nonbalance terms describe processes of diffusion and of drift, respectively, in momentum space. In scattering by magnetic spots, the perturbations $\delta f_{\mathbf{k}}$ drift in the mean magnetic field and slowly spread out. In scattering by a noncentral potential, the situation is the opposite. The perturbations spread out rapidly, while the detailed-nonbalance terms produce a small asymmetric distortion of their shape.

5. We shall discuss briefly the problem of describing, on the basis of (4), transport phenomena produced in **R** space by the absence of detailed balancing. We define the particle current I in coordinate space as $\int \mathbf{k} f_{\mathbf{k}} d\mathbf{k}$. Then we have from (4)

$$\frac{\partial I}{\partial t} = \int j_{\mathbf{k}}\, d\mathbf{k}. \tag{10}$$

At the initial instant, let there be a currentless perturbation, $\delta f_{\mathbf{k}} = \delta f_{-\mathbf{k}}$. Because of the different parity of the detailed-balance and nonbalance terms in the current $\mathbf{j}_{\mathbf{k}}$, it follows immediately from (10) that the transitional process in the absence of detailed balance will be accompanied by transport of particles. But if there is a source that maintains the symmetric perturbations, $\delta f_{\mathbf{k}} = \delta f_{-\mathbf{k}}$ (for example, a high-frequency field), then the additional terms in the FP equation will produce a constant flow of particles (electric current). Such a photogalvanic effect (and also the anomalous Hall effect[6]) can be immediately described by means of the modified FP equation in terms of the coefficients A_i and B_{ijl}.

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[1)]The idea of cycles goes all the way back to Boltzmann.[9]
[2)]Scattering at small angles may be considered quasiclassical.

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Use of averaging method in problems of high-resolution nuclear magnetic resonance in solids

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The Krylov-Bogolyubov-Mitropol'skiĭ averaging method is used to derive an expression for the average Hamiltonian that describes the evolution of a spin system under the influence of pulse sequences. It is shown that the equation customarily employed for the average Hamiltonian and based on the Magnus expansion is nonsecular in the higher orders of perturbation theory, i.e., the contribution of the latter to the line shape corresponds to satellites at frequencies that are multiples of the fundamental frequency. Some concrete situations are considered where the use of the Magnus expansion leads to incorrect physical results. The limits of applicability of the theory of the average Hamiltonian is investigated.

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New methods of NMR in solids, based on the work of J.S. Waugh and co-workers,[1] have been attracting much attention recently. The idea of the new methods is that a periodic sequence of pulses is applied to a spin system and averages out a definite part of the spin-spin interactions, thus leading to an effective narrowing of the magnetic-resonance lines. It is important to note that by suitably choosing the pulse sequence we can selectively suppress one part of the spin-spin interactions or another, so that the method can provide an increased amount of information.

The response of a spin system to a pulse sequency is usually analyzed mathematically by the average-

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Hamiltonian method developed in detail in Refs. 1 and 2. This method is based on the application of the Magnus expansion[3] to the spin-system evolution operator. Heberlen and Waugh[1] have shown that if measurements are made at instants of time t_c (the period of the pulse sequence), then the evolution of the spin system can be approximately regarded as taking place under the influence of a time-independent average Hamiltonian. This simplifies greatly the solution of the problem which now becomes conservative, compared with the initial formulation.

Recent experiments,[4] however, yielded results that conflicted with the indicated theory. It was therefore stated in Refs. 5 and 6 that the average-Hamiltonian field is not applicable at all at $t \gtrsim T_2$ (where T_2 is the transverse-relaxation time), and the spin system cannot be regarded as conservative. Since the Waugh theory describes well a large number of experiments, we doubt the validity of this statement.

On the other hand, methods of investigating the behavior of a system under the action of a periodic perturbation are well known and mathematically corroborated in mechanics (e.g., the widely employed Krylov-Bogolyubov-Mitropol'skiĭ averaging method[7]). The averaging method is based on ideas utterly different from those of the Waugh theory, which is based on the Magnus expansion. The averaging method is connected with the existence of a certain change of variables, whereby it becomes possible to eliminate the explicit time dependence with any degree of accuracy relative to a small parameter, i.e., it permits the solution of the exact problem to be approximated by the solution of a corresponding conservative problem much simpler than the initial one. From this point of view the averaging method and the Waugh theory should lead to similar results, and the comparison of results obtained by different methods is of considerable interest. Furthermore, it is possible to investigate within the framework of the averaging method the already mentioned fundamental question of the limits of applicability of the average-Hamiltonian theory and to ascertain the causes of the deviation of Waugh's theory from experiment.

We consider the bahavior of a system under the action of a periodic perturbation (a particular case of which is a pulse sequence). The evolution of the system is determined by the Liouville equation

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

where H is the spin-spin interaction operator and $V(t)$ is the periodic perturbation.

Following Haberlen and Waugh,[1] we introduce the unitary transformation

$$\tilde{\rho}=U(t)\rho U^{-1}(t),$$

where the operator U satisfies the equation

$$dU/dt=iUV(t).$$

The equation for $\tilde{\rho}$ takes the form

$$\frac{d\tilde{\rho}}{dt}=i[\tilde{\rho},\tilde{H}(t)], \quad \tilde{H}(t)=U(t)HU^{-1}(t). \tag{2}$$

Following Ref. 1, we assume that the perturbation has periodicity and cyclicity properties (i.e., $V(t+Nt_c)=V(t)$ and $U(Nt_c)=1$), so that $\tilde{H}(t)$ is also a periodic function with period t_c. If, in analogy with the method of Bogolyubov and Mitropol'skiĭ,[7] we change variables in (2) by introducing the "dimensionless time" $x=t/t_c$ then the right-hand side of the equation is of the order of $t\|H\|$ (the double bars mark quantities in frequency units). The pulse sequences are chosen in the experiment such as to satisfy the condition $t_c\|H\| \ll 1$, for only in this case can the evolution of the spin system be described by the average-Hamiltonian theory. Consequently the right-hand side of Eq. (2), written in dimensionless form, is proportional to the small parameter $\varepsilon=t_c\|H\|$ and is of the same form as the equation in the standard formulation.[7] In order not to clutter up the exposition, we shall not make the indicated change of variables, but will seek the solution of (2) in the form of a series in powers of H (and it will be seen from the final equations that the actual expansion parameter is indeed $t\|H\|$).

Thus, in accord with the averaging method,[7] we seek the solution of (2) in the form

$$\tilde{\rho}(t)=\xi(t)+\rho^{(1)}(t,\xi)+\rho^{(2)}(t,\xi)+\ldots, \tag{3}$$

where the operator $\xi(t)$ satisfies the closed equation

$$d\xi/dt=A^{(1)}(\xi)+A^{(2)}(\xi)+\ldots. \tag{4}$$

The dependences of the quantities $\rho^{(n)}$ and $A^{(n)}$ on ξ in Eqs. (3) and (4) is linear, since Eq. (2) is linear in $\tilde{\rho}$.

Since $\tilde{H}(t)$ is a periodic function, it can be expanded in a Fourier series

$$\tilde{H}(t)=\sum_{n=-\infty}^{\infty} H_n e^{i\omega_n t}, \qquad \omega_n=\frac{2\pi}{t_c}n, \quad H_n=\frac{1}{t_c}\int_0^{t_c} dt\tilde{H}(t)e^{-i\omega_n t}. \tag{5}$$

Following the averaging method, we also expand $\rho^{(m)}$ in Fourier series:

$$\rho^{(m)}(\xi,t)=\sum_{n\neq 0}\rho_n^{(m)}(\xi)e^{i\omega_n t}. \tag{6}$$

The absence of zeroth harmonics from the expansion (6) means that the entire slow dependence on the time is contained in $\xi(t)$. Differentiating (3) with respect to time with (4)–(6) taken into account, and substituting in (2), we obtain

$$A^{(1)}=-i[H_0,\xi], \quad \rho_n^{(1)}=-\frac{1}{\omega_n}[H_n,\xi],$$
$$A^{(2)}=-i\sum_{n\neq 0}\frac{1}{\omega_n}[H_n[H_{-n},\xi]].$$

The expression for $A^{(2)}$ can be transformed into

$$A^{(2)}=-i\sum_{n\neq 0}\frac{1}{2\omega_n}[[H_n,H_{-n}]\xi].$$

It is seen from the expressions for $\rho_n^{(1)}$ and $A^{(2)}$ that the expansion parameter is indeed the quantity $t\|H\|$. Thus, in second-order in the perturbation, we can write the equation for $\xi(t)$ in the form

$$d\xi/dt=-i[\bar{H},\xi], \tag{7}$$

where

$$\bar{H}=H_0+\sum_{n\neq 0}\frac{1}{2\omega_n}[H_n, H_{-n}] \tag{8}$$

has the meaning of a Hamiltonian. If we now replace the quantum Poisson brackets by classical ones, then the obtained expression coincides with the expression for the average Hamiltonian, obtained in the classical case by using the averaging method in the canonical formalism.[7]

Obviously, expression (8) is valid at all times, whereas the analogous expression obtained on the basis of the Magnus expansion is meaningful only for times that are multiples of t_c.

It is shown in Ref. 7 that if the average Hamiltonian is calculated accurate to second order, then it is sufficient to retain in the expansion for $\bar{\rho}(t)$ the first-order terms. It was noted above that the entire slow dependence on the time is contained in $\xi(t)$ and $\rho^{(1)}(t)$ yields rapid oscillations.

We discuss now the limits of applicability of the employed method. In the averaging method this question is dealt with the first fundamental theorem of Bogolyubov[7] (a generalization of this theorem to include infinite-dimensional Hilbert space is given by Los'[8]). As applied to our case, this theorem states that, subject to rather general restrictions on $\tilde{H}(t)$, the solution $\xi(t)$ taken in first approximation is asymptotically close to the solution of Eq. (2) in the dimensionless-time interval $0 < x < L/\varepsilon$, where the number L can be made arbitrarily large at sufficiently small ε. In the usual time units, this corresponds to the time interval $0 < t < LT_2 (T_2 = \|H\|^{-1})$. The system can thus be regarded as conservative overtime intervals much longer than T_2. This statement is all the more valid for the higher orders.

We compare now (8) with the expression obtained by Waugh[1] for the average Hamiltonian. It is of the form

$$\bar{H}=\frac{1}{t_c}\int_0^{t_c}\tilde{H}(t)\,dt-\frac{i}{2t_c}\int_0^{t_c}\int_0^{t_1}[\tilde{H}(t_2),\tilde{H}(t_1)]\,dt_2\,dt_1.$$

Changing to the Fourier representation, we get

$$\bar{H}=H_0+\sum_{n\neq 0}\frac{1}{2\omega_n}[H_n, H_{-n}]+\sum_{n\neq 0}\frac{1}{\omega_n}[H_0, H_n]. \tag{9}$$

We see that expressions (8) and (9) coincide in first-order approximation. Consequently, in problems where the first approximation is sufficient, Waugh's theory is valid at times $t \gg T$. At $H_0 = 0$ expressions (8) and (9) also agree up to second order, and consequently yield identical results, so that Waugh's theory describes correctly the results of experiments in which the width is determined by H_0 or $H^{(1)}$ (at $H_0 = 0$). At $H_0 \neq 0$, however, there appears in (9), in contrast to the result obtained by the averaging method, a nonsecular term in the form

$$\sum_{n\neq 0}\frac{1}{\omega_n}[H_0, H_n]. \tag{10}$$

A similar situation will be encountered also in the higher orders. We consider below examples from which it follows that it is precisely the presence of nonsecular terms in the higher orders which is the reason why the Waugh theory does not agree in a number of cases with the experimental data (and not that the theory is incorrect at $t \gtrsim T_2$, as is stated in Refs. 5 and 6).

1) We consider a system of spins that interact in dipole-dipole fashion and are situated in a constant magnetic field. It is well known (see, e.g., Ref. 9) that if the constant field is much stronger than the local field produced at the nuclei by the dipole-dipole interaction, then to determine the line shape it is necessary to take into account only the secular part of the dipole-dipole interaction. This part can be separated with the aid of the method described above. In this case

$$V(t)=\omega_0 I_z, \quad H=H_d^{(0)}+\sum_{m=\pm 1,\pm 2}H_d^{(m)}.$$

The explicit form of $H_d^{(m)}$ can be found, e.g., in Ref. 9. The operator $U(t)$ takes the form

$$U(t)=\exp(i\omega_0 t I_z)$$

and consequently the cyclicity condition will be satisfied at $t_c = 2\pi/\omega_0$. The average Hamiltonian calculated with the aid of (8) is

$$\bar{H}_d=H_d^{(0)}+\sum_{n\neq 0}\frac{1}{2n\omega_0}[H_d^{(n)}, H_d^{(-n)}]. \tag{11}$$

This expression was derived earlier by other methods by Jeener *et al.*[10] On the other hand if we use (9), then an additional nonsecular term appears in second order, namely

$$\sum_{n\neq 0}\frac{1}{n\omega_0}[H_d^{(0)}, H_d^{(n)}],$$

and inclusion of this term in the calculation of the line shape gives an incorrect result, corresponding to satellites at frequencies that are multiples of the fundamental frequency.

2) We consider now the damping of the transverse magnetization (i.e., the x component) under the influence of a pulse sequence

$$90°_y-(\tau-\varphi_x-\tau)^n, \tag{12}$$

which was investigated by Ivanov, Provotorov, and Fel'dman.[5] In multipulse NMR experiments one usually investigates the Fourier transform of the x component of the magnetization. The line shape should be determined in this case by the average Hamiltonian (8). In fact, the central component of the line is determined by the Fourier transform of that part of the transverse magnetization which depends slowly on the time, while the fast oscillations are determined by the line satellites. In other words, to determine the line shape it suffices to retain in the expansion (3) the first term $\xi(t)$. But $\xi(t)$ satisfies Eq. (7) with time-independent Hamiltonian $\bar{H}$. Thus, according to the general theorem,[11] the line width is indeed determined by the average Hamiltonian (8).

We now ascertain the results obtained for the pulse sequence (12) from the Waugh theory and from the averaging methods. Both methods can be used at $\varphi=\pi/m$ (where m is an integer), so as to satisfy the cyclicity and periodicity condition. Using the results of Ivanov *et al.*,[5] we write the Hamiltonian of the dipole-dipole interaction in the form

$$H_d(t)=-\frac{1}{2}H_d^x+\sum_{n=-\infty}^{\infty}C_n\left(H_d^2\exp\left\{-\frac{i(mn+1)\pi t}{m\tau}\right\}\right.$$
$$\left.+H_d^{-2}\exp\left\{\frac{i(mn+1)\pi t}{m\tau}\right\}\right),$$

where

$$C_n=\frac{(-1)^n m\sin(\pi/m)}{\pi(mn+1)}$$

After the action of the 90°_y pulse, the initial state takes the form

$$\rho(0)=1-aI_x.$$

The average Hamiltonian calculated with the aid of expression (8) is

$$\bar{H}=-\frac{1}{2}H_d^x+\tau A_m[H_d^{-2},H_d^2],\tag{13}$$

where

$$A_m=\frac{m^3\sin^2(\pi/m)}{2\pi}\sum_{n=-\infty}^{\infty}\frac{1}{(mn+1)^3}.$$

Since $[\bar{H},I_x]=0$, the initial state does not change with time. On the other hand if we use expression (9) to calculate the average Hamiltonian, then we obtain in second order an additional nonsecular term in the form

$$H_{ns}=\tau B_m[H_d^x,\ H_d^2-H_d^{-2}],$$

where

$$B_m=\frac{m^2\sin(\pi/m)}{2\pi}\sum_{n=-\infty}^{\infty}\frac{(-1)^n}{(mn+1)^2}.$$

It is easily seen that $B_m=0$ at $m=2$, i.e., the result agrees with (13). At $m\neq 2$, however, we have $B_m\neq 0$ and the Waugh Hamiltonian takes in second order the form $H'=\bar{H}+H_{ns}$, and since $\|H\|\gg\|H_{ns}\|$, the situation here is analogous to exchange narrowing.[9] It is easy to estimate the order of the damping due to H_{ns}. It is of the form

$$1/T_{2e}\sim\tau^2/T_2^3.$$

This expression does not agree with the available experimental data[4] (a relation of the type $1/T_{2e}\propto\tau^4/T_2^5$ is observed in experiment). We emphasize once more that this contradiction is due to the nonsecular character of the Magnus expansion.

The experimentally observed damping[4] can be taken into account within the framework of the method described above in the following manner. Since $[\bar{H},I_x]=0$, it follows from the general premises of nonequilibrium thermodynamics[12] that after a time of the order of T_2 there will be established in the system a quasi-equilibrium state, which is characterized in this case by two quasi-integrals of motion, I_x and $\frac{1}{2}H_d^x$. The subsequent relaxation of the system proceeds with a time much longer than T_2. To determine the behavior of the system during this stage we can no longer confine ourselves to expression (8) for the average Hamiltonian, but must take into account the influence of the non-averaged part of the dipole-dipole interaction. This program was actually effected by another method in Refs. 5 and 6.

3) As the third example, we consider the effect of radiative magnetic-resonance line shift in the case when the RF field acting on the system oscillates in a plane perpendicular to the constant field (the Bloch-Siegert shift). This case can also be analyzed on the basis of the average-Hamiltonian theory. The system under consideration is described by the Hamiltonian

$$H=\omega_0 I_z+2\omega_1 I_x\cos\omega_0 t.$$

The small parameter in our problem is the ratio of the amplitude of the laternating field to that of the constant field, $\varepsilon=\omega_1/\omega_0$. We change to a coordinate frame that rotates with frequency ω_0. In this system, the Hamiltonian takes the form

$$\tilde{H}(t)=\omega_1 I_x+{}^1/_2\omega_1(I^+e^{2i\omega_0 t}+I^-e^{-2i\omega_0 t}).$$

It is seen from this expression that in our case

$$H_0=\omega_1 I_x,\quad H_2={}^1/_2\omega_1 I^+,\quad H_{-2}={}^1/_2\omega_1 I^-.$$

The average Hamiltonian calculated with the aid of (8) is

$$\bar{H}=\omega_1 I_x+\frac{\omega_1^2}{4\omega_0}I_z.$$

We see therefore that the shifted frequency, to which the line center corresponds, is

$$\omega=\omega_0+\omega_1^2/4\omega_0.$$

This is a well known result (see the review of Novikov and Skrotskiĭ[13] and the references therein). But if we use (9), the shifted frequency is

$$\omega=\omega_0-\omega_1^2/4\omega_0,$$

so that in this example the Waugh theory yields a most incorrect result.

We note finally that the averaging method described above is valid not only for periodic perturbations (as is the Waugh theory), but also for an arbitrary time dependence. All that matters here is the existence of an average value[7]

$$H_0=\lim_{t_c\to\infty}\frac{1}{t_c}\int_0^{t_c}\tilde{H}(t)\,dt,$$

so that the results obtained above are valid also for stochastic processes if the corresponding correlation times are short enough.

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Microstructure of a resistive layer on an aluminum surface

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The microstructure of the resistive layer formed on the surface of superconducting aluminum after switching off an external magnetic field $H_0 > H_c$ is investigated by using point junctions of size $d_0 \ll \xi_0$ (ξ_0 is the superconducting coherence length in aluminum. The macroscopic properties of the layer are close to the well-known properties of a two-dimensional mixed (TDM) state in type-*I* superconductors [Landau and Sharvin, JETP Lett. **10**, 121 (1969)]. It is found that, under various conditions, three types of structure exist in the layer, viz., stationary laminar, stationary island, and nonstationary island. The laminar structure is close to the model of the TDM state proposed by Gor'kov and Dorokhov [Sov. Phys. JETP **40**, 956 (1975)]. It is found that the structures move along the surface and that the dynamics of the structures is qualitatively the same as in the intermediate state [Gubankov and Margolin, JETP Lett. **29**, 673 (1979)]. On the basis of an analysis of the waveforms of the signals from the point junctions it is concluded that regions exist in which the order parameter varies from zero up to the superconducting value. The measured layer thickness $d \sim \xi_0$. The surface impedance differs from that corresponding to the pure superconducting state.

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Among the resistive states of type-I superconductors, particular interest attaches to the two-dimensional mixed (TDM) state observed by I. Landau and Sharvin.[1] This state is produced on the inner surface of a hollow cylinder under the influence of a strong current flowing through it, when the ordinary intermediate-state structure is no longer present in the sample. An electric field is present in the TDM layer, and the current flowing through it produces a magnetic-field discontinuity $\Delta H \ll 2H_c$ across the layer. Such a layer was subsequently produced in the interior and on the outer surface of a hollow cylinder.[2] The presence of the TDM state causes paramagnetic effects in solid[3] and hollow[4] current-carrying cylinders.

The study of the microscopic structure of the TDM state is of great interest because the various employed theoretical models[5-8] predict different microscopic arrangements. A possible criterion of the proximity of a layer to the TDM state may be the relation between its characteristic dimensions and the superconducting coherence length ξ_0. Consequently the most convenient for structural investigations of the TDM state are superconductors with large ξ_0, particularly aluminum ($\xi_0 = 1.36 \times 10^{-4}$ cm, Ref. 9).

We have previously noted[10] that a layer with properties close to those of the TDM state can be produced on the surface of a type-I superconductor when the external magnetic field $H_0 > H_c$ is turned off. In fact, the field outside the sample drops rapidly to zero, whereas in the interior of the sample, owing to the eddy currents, it remains equal to H_0 for a sufficiently long time. It follows from the continuity of the tangential component that the magnetic field is equal to zero also on the sample surface parallel to $\mathbf{H}_0$. The region near the surface, where $H < H_c$, should become superconducting. The produced layer cannot trap in the sample the magnetic flux, which at that time is larger than critical. The change of the magnetic flux passing through the sample leads to the appearance of a solenoidal electric field in the layer. Thus, a rather thin resistive layer should exist on the surface of the sample.

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