it possible to obtain the contribution of the oscillating nonsecular dipole interactions to the dephasing of the spins, and do not change the contribution of these terms to the processes involving absorption of the external-field energy by the system. This conclusion is general and is connected with the following circumstance. In multipulse experiments, the overwhelming majority of spins are located in local fields $\omega_{\rm loc}\ll 2\pi/t_c$. There is, however, a small number of spins in local fields $\omega\sim 2\pi/t_c$ [their fraction of the total number of spin nuclei is $\sim\exp(-\omega^2/6\omega_{\rm loc}^2)$, Ref. 15]. In the canonical transformations we neglect spins in the strong local fields, since their number is small. At the same time, these spins play an important role in the absorption of the energy of the external fields by the system. The rate of energy absorption on account of the oscillating nonsecular terms is determined by the energy δ that must be transferred to the dipole-dipole interaction pool and by the number of absorbing spins, and is estimated approximately[16] at

$$\frac{1}{T_{2e}}\sim t_c^{2n-4}\ \omega_{\rm loc}^{2n-3}\ \exp\left(-\frac{\delta^2}{6n\omega_{\rm loc}^2}\right)$$

with account taken here of the fact that in the interval between the pulses the dipole-dipole interaction does not depend on the time and $\propto\omega_{\rm loc}$.

These multispin energy-absorption processes determine the damping of the magnetization over times $t\gg 1/\omega_{\rm loc}^{\rm eff}$ ($1/\omega_{\rm loc}^{\rm eff}$ is the time of establishment of quasi-equilibrium in the system). It was shown earlier[9] that when several multispin energy-absorption processes take place simultaneously, the system becomes heated until the magnetization vanishes completely, as confirmed by experimental data.[6,7] The main shortcoming of the average-Hamiltonian theory is the neglect of the here-noted multispin absorption of the energy of the external fields, which in fact leads in a number of cases to a discrepancy with the experimental data.[5-7] At the same time, the average-Hamiltonian theory[2] yields the correct value of the first nonvanishing term of the effective Hamiltonian, and this made it possible for the theory to explain correctly the cause of the NMR line narrowing in multipulse experiments. Buishvili and Menabde,[10,11] by applying the averaging method[12,13] to multipulse problems, succeeded in obtained the correct effective Hamiltonian (up to second order in ε), but just as in Ref. 2 did not consider the thermodynamic effects noted here.

2. THE PULSE TRAIN OF WAUGH, HUBER AND HAEBERLEN (WHH-4)

We consider the pulse train[1] WHH-4, defined for formula (2), where

$$k=4,\quad t_c=6\tau,\quad t_{2i-1}=\tau,\quad t_{2i}=2\tau\ (i=1,2),$$
$$-\varphi_1=\varphi_2=\varphi_3=-\varphi_4=\pi/2,\quad \mathbf{n}_i=\mathbf{n}_x\ (i=1,2),\quad \mathbf{n}_i=\mathbf{n}_y\ (i=3,4).$$

Choosing $\mathbf{n}_e$ in the direction of the (111) axis, we obtain

$$\theta=0,\quad \chi_0(t)=0,\quad \chi_2(t)=(\alpha_2/\alpha_1^*)\chi_1^*(t),$$
$$\alpha_1=-\frac{\sqrt{3}-1+i(\sqrt{3}+1)}{4},\quad \alpha_2=-\frac{\sqrt{3}-i}{4}, \tag{27}$$

$$\chi_1^n=\frac{\sqrt{3}}{2\pi n}[e^{\pi in/3}+(-1)^{n+1}]\cdot\begin{cases}\sqrt{3}/i, & n\text{—even}\\ 1, & n\text{—odd}\end{cases}. \tag{28}$$

Since $\chi_m^0=0$ ($m=0,\pm1,\pm2$), it follows from (14) that $\hat{V}_{\text{eff}}^{(1)}=0$. With the aid of (16), (27), and (28) we establish that $s_{mn}^0=0$ ($m,n=0,\pm1,\pm2, m>n$). Therefore $\hat{V}_{\text{eff}}^{(2)}=0$. Formula (21) yields $u_{m,0}(t)=0$ ($m=1,2$), and from (22), taking (13), (24), and (27) into account, we find that $u_{1,1}^0=0$.

Thus, the secular term in the effective Hamiltonian [relative to the (111) axis], which is proportional to ε^3, vanishes. We now calculate the nonsecular terms proportional to ε^3. We consider by way of example $\hat{R}_s^{(4)}(t)$. By virtue of (13), (16), (23), (24), and (27) we find that

$$v_1^s=\frac{1}{2}\frac{\alpha_2}{\alpha_1^*}\int_0^1\chi_1^*(t)\left[\int_0^t\chi_1(t')\,dt'\right]^2dt=-\frac{1-i\sqrt{3}}{1728},\quad v_2^s=0. \tag{29}$$

We can analogously obtain also the other nonsecular terms $\hat{R}_s^{(i)}(t)$ ($i=\pm1,\pm2,\pm3$), and determine $\hat{V}_{\text{eff}}^{(3)}$ with the aid of (18). The effective Hamiltonian obtained here coincides with that obtained in the average-Hamiltonian theory.[2]

We compare now the results with the experimental data. In the absence of detuning, an exponential decrease[17] is observed with a damping time determined by the effective Hamiltonian. In the presence of detuning, the damping time of the transverse magnetization component is somewhat lengthened, and the fall-off time of the longitudinal component (relative to the effective field), which in the absence of detuning coincided with the damping time of the transverse component, increases by several orders of magnitude.[17] The cause of the damping of the longitudinal magnetization component is not fully explained in the average-Hamiltonian theory and consists in the following. The dipole interactions between spins situated in local fields $\sim2\pi/t_c$ and other spins are not averaged out by the pulse train. The local fields at such spins therefore correspond to the initial dipole-dipole interactions and $\sim\omega_{\text{loc}}$.

In the presence of a detuning δ, multispin absorption of the energy of the external fields takes place. Let us estimate the probability of energy absorption in a four-spin process on account of the effective-Hamiltonian term $\hat{R}_s^{(4)}(t)$. The energy fed to the dipole-dipole pool should then be 4δ, and the time $T_\parallel$ of this process can be approximately estimated from the formula (see the estimate of T_{2e} above)

$$T_\parallel=T_\perp\exp\left(\frac{(4\delta)^2}{2\bar{\omega}^2_{\text{loc}}}\right), \tag{30}$$

where $T_\perp$ is the damping time of the transverse magnetization component and $\bar{\omega}_{\text{loc}}$ is the value of the local field at the spins that absorb the energy of the external fields. Using for the estimate the values of $T_\perp$ and δ from Ref. 17 ($T_\perp\sim5\times10^{-13}$ sec, $\delta=2\times10^3$ Hz) and putting $\bar{\omega}_{\text{loc}}\sim1.3\times10^4$ rad/sec, we obtain $T_\parallel\sim0.9$ sec, in agreement with the experimental data.[17] Thus, allowance for the spins in strong local fields explains the slow damping of the longitudinal component of the magnetization in the WHH-4 multipulse experiment.

3. UNIAXIAL ANALOGS OF THE WHH-4 PULSE TRAIN AND OF ITS MODIFICATIONS

We shall show that the behavior of a spin system in the multipulse experiments WHH-4,[1] of Haeberlen and Waugh (HW-8),[2] and of Mansfield, Rhim, Elleman, and Vaughn (MREV-8)[18] agrees in the main with the dynamics of a system acted upon by a pulse train with the RF pulse fields directed along one axis in the rotating coordinate system.[19,28] We consider for the sake of argument the HW-8 pulse train,[2] which is defined by formula (2) with

$$k=8,\quad t_{2i-1}=\tau,\quad t_{2i}=2\tau\ (i=1,2,3,4);$$

the directions $\mathbf{n}_1$ and $\mathbf{n}_6$ coincide with the $(-y)$ axis, $\mathbf{n}_2$ and $\mathbf{n}_5$ with the y axis, $\mathbf{n}_3$ and $\mathbf{n}_8$ with the x axis, and $\mathbf{n}_4$ and $\mathbf{n}$ with the $(-x)$ axis; $\varphi_i=\pi/2$ ($i=1,2,\ldots,8$).

We carry out a canonical transformation of Eq. (1):

$$\tilde{\rho}(t)=\exp\left(-i\frac{\pi}{2\tau}t\hat{S}_z\right)\rho(t)\exp\left(i\frac{\pi}{2\tau}t\hat{S}_z\right). \tag{31}$$

The density matrix $\tilde{\rho}(t)$ satisfies in this case an equation similar to (1), in which the detuning Δ is replaced by $\Delta+\pi/2\tau$, and the pulse train HW-8 is replaced by a train of 90° pulses turned on at the same instant of time, but the fields of all the RF pulses are applied only along the x axis. We shall call the corresponding pulsed sequence the uniaxial analog of the HW-8 multipulse train. We can similarly obtain the uniaxial analogs of other modifications of WHH-4.[19,20] We note that such sequence were obtained independently by von Müller and Scheler.[21] It is more convenient to study the dynamics of a spin system acted upon by the HW-8 pulsed sequence by using a uniaxial analogy of HW-8.

4. UNIAXIAL ANALOG OF THE HW-8 PULSE TRAIN

The uniaxial analog of HW-8 is defined by formula (2) with

$$k=2,\quad t_c=3\tau,\quad \varphi_1=\varphi_2=\pi/2,\quad t_1=\tau,\quad t_2=2\tau;$$

the directions $\mathbf{n}_1$ and $\mathbf{n}_2$ coincide with the x axis. From (3) we obtain the magnitude and direction of the effective field:

$$\cos\frac{\theta}{2}=\cos\frac{3\tau\omega_e}{2}=-\sin\frac{\Delta\tau}{2}\sin\Delta\tau=-\sin\frac{\bar{\Delta}}{6}\sin\frac{\bar{\Delta}}{3},$$
$$n_x=\cos\frac{\bar{\Delta}}{3}\cos\frac{\bar{\Delta}}{6}\Big/\sin\frac{\theta}{2},\quad n_y=\sin\frac{\bar{\Delta}}{3}\sin\frac{\bar{\Delta}}{6}\Big/\sin\frac{\theta}{2}. \tag{32}$$
$$n_z=\cos\frac{\bar{\Delta}}{3}\sin\frac{\bar{\Delta}}{6}\Big/\sin\frac{\theta}{2}\quad(\bar{\Delta}=\Delta t_c)$$

The Fourier coefficients of the functions $\chi_m(t)$ ($m=0, \pm 1, \pm 2$) are defined here in the following manner:

$$\chi_0^0=\frac{n_z^2-n_x^2}{2}, \quad \chi_0^k=\frac{3(e^{2\pi ik/3}-1)}{4\pi ik}(n_y^2-n_z^2) \quad (k\neq 0),$$
$$\chi_1^k=3\frac{qn_y[e^{\frac{1}{3}i(2\pi k+\theta)}-1]+pn_z e^{i\theta/3}[e^{\frac{2}{3}i(\pi k-\theta)}-1]}{i(2\pi k+\theta)}, \tag{33}$$
$$\chi_2^k=3\frac{q^2[e^{\frac{2}{3}i(\pi k+\theta)}-1]+p^2[e^{2i\theta/3}-e^{\frac{2}{3}i(\pi k-\theta)}]}{2i(\pi k+\theta)},$$
$$p=\frac{1}{2}\left[\frac{n_y n_z}{1+n_x}+i\left(n_x+\frac{n_y^2}{1+n_x}\right)\right], \quad q=\frac{1}{2}\left[n_x+\frac{n_z^2}{1+n_x}+i\frac{n_y n_z}{1+n_x}\right]. \tag{34}$$

We confine ourselves to the case $\bar{\Delta}=3\pi/2+\bar{\delta}$ ($\bar{\delta}=\delta t_c \ll 1$), i.e., we consider a uniaxial analog of the HW-8 pulse sequence with small detuning δ. With the aid of (16) and (33) we find that

$$\chi_0^0\sim\bar{\delta}^3, \quad s_{1,-1}^0\sim\bar{\delta}^2, \quad s_{2,-2}^0\sim\bar{\delta}, \quad u_{1,0}^0\sim\bar{\delta}, \quad u_{2,0}^0\sim 1, \quad u_{1,1}^0\sim\bar{\delta}. \tag{35}$$

Here $\theta\approx 3\pi/2$, and the dynamics of the spin system is strongly influenced by a four-spin resonant process[9] due to spin transitions between the levels of the effective field, caused by resonant (relative to the effective fields) harmonics of the four-spin nonsecular terms $\hat{R}_s^{(4)}(t)$ and by the transfer of part of the energy $\sim 2\pi/t_c - 4\omega_e$ to the dipole-dipole interaction pool. Estimating the resonant part of $\hat{R}_s^{(4)}(t)$ by formula (23), we find that $\bar{v}_1^{-3}\sim\bar{\delta}^2$ and $\bar{v}_2^{-3}\sim 1$.

We retain in the equation for the density matrix only the most significant terms at $\delta \ll 1$; we use here

$$i\frac{d\tilde{\rho}(t)}{dt}=\Big[\Big(\theta-\frac{3\pi}{2}\Big)\hat{S}_{n_e}+\varepsilon^3(u_{2,0}^0[\hat{V}_d^2,[\hat{V}_d^0,\hat{V}_d^{-2}]]$$
$$+\bar{v}_2^{-3}[\hat{V}_d^2,[\hat{V}_d^0,\hat{V}_d^2]])+\text{H.c.}, \tilde{\rho}(t)\Big], \tag{36}$$

where $\theta-3\pi/2\sim\bar{\delta}$. At $\bar{\delta}\lesssim\varepsilon^3$ the damping of the magnetization takes place over times $\sim 1/|\hat{H}^{\mathrm{eff}}|$ (Ref. 22), where $\hat{H}^{\mathrm{eff}}$ is the Hamiltonian in (36).

At $\varepsilon\gg\bar{\delta}\gg\varepsilon^3$ the damping times of the longitudinal and transverse (relative to the effective field) magnetization components become substantially different.[22] The (several fold) increase of the damping time of the transverse magnetization component stems from the partial averaging of the nonsecular terms in (36) by the "strong" field δ. This is the gist of the second averaging principle established by Haeberlen, Ellett, and Waugh,[17] according to which the residual dipole-dipole interaction (which is not averaged by the pulse train) is additionally averaged by the detuning field. However, the second-averaging principle[17] does not explain the damping of the longitudinal component of the magnetization, which can exceed that of the transverse magnetization component by several orders of magnitude. The mechanism of the damping of the longitudinal component is the same as in the WHH-4 multipulse experiment, and is due to absorption of the energy of the external fields by the spin system.

Let us explain the experimentally observed[22] dependence of the damping time of the transverse magnetization component on the detuning δ. If Eq. (36) is subjected at $\varepsilon\gg\bar{\delta}\gg\varepsilon^3$ to a canonical transformation that decreases the amplitudes of the nonsecular terms,[15] then in the next higher order of perturbation theory there appear secular terms $\sim t_c^4\omega_{\mathrm{loc}}^6/\delta$, which determine the dependence of the damping time on the detuning. At $\bar{\delta}\sim\varepsilon$ the damping of the transverse magnetization component is determined by the dephasing of the spins in the residual dipole fields $\sim\varepsilon^2$, and the damping time is $\sim\delta^{-1}t_c^{-2}$. The degree of averaging of the dipole-dipole interaction at $\bar{\delta}\sim\varepsilon$ begins to decrease. The results agree with the experimental data and with the qualitative estimates.[22]

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[1)] The expressions for $\hat{R}_s^{(i)}(t)$ ($i=\pm 1, \pm 2, \pm 3$) are too cumbersome to present here.

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Stochastic inhomogeneous structures in nonequilibrium systems

B. S. Kerner and V. V. Osipov

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It is shown that stable inhomogeneous states of a complicated type, namely stochastically inhomogeneous structures (SIS), can arise spontaneously in kinetic phase transitions in homogeneous nonequilibrium systems, i.e., at the points when their homogeneous state becomes unstable. The phase portrait of the SIS has even in the one-dimensional case a set of nonisolated limit cycles, at some point of which a phase trajectory can go over randomly from one cycle to another. The onset of SIS is established by analyzing a system of two nonlinear differential equations of the diffusion type, which describe a definite class of nonequilibrium systems. The latter, in particular, include an electron-hole plasma uniformly heated by electromagnetic radiation, a weakly ionized gas plasma, nonequilibrium superconductors, as well as a number of important chemical and biological systems whose properties are determined by autocatalytic reactions. Static as well as traveling SIS can be excited in the systems under consideration also by a finite inhomogeneous perturbation. Methods are developed for a self-consistent qualitative derivation of one-dimensional and radially symmetrical stationary solutions and of the analysis of their stability. The form and velocity of the traveling one-dimensional SIS are found. General requirements on the form of two- and three-dimensional SIS are formulated on the basis of the stability analysis. It is shown that under the same conditions there exist in the system a number of different SIS, and the distinguishing features of the evolution of their instability with changing state of the system are analyzed. Explanations are offered for the experimental data and for the results of numerical investigations of a number of systems in which spatial dissipative structures arise.

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1. INTRODUCTION

The onset of a new structure in a system under thermodynamic equilibrium in the course of a phase transition can be regarded as the result of the growth of the order-parameter fluctuations on going through the point at which the initial phase loses stability. There can also be produced in this case spatially inhomogeneous distributions of the order parameter, for example multidomain states, noncommensurate phases,[1,2] or a substructure of heterophase alloys.[3] In a certain sense, similar phenomena occur in nonequilibrium homogeneous systems when their homogeneous state becomes unstable. Such a kinetic phase transition, however, leads to more varied effects: homogeneous and inhomogeneous oscillations can arise in nonequilibrium systems, traveling pulses and nonlinear waves are excited, or complicated stable inhomogeneous structures (IS) can be formed.[4-17]

In contrast to a true phase transition, in which new coherent states are established as a result of effective long-range interaction, in the here considered nonequilibrium systems the IS are produced as a result of diffusion processes.[6,9,12,14-17] The spontaneous formation of IS as a result of diffusion instability can be described in unified fashion for a large class of physical, chemical, and biological systems whose properties depend on two parameters θ and η that differ in their spatial dispersion.[14-17] The layering in such systems is due to the spatial decoupling of the "rapidly varying" parameter θ from the "slowly varying" parameter η when the system is unstable to θ at constant η. A nonlinear theory of one-dimensional IS (layers) for this class of systems was developed in preceding papers,[16,17] in which principal attention was paid to spatially periodic structures, as well as to IS in the form of single layers.

The properties of the considered systems are described by two nonlinear equations of the diffusion type:

$$\tau_\theta\frac{\partial\theta}{\partial t}=l^2\Delta\theta-q(\theta,\eta,A,\ldots,G), \qquad (1)$$

$$\tau_\eta\frac{\partial\eta}{\partial t}=L^2\Delta\eta-Q(\eta,\theta,A,\ldots,G) \qquad (2)$$

with cyclic boundary conditions or with boundary conditions

$$\mathbf{n}\nabla\theta|_S=\mathbf{n}\nabla\eta|_S=0, \qquad (3)$$

corresponding to the absence of fluxes through the surface S of the system. These are the basic equations for the study of IS and of the propagation of perturbations in biological systems.[6-12] They correspond, in

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