Theory of magnetic resonance in the memory-function formalism

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The equations of motion for the x, y, and z components of the total spin and for the secular part of the spin dipolar interactions under magnetic-resonance conditions are obtained using memory functions, and their stationary solution is presented. The results obtained supplement and expand the scope of the Provotorov and Bloch theories. © *1996 American Institute of Physics.* [S1063-7761(96)02508-5]

1. There is a fairly extensive class of magnetic-resonance problems in which a significant role is played by secular dipolar interactions. The successful solution of these problems became possible with the appearance of Provotorov's theory,[1] according to which the secular dipolar interactions are isolated in a separate subsystem and influence the redistribution of the energy of the variable magnetic field and other processes, determining the magnetic-resonance linewidth (shape). The Provotorov theory, which has been confirmed by numerous experiments,[2–4] was represented in the original paper[1] by two equations for the average values of the "Zeeman" operator $\mathcal{H}^z(t)$ and the part $\mathscr{H}^d(t)$ of the dipolar interactions that is secular with respect to $\mathscr{H}^z(t)$:

$$\frac{d\mathscr{H}^z(t)}{dt}=-\omega_1^2\pi g(\Delta)[\mathscr{H}^z(t)-\varepsilon\mathscr{H}^d(t)],\tag{1}$$

$$\frac{d\mathscr{H}^d(t)}{dt}=-\frac{d\mathscr{H}^z(t)}{dt},\tag{2}$$

where ω_1 is the amplitude of the variable field, $g(\Delta)$ is the line shape for the resonant absorption of energy from the external variable magnetic field, $\varepsilon=\Delta^2/D^2$, $\Delta=\omega_0-\omega$ is the detuning of the frequency ω of the external variable magnetic field relative to the central resonant Zeeman frequency ω_0, $D^2=\mathrm{Tr}(\mathscr{H}^d)^2/\mathrm{Tr}(I^z)^2$, and I^z is the z component of the total spin.

On the other hand, in the 1970s the work of Parker, Mehring, and Rado laid the foundation for the magnetic-resonance application of the so-called memory-function formalism (see Refs. 3, 5, and 6 and the literature cited therein). This formalism, being one of the methods of nonequilibrium statistical mechanics applied to certain magnetic-resonance problems, can probably also be related in a more general sense to the ideas of Liouville an von Neumann, who proposed the fundamental equations of motion for the distribution function and the density matrix of a statistical operator, as well as Zwanzig, who first introduced the projection operator into nonequilibrium statistical mechanics and derived the fundamental kinetic equation for the statistical operator $\rho(t)$ [Eqs. (1) and (2) were obtained by just this method], and Mori, who proposed the method for constructing a projection operator (superoperator) that leads to modified nonequilibrium dynamics.[7–9] In particular, using the memory-function formalism the magnetic-resonance line shape $g(\Delta)$ can be expressed in terms of the cosine and sine Fourier transforms of memory functions, $k'(\Delta)$ and $k''(\Delta)$ (Refs. 3 and 5):

$$g(\Delta)=k'(\Delta)\{[k'(\Delta)]^2+[\Delta-k''(\Delta)]^2\}^{-1}.\tag{3}$$

It can be assumed that the quantity $g(\Delta)$ in (1) and (2) should have the form (3). As will be shown below, this assumption is correct and follows naturally from the main problem solved herein, in which an attempt is made to show that the memory-function formalism makes it possible to describe the interrelated macroscopic dynamics of both the diagonal operators ($\mathscr{H}^z$ and $\mathscr{H}^d$), i.e., the "good" thermodynamic coordinates, and the off-diagonal operators, i.e., the x and y components of the total spin, I^x and I^y, which, although they are not good (in the thermodynamic sense, since they do not commute with $\mathscr{H}^d$), are still macroscopically observable quantities (the inflow of energy from the variable magnetic field and the observation of the dispersion signal are provided "in terms of" I^x, and the resonant absorption signal is attributed to I^y). This is also the purpose of the present work, i.e., the derivation and stationary solution of a system of equations that describe the dynamics of the spin system of a solid under magnetic-resonance conditions using components of the total spin together with secular dipolar interactions within the memory-function formalism. We note that a similar problem, but without consideration of the secular dipolar interactions and memory effects, i.e., the derivation of equations that describe the interrelated dynamics of the x, y, and z components of the magnetization (the phenomenological Bloch equations) by one of the methods of nonequilibrium statistical physics was solved in Refs. 10 and 11, and in Refs. 12 and 13 these equations were modified with the consideration of memory effects.

2. Before preceding to the solution of the problem posed, we note the following. In one of the productive methods of nonequilibrium mechanics, viz., the Zwanzig projection operator method, a nonequilibrium process is treated in a closed (isolated) system of weakly interacting particles.[7–9] Therefore, it is natural that the diagonal part of the total statistical operator ρ is taken as the relevant (quasiequilibrium) statistical operator ρ_1 [accordingly, the projection operator P^0 isolates the diagonal part from ρ, i.e., $\rho_1=P^0\rho$, and the operator $1-P^0$ isolates the off-diagonal part from ρ, i.e., $\rho_2=(1-P^0)\rho$]. There is usually interest specifically in the diagonal or so-called slowly varying operators, and the off-diagonal (rapidly varying) operators are considered insignificant. The diagonal and off-diagonal variables then develop with time completely independently.

A different situation arises when an open system, in which the external conditions are maintained constant for a long time, is considered. In our case we have the continuous action of a weak resonant variable magnetic field aligned parallel to the x axis and perpendicularly to a strong constant magnetic field on a spin system. This situation, which is standard in magnetic resonance, corresponds to what is characterized in nonequilibrium statistical mechanics as an "equilibrium" in a nonequilibrium state (a steady nonequilibrium process). In this case the variable field creates constant fluxes that maintain a nonequilibrium state, in which the macroscopic state does not vary, while the microscopic states undergo rapid reversible changes.[9] Such a nonequilibrium state can be described within the memory-function formalism using observable macroscopic diagonal and off-diagonal operators, since this formalism makes it possible to replace the terms like I^z/T_2 in the equations of motion by integrals with relaxation kernels, i.e., memory functions, as was done *a priori* in Refs. 12 and 13 [a similar integrodifferential equation for I^x makes it possible to define the magnetic-resonance line shape in terms of memory functions like (3)]. Here T_2 is the spin-spin relaxation time.

Thus, to investigate the nonequilibrium states described above using memory functions, along with the obvious choice of the average values $\langle \mathcal{H}^z(t)\rangle$ and $\langle \mathcal{H}^d(t)\rangle$ of the diagonal operators, we can choose the average values $\langle I^x(t)\rangle$ and $\langle I^y(t)\rangle$ of the off-diagonal operators as relevant functions, and we can select the operator P, which is composed of all those operators simultaneously, as the Mori projection superoperator. The condition that the production of entropy[1)] in the stationary nonequilibrium process under consideration be minimal is satisfied, although the off-diagonal operators ($\langle I^x(t)\rangle$ and $\langle I^y(t)\rangle$), which are associated with the source of the variable field, are not constants of motion, since the conjugate thermodynamic parameter is minimal (the inverse temperature of the source of the variable field tends to zero).

Attempting to generalize the foregoing statements, we note that here we are actually following Ref. 9, where the use of the diagonal operators as conserved quantities was proposed to characterize an arbitrary nonequilibrium state, and some off-diagonal operators can be regarded as relevant, or, according to the terminology in Refs. 3 and 5, operators of interest for a particular nonequilibrium state. According to Ref. 9, there are no general criteria for choosing the relevant set of operators in modern nonequilibrium statistical mechanics, and while a surplus of operators causes no harm, a shortage can lead to errors. If, for example, in the well-known problem of cross relaxation between two spin systems with similar frequencies only the operators of the Zeeman subsystem are chosen as the operators of interest, incorrect results are obtained,[3] whereas if the Hamiltonian of the dipolar interaction, which commutes with both Zeeman operators, is added as a relevant operator, the correct results presented in Ref. 4 can be obtained.

Thus, we must next investigate the interrelated dynamics of the macroscopic, observable diagonal ($\langle I^z(t)\rangle$ and $\langle \mathcal{H}^d(t)\rangle$) and off-diagonal ($\langle I^x(t)\rangle$ and $\langle I^y(t)\rangle$) parts of the Hamiltonian when energy is absorbed from the variable magnetic field by the spin system. For this purpose, we introduce a projection operator containing all these operators:

$$P=P^0+P', \tag{4}$$

where

$$P^0=P^z+P^d=\frac{|\mathcal{H}^z\rangle\langle\mathcal{H}^z|}{\langle\mathcal{H}^z|\mathcal{H}^z\rangle}+\frac{|\mathcal{H}^d\rangle\langle\mathcal{H}^d|}{\langle\mathcal{H}^d|\mathcal{H}^d\rangle}, \tag{5}$$

$$P'=P^x+P^y=\frac{|I^x\rangle\langle I^x|}{\langle I^x|I^x\rangle}+\frac{|I^y\rangle\langle I^y|}{\langle I^y|I^y\rangle}=\frac{|I^+\rangle\langle I^-|}{\langle I^+|I^-\rangle}+\frac{|I^-\rangle\langle I^+|}{\langle I^+|I^-\rangle}, \tag{6}$$

$|Q^j\rangle$ is an operator in Liouville space, $\langle Q^j|Q^j\rangle=\mathrm{Tr}(Q^j)^2$, and $I^\pm=I^x\pm iI^y$. Thus, the operator P isolates the part of ρ that is significant in our problem, while $1-P$ isolates the insignificant direct and indirect interactions. In addition, $P^2=P$.

Following the memory-function formalism in the form in which it was presented in the Appendix to Mehring's monograph,[5] we obtain a system of equations for the operators of interest $\langle Q^k(t)\rangle=\langle I^x(t)\rangle$, $\langle I^y(t)\rangle$, $\langle I^z(t)\rangle$, and $\langle \mathcal{H}^d(t)\rangle$:

$$\frac{d}{dt}\langle Q^k(t)\rangle=K+L+M, \tag{7}$$

where

$$K=-i\langle Q^k|\mathcal{H}P|\rho\rangle=-i\sum_j \frac{\langle Q^k|\mathcal{H}|Q^j\rangle}{\langle Q^j|Q^j\rangle}\langle Q^j(t)\rangle, \tag{8}$$

$$L=-i\langle Q^k|\mathcal{H}S(t,0)(1-P)|\rho(0)\rangle, \tag{9}$$

$$M=-\sum_j (\langle Q^j|Q^j\rangle)^{-1}\int_0^t dt'\langle Q^k|\mathcal{H}S(\tau)(1-P)\mathcal{H}|Q^j\rangle\langle Q^j(t')\rangle, \tag{10}$$

$$S(\tau)=S(t-t')=\exp[-i(t-t')(1-P)\mathcal{H}]. \tag{11}$$

The expressions (7)–(11) coincide exactly in form with the analogous equations from Refs. 3 and 5; however, there is a significant difference associated with the form of the projection operator (4). In deriving Eqs. (7)–(11), it was assumed that the Hamiltonian $\mathcal{H}$ does not depend on time and that the relevant operators of interest $\langle Q^k(t)\rangle$, from which the projection operator P is composed, are not the complete set, since we would otherwise have $M=0$, because $1-P=0$, and the system would have no "memory."

To be specific, we consider the system of nuclear spins of a nonmagnetic solid under magnetic-resonance conditions, whose Hamiltonian in a reference frame rotating with the frequency ω of the variable magnetic field has the standard form

$$\mathscr{H}=\mathscr{H}^0+V=\mathscr{H}^z+\mathscr{H}^d+V=\Delta I^z+\mathscr{H}^d+\omega_1 I^x. \tag{12}$$

The variable field $V=\omega_1 I^x$ is treated as a small perturbation. In addition, for the sake of convenience and unity regarding the dimensions in (7)–(11), the operators I^x, I^y, and I^z are replaced by $\mathscr{H}^{\pm}=I^{\pm}\omega_1/2$ and $\mathscr{H}^z$, so that we have the following set as the operators of interest:

$$Q^k=\mathscr{H}^+,\ \mathscr{H}^-,\ \mathscr{H}^z,\ \mathscr{H}^d.$$

Let us now turn to Eqs. (7)–(11). When only operators that commute with one another (for example $\mathscr{H}^z$ and $\mathscr{H}^d$) or the one single operator I^x are chosen as relevant operators, the term K, which represents a trivial contribution to the evolution of $\langle Q^k(t)\rangle$, is found to vanish,[3,5] while in our case it is obvious that it is nonzero for $\langle I^x(t)\rangle$, $\langle I^y(t)\rangle$, and $\langle I^z(t)\rangle$ [it is equal to zero for $\langle\mathscr{H}^d(t)\rangle$, because $\mathrm{Tr}[Q^j,Q^k]\mathscr{H}^d=0$ holds] and gives trivial (drift) terms that correspond to Hamilton dynamics. The term L can be set equal to zero on the basis of arguments that can be found, for example, in several books.[3,5,7–9] As for the third term, M, it is non-Markovian—it has memory, i.e., the temporal variation of $\langle Q^k(t)\rangle$ is determined not only by the particular state, but also by the macroscopic states of the system in all the preceding moments in time $t'\leqslant t$: the integration is carried out over the past time, and the corresponding kernel, which is a tensor in the general case, is called the memory function or the relaxation kernel.

Before proceeding to specific calculations involving the identification of memory functions (there are 16 in our case) and solving Eqs. (7), we make the following remark. The multiplier

$$\sum_j \frac{(1-P)\mathscr{H}|Q^j\rangle}{\langle Q^j|Q^j\rangle}\langle Q^j(t')\rangle \tag{13}$$

is common to all four equations (7)–(10). It is easy to see that

$$(1-P)\mathscr{H}|\mathscr{H}^z\rangle(\langle\mathscr{H}^z|\mathscr{H}^z\rangle)^{-1}\langle\mathscr{H}^z(t')\rangle=0,$$

since

$$(1-P)\mathscr{H}|\mathscr{H}^z\rangle=V|\mathscr{H}^z\rangle-P'V|\mathscr{H}^z\rangle=0, \tag{14}$$

and this is just as inadmissible in the equations for $\mathscr{H}^z$ and $\mathscr{H}^d$ from (7), as the absence of the term with $\mathscr{H}^z(t)$ on the right-hand sides of Eqs. (1) and (2). In addition, substituting the remaining three terms from (13) into (7), neglecting the perturbation V in the argument of the exponential, and expanding the corresponding memory functions, we can easily see that in the equation for $\langle\mathscr{H}^+(t)\rangle$ the terms with memory vanish completely, i.e., roughly speaking, the term $\sim\langle\mathscr{H}^+(t)\rangle/T_2$ vanishes. In the equation for $\langle\mathscr{H}^-(t)\rangle$ the terms with memory for $\langle\mathscr{H}^-(t')\rangle$ and $\langle\mathscr{H}^d(t')\rangle$ remain. In the equation for $d\langle\mathscr{H}^z(t)\rangle/dt$, in addition to the term with $\langle\mathscr{H}^z(t')\rangle$ that vanishes because of (14), the nontrivial term with memory for $\langle\mathscr{H}^d(t')\rangle$ also vanishes. Finally, in the equation for $\langle\mathscr{H}^d(t)\rangle$ all the nontrivial terms, except the term just mentioned with $\langle\mathscr{H}^z(t')\rangle$, remain. It is seen that the presence of the projection operator P in the memory functions leads to obviously incorrect equations, although the "energy conservation law"

$$\frac{d\langle\mathscr{H}^+(t)\rangle}{dt}+\frac{d\langle\mathscr{H}^-(t)\rangle}{dt}+\frac{d\langle\mathscr{H}^z(t)\rangle}{dt}+\frac{d\langle\mathscr{H}^d(t)\rangle}{dt}=0$$

formally remains in force. Therefore, to retain the significant terms in (10) we must replace P by P^0. It is noteworthy that the above arguments are not the basis for the replacement of P with P^0, which relies on general physical principles or internal mathematical logic. The replacement, which is performed *a priori*, takes into account the results of the Provotorov theory and restores the traditional, classical form[3,5–9] of the integral kernels, i.e., the memory functions.

Thus, the following system of equations can be obtained from (7):

$$\frac{d\langle Q^k(t)\rangle}{dt}=-i\sum_j\frac{\langle Q^k|\mathscr{H}|Q^j\rangle}{\langle Q^j|Q^j\rangle}\langle Q^j(t)\rangle-\sum_j\int_0^t dt' \times\frac{\langle Q^k|\mathscr{H}\exp[-i(1-P^0)\mathscr{H}\tau](1-P^0)\mathscr{H}|Q^j\rangle}{\langle Q^j|Q^j\rangle} \times\langle Q^j(t')\rangle, \tag{15}$$

or, in the Hilbert notation,

$$\frac{d\langle Q^k(t)\rangle}{dt}=-i\sum_j\frac{\mathrm{Tr}[Q^j,Q^k]\mathscr{H}}{\mathrm{Tr}(Q^j)^2}\langle Q^j(t)\rangle -\sum_j\int_0^t dt'\frac{\mathrm{Tr}[Q^k,\mathscr{H}]\exp[-i(1-P^0)\mathscr{H}\tau](1-P^0)[\mathscr{H},Q^j]\exp[i(1-P^0)\mathscr{H}\tau]}{\mathrm{Tr}(Q^j)^2}\langle Q^j(t')\rangle, \tag{16}$$

f, for simplicity, we now replace $\langle Q^j(t)\rangle$ by $Q^j(t)$ from (15), we obtain the following system of "exact" equations:

$$\frac{d\mathcal{H}^{\pm}(t)}{dt}=\frac{d\mathcal{H}^{\pm}_B(t)}{dt}-\langle\mathcal{H}^z|\mathcal{H}^z\rangle^{-1}\int_0^t dt'\langle\mathcal{H}^{\pm}|\mathcal{H}^0 \times\exp[-i(1-P^0)\mathcal{H}\tau] \times V[|\mathcal{H}^z\rangle\mathcal{H}^z(t')+\varepsilon|\mathcal{H}^d\rangle\mathcal{H}^d(t')], \quad (17)$$

$$\frac{d\mathcal{H}^z(t)}{dt}=\frac{d\mathcal{H}^z_B(t)}{dt}+\frac{d\mathcal{H}^z_P(t)}{dt} -\langle\mathcal{H}^+|\mathcal{H}^-\rangle^{-1}\int_0^t dt'\langle\mathcal{H}^z|V \times\exp[-i(1-P^0)\mathcal{H}\tau]V[|\mathcal{H}^+\rangle\mathcal{H}^-(t') +|\mathcal{H}^-\rangle\mathcal{H}^+(t')], \quad (18)$$

$$\frac{d\mathcal{H}^d(t)}{dt}=\frac{d\mathcal{H}^d_P(t)}{dt}-\langle\mathcal{H}^+|\mathcal{H}^-\rangle^{-1}\int_0^t dt'\langle\mathcal{H}^d|V \times\exp[-i(1-P^0)\mathcal{H}\tau]V[|\mathcal{H}^+\rangle\mathcal{H}^-(t') +|\mathcal{H}^-\rangle\mathcal{H}^+(t')], \quad (19)$$

where

$$\frac{d\mathcal{H}^{\pm}_B(t)}{dt}=\pm i\Delta\mathcal{H}^{\pm}(t)\pm\frac{\omega_1^2}{2i\Delta}\mathcal{H}^z(t) -\langle\mathcal{H}^+|\mathcal{H}^-\rangle^{-1}\int_0^t dt'\langle\mathcal{H}^{\pm}|\mathcal{H}^0 \times\exp[-i(1-P^0)\mathcal{H}\tau]\mathcal{H}^0|\mathcal{H}^{\mp}\rangle\mathcal{H}^{\pm}(t'), \quad (20)$$

$$\frac{d\mathcal{H}^z_B(t)}{dt}=-i\Delta[\mathcal{H}^+(t)-\mathcal{H}^-(t)]-\frac{\mathcal{H}^z(t)-\mathcal{H}^z_0}{T_z}, \quad (21)$$

i.e., the Bloch equations with memory,[6,12] from which it is easy to obtain the phenomenological Bloch equations,[11] if the upper limit in (20) is replaced by ∞, $\mathcal{H}^{\pm}(t)$ is taken out of the integral sign, and the remaining integral is denoted by T_2^{-1} [the term describing spin-lattice relaxation, i.e., the tendency of $\mathcal{H}^z(t)$ to attain its equilibrium value $\mathcal{H}^z_0$ with the time T_z, was introduced phenomenologically into (21), although it can be taken into account rigorously in the memory-function formalism[3]]:

$$\frac{d\mathcal{H}^z_P(t)}{dt}=-\langle\mathcal{H}^z|\mathcal{H}^z\rangle^{-1}\int_0^t dt'\langle\mathcal{H}^z|V \times\exp[-i(1-P^0)\mathcal{H}\tau]V[|\mathcal{H}^z\rangle\mathcal{H}^z(t') +|\mathcal{H}^d\rangle\varepsilon|\mathcal{H}^d(t')], \quad (22)$$

$$\frac{d\mathcal{H}^d_P(t)}{dt}=-\langle\mathcal{H}^z|\mathcal{H}^z\rangle^{-1}\int_0^t dt'\langle\mathcal{H}^d|V \times\exp[-i(1-P^0)\mathcal{H}\tau]V[|\mathcal{H}^z\rangle\mathcal{H}^z(t') +|\mathcal{H}^d\rangle\varepsilon|\mathcal{H}^d(t')], \quad (23)$$

i.e., the equations from which, following Ref. 3 exactly, we can obtain the generalized Provotorov equations.

The system of equations (17)–(19), whose derivation is the main purpose of the present work, describes the coupled trivial and nontrivial (specified by memory functions) dynamics of the operators of interest I^x, I^y, I^z, and $\mathcal{H}^d$. We stress that this system of equations simultaneously includes both the Bloch equations with memory and the generalized Provotorov equations in the form of Eqs. (20) and (21) and Eqs. (22) and (23), respectively. If the spin-lattice relaxation is not taken into account, from (17)–(19) it is easy to find that

$$\frac{dV(t)}{dt}+\frac{d\mathcal{H}^z(t)}{dt}+\frac{d\mathcal{H}^d(t)}{dt}=0, \quad (24)$$

i.e., the energy is conserved. Finally, we note that in (17) we discarded the term

$$\pm\frac{\omega_1^2}{2\Delta}\sum_j\langle\mathcal{H}^z|\exp[-i(1-P^0)\mathcal{H}\tau]\mathcal{H}^0|Q^j\rangle(\langle Q^j|Q^j\rangle)^{-1},$$

since, if the perturbation V is discarded in the exponential (which will be done below), the corresponding integral kernel, i.e., memory function, vanishes, and, in addition, the terms proportional to dV/dt in (17) cancel out exactly.

3. Let us now move on to the solution of the system of equations (17)–(19) in the stationary case. We neglect the perturbation V everywhere in the exponential. While this is a generally accepted assumption for the last four integrals in Eqs. (17)–(19), i.e., for the integrals from (22) and (23), since the corresponding integral kernels already contain multipliers that are second-order with respect to the perturbation,[3,7] it is a somewhat stronger requirement for the remaining memory functions, which is still acceptable, since V is small. Then, from (17)–(19) we obtain

$$\frac{d\mathcal{H}^{\pm}(t)}{dt}=\pm i\Delta\mathcal{H}^{\pm}(t)\pm\frac{\omega_1^2}{2i\Delta}\mathcal{H}^z(t)-\int_0^t dt'g(\tau)e^{\pm i\Delta\tau} \times\{4\Delta^2\mathcal{H}^{\pm}(t')-\omega_1^2[\mathcal{H}^z(t')+\varepsilon\mathcal{H}^d(t')]\}, \quad (25)$$

$$\frac{d\mathcal{H}^z(t)}{dt}=-i\Delta[\mathcal{H}^+(t)-\mathcal{H}^-(t)]+2\Delta^2\int_0^t dt'g(\tau) \times[e^{-i\Delta\tau}\mathcal{H}^-(t')+e^{i\Delta\tau}\mathcal{H}^+(t')]-\omega_1^2 \times\int_0^t dt'g(\tau)\cos\Delta\tau[\mathcal{H}^z(t')+\varepsilon\mathcal{H}^d(t')], \quad (26)$$

$$\frac{d\mathcal{H}^d(t)}{dt}=2\Delta^2\int_0^t dt' g(\tau)[e^{-i\Delta\tau}\mathcal{H}^-(t')+e^{i\Delta\tau}\mathcal{H}^+(t')]-\omega_1^2\int_0^t dt' g(\tau)\cos\Delta\tau[\mathcal{H}^z(t')+\varepsilon\mathcal{H}^d(t')],\quad(27)$$

where

$$g(\tau)=\mathrm{Tr}(\mathcal{H}^+(\tau)\mathcal{H}^-)/\mathrm{Tr}(\mathcal{H}^+\mathcal{H}^-).\quad(28)$$

In obtaining Eqs. (25)–(27) we introduced new notation and performed several transformations, some of which are presented below as examples:

$$g(\tau)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{i\Delta\tau}g(\Delta)d\Delta,$$

$$\int_0^t dt'\frac{\langle\mathcal{H}^+|\mathcal{H}^0e^{-i\mathcal{H}^0\tau}\mathcal{H}^0|\mathcal{H}^-\rangle}{\langle\mathcal{H}^+|\mathcal{H}^-\rangle}\mathcal{H}^+(t')$$

$$=\int_0^t dt'\left\{\Delta^2\frac{\mathrm{Tr}\mathcal{H}^+\mathcal{H}^-(\tau)}{\mathrm{Tr}\mathcal{H}^+\mathcal{H}^-}-2i\Delta\frac{\mathrm{Tr}\mathcal{H}^+\mathcal{H}^-(\tau)}{\mathrm{Tr}\mathcal{H}^+\mathcal{H}^-}-\frac{\mathrm{Tr}\mathcal{H}^+\mathcal{H}^-(\tau)}{\mathrm{Tr}\mathcal{H}^+\mathcal{H}^-}\right\}e^{i\Delta\tau}\mathcal{H}^+(t')$$

$$=\int_0^t dt'[\Delta^2g(\tau)+2\Delta^2g(\tau)+\Delta^2g(\tau)]e^{i\Delta\tau}\mathcal{H}^+(t')$$

$$=4\Delta^2\int_0^t dt' e^{i\Delta t}g(\tau)e^{-i\Delta t'}\mathcal{H}^+(t'),$$

etc. Adding the spin-lattice term $[\mathcal{H}^d(t)-\mathcal{H}_0^d]/T_d$ to (27), utilizing the analogous term from (21) in (26) [$\mathcal{H}_0^d$ is the equilibrium value of the "energy" of the dipolar subsystem, T_d is the spin-lattice relaxation time, and $T_d^{-1}\approx 2T_z^{-1}$ to $3T_z^{-1}$ (Ref. 4)], and employing the Laplace transformation while utilizing the convolution and displacement theorems, we readily obtain the following system of algebraic equations

$$S\mathcal{H}^{\pm}(S)=\pm i\Delta\mathcal{H}^{\pm}(S)\pm\frac{\omega_1^2}{2i\Delta}\mathcal{H}^z(S)-4\Delta^2g(S\mp i\Delta)\mathcal{H}^{\pm}(S)+\omega_1^2g(S\mp i\Delta)\times[\mathcal{H}^z(S)+\varepsilon\mathcal{H}^d(S)],\quad(29)$$

$$S\mathcal{H}^z(S)-\mathcal{H}_0^z=-i\Delta[\mathcal{H}^+(S)-\mathcal{H}^-(S)]+2\Delta^2\times[g(S+i\Delta)\mathcal{H}^-(S)+g(S-i\Delta)\mathcal{H}^+(S)]-\frac{\omega_1^2}{2}[g(S+i\Delta)+g(S-i\Delta)][\mathcal{H}^z(S)+\varepsilon\mathcal{H}^d(S)]-\frac{\mathcal{H}^z(S)}{T_z}+\frac{1}{S}\frac{\mathcal{H}_0^z}{T_z},\quad(30)$$

$$S\mathcal{H}^d(S)-\mathcal{H}_0^d=2\Delta^2[g(S+i\Delta)\mathcal{H}^-(S)+g(S-i\Delta)\mathcal{H}^+(S)]-\frac{\omega_1^2}{2}[g(S+i\Delta)+g(S-i\Delta)][\mathcal{H}^z(S)+\varepsilon\mathcal{H}^d(S)]-\frac{\mathcal{H}^d(S)}{T_d}+\frac{1}{S}\frac{\mathcal{H}_0^d}{T_d},\quad(31)$$

where S is the Laplace transformation variable. We note that the multiplier $1/S$ permits finding the stationary solution without any hypotheses regarding the form of the correlation function $g(\tau)$. After the simple calculations of the determinants written on the basis of Eqs. (29)–(31), for the stationary values of the operators of interest we ultimately obtain

$$\mathcal{H}_{st}^{\pm}=\left\{\frac{\mathcal{H}_0^z\omega_1^2}{2\Delta^2}+4\pi^2\omega_1^2(g^2+g'^2)(\mathcal{H}_0^z+\varepsilon\mathcal{H}_0^d)+\frac{\omega_1^2}{2\Delta^2}\varepsilon W(\Delta)(\mathcal{H}_0^zT_d+\mathcal{H}_0^dT_z)-\pi\omega_1^2\Delta^{-1}g'\times(3\mathcal{H}_0^z-\varepsilon\mathcal{H}_0^d)\mp i\Delta^{-1}W(\Delta)(\mathcal{H}_0^z-\varepsilon\mathcal{H}_0^d)\right\}\{(4\pi g\Delta)^2+(1-4\pi g'\Delta)^2+W(\Delta)(T_z+\varepsilon T_d)\}^{-1},\quad(32)$$

$$\mathcal{H}_{st}^z=\frac{[(4\pi\Delta g)^2+(1-4\pi g'\Delta)^2]\mathcal{H}_0^z+W(\Delta)(\mathcal{H}_0^zT_d+\mathcal{H}_0^dT_z)}{(4\pi g\Delta)^2+(1-4\pi g'\Delta)^2+W(\Delta)(T_z+\varepsilon T_d)},\quad(33)$$

$$\mathcal{H}_{st}^d=\frac{[(4\pi g\Delta)^2+(1-4\pi g'\Delta)^2]\mathcal{H}_0^d+W(\Delta)(\mathcal{H}_0^zT_d+\mathcal{H}_0^dT_z)}{(4\pi g\Delta)^2+(1-4\pi g'\Delta)^2+W(\Delta)(T_z+\varepsilon T_d)},\quad(34)$$

where $g(\Delta)$ and $g'(\Delta)$ are the cosine and sine Fourier transforms of the correlation function (28), and $W(\Delta)=\pi\omega_1^2g(\Delta)$ is the probability of transitions caused by the variable magnetic field.

Neglecting $\mathcal{H}_0^d$ in comparison with $\mathcal{H}_0^z$ and taking into account that

$$\mathcal{H}_{st}^{\pm}=(I_{st}^x\pm iI_{st}^y)\omega_1/2,\mathcal{H}_{st}^z=\Delta I_{st}^z,$$

for the stationary values of the components of the total spin and the secular dipolar interactions we ultimately have

$$I^x_{st} \approx \omega_1 I^z_0 \frac{W_m T_d \Delta / D^2 + W W_m^{-1}\{-6\pi g' + \Delta^{-1}[1-8\Delta^2(g^2+g'2)]\}}{1+W_m(T_z+\varepsilon T_d)}, \quad (35)$$

$$I^y_{st} \approx -\frac{I^z_0}{\omega_1}\frac{2W_m}{1+W_m(T_z+\varepsilon T_d)}, \quad (36)$$

$$I^z_{st} \approx I^z_0 \frac{1+W_m \varepsilon T_d}{1+W_m(T_z+\varepsilon T_d)}, \quad (37)$$

$$\mathscr{H}^d_{st} \approx \mathscr{H}^z_0 \frac{W_m \varepsilon T_d}{1+W_m(T_z+\varepsilon T_d)}, \quad (38)$$

where

$$W_m = \frac{\omega_1^2}{4}\frac{K'(\Delta)}{[K'(\Delta)]^2+[\Delta - K''(\Delta)]^2} \quad (39)$$

is the probability of transitions with "memory," in which for greater familiarity, i.e., for correspondence with (3), we introduced the symbols $K'(\Delta)=4\pi\Delta^2 g(\Delta)$ and $K''(\Delta)=4\pi\Delta^2 g'(\Delta)$. It is seen that Eqs. (35)–(38) simultaneously describe phenomena which can be explained both by the Provotorov theory and by the Bloch theory with memory. In particular, the term $\sim \pi\omega_1^2 g(T_z+\varepsilon T_d)$ and the multiplier $\sim W_m$ point to the narrowing of the magnetic-resonance absorption line with increasing ω_1 and the nontrivial ("non-Gaussian" and "non-Lorentzian") character of its shape, which are characteristic of both the Provotorov theory and the theory of the line shape in the memory-function formalism.

Thus, the result of the Provotorov theory pertaining to the magnetic-resonance line shape and apparently the Provotorov theory as a whole can be combined with the results in Refs. 3, 5, 6, 12, and 13 within the memory-function formalism, which is actually the Zwanzig projection-operator technique used in the Provotorov theory plus the method of constructing projection superoperators proposed by Mori. Stated differently, the addition of Mori's method to the Zwanzig approach, i.e., the memory-function formalism, stipulates a corresponding addition and expansion of the scope of the Provotorov and Bloch theories.

4. Let us now test the hypothesis regarding the replacement of $g(\Delta)$ by the expression (3) in (1) and (2). The validity of this hypothesis can be seen at once from Eqs. (33) and (34) and Eqs. (37) and (38), which are stationary solutions of Eqs. (1) and (2) with spin-lattice terms, in which W is replaced by W_m. However, we utilize the principle of subordination,[14] i.e., we set $d\mathscr{H}^{\pm}(t)/dt=0$ in Eqs. (25)–(27). Then, determining $\mathscr{H}^{\pm}(S)$ from (27), substituting the result into (30), and performing the inverse Laplace transformation, we easily obtain

$$\frac{d\mathscr{H}^z(t)}{dt} = -\frac{d\mathscr{H}^d(t)}{dt}, \quad (40)$$

which would be expected in view of (24). Thus, the subordination of the "secondary" quantities $\mathscr{H}^{\pm}$ with respect to the primary quantities $\mathscr{H}^z$ and $\mathscr{H}^d$ in the present case enables us only to take into account the slowness of $\mathscr{H}^z$ and $\mathscr{H}^d$, to eliminate the trivial term from (26), and to thereby symmetrize this equation relative to (27), while the same principle makes it possible to obtain the Bloembergen-Purcell-Pound equation from the phenomenological Bloch equations.[11]

Now treating the off-diagonal operators as stationary operators, i.e., setting $S=0$ in Eqs. (29)–(31) only for the off-diagonal operators, obtaining the expressions for the stationary values of $\mathscr{H}^{\pm}(0)=\mathscr{H}^{\pm}_{st}$ from (29), and substituting the latter into (31) and the Laplace transform of Eq. (40), after some lengthy, but simple transformation we can obtain

$$\frac{d\mathscr{H}^z(t)}{dt} = -W_m(\mathscr{H}^z - \varepsilon\mathscr{H}^d), \quad (41)$$

$$\frac{d\mathscr{H}^d(t)}{dt} = W_m(\mathscr{H}^z - \varepsilon\mathscr{H}^d), \quad (42)$$

i.e., Eqs. (1) and (2), in which $g(\Delta)$ is represented by (3). Q.E.D.

5. Thus, using the memory-function formalism, we have obtained equations describing the interrelated dynamics of the components of the total spin and the secular dipolar interactions, from which the Bloch equations with memory can easily be obtained, if the role of the secular dipolar interactions is not taken into account. It has been shown that the Provotorov equations, which are distinguished from the original equations (1) and (2) by the specific form of the absorption line shape (3), follow from the equations obtained when the subordination principle is employed.

Stationary solutions, from which the stationary solutions of both the Bloch and Provotorov equations are obtained under appropriate assumptions, have been obtained.

The results obtained can be detected when magnetic resonance is observed using a detection device with a decay time far shorter than T_2. It is also noteworthy that, in principle, the equations for the spin degrees of freedom can be supplemented by Maxwell's equations, particularly by the equations for the field in the cavity.[15]

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[1)]We use the definition of the entropy of a nonequilibrium state adopted in Refs. 7 and 9.

[1] B. N. Provotorov, Zh. Éksp. Teor. Fiz. **41**, 1582 (1961) [Sov. Phys. JETP **14**, 1126 (1962)].
[2] V. A. Atsarkin, Zh. Éksp. Teor. Fiz. **58**, 1884 (1970) [Sov. Phys. JETP **31**, 1012 (1970)].

[3]A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Clarendon Press, Oxford, 1982) [Russ. transl., Mir, Moscow, 1984].
[4]M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon Press, Oxford, 1970) [Russ. transl., Mir, Moscow, 1972].
[5]M. Mehring, *High Resolution NMR Spectroscopy in Solids* (Springer-Verlag, Berlin–Heidelberg–New York, 1976) [Russ. transl., Mir, Moscow, 1980].
[6]É. Kh. Khalvashi, Doctoral Dissertation, Tbilisi State University, Tbilisi (1993).
[7]D. N. Zubarev, *Modern Methods of the Statistical Theory of Nonequilibrium Processes (Results of Science and Technology. Current Problems in Mathematics, Vol. 15)* [in Russian] (VINITI, Moscow, 1980), p. 131.
[8]R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975) [Russ. transl., Vol. 2, Mir, Moscow, 1978].
[9]G. Röpke, *Statistische Mechanik für das Nichtgleichgewicht* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1987) [Russ. transl., Mir, Moscow, 1990].
[10]N. N. Korst, Zh. Éksp. Teor. Fiz. **40**, 249 (1961) [Sov. Phys. JETP **13**, 171 (1961)].
[11]I. V. Aleksandrov, *Theory of Magnetic Relaxation, Relaxation in Liquid and Solid Nonmetallic Paramagnetic Substances* [in Russian] (Nauka, Moscow, 1975).
[12]L. L. Buishvili, M. D. Zviadadze, and É. Kh. Khalvashi, Zh. Éksp. Teor. Fiz. **91**, 310 (1986) [Sov. Phys. JETP **64**, 181 (1986)].
[13]É. Kh. Khalvashi, Izv. Vyssh. Uchebn. Zaved., Radiofiz. **32**, 923 (1989).
[14]H. Haken, *Light, Vol. 2. Laser Light Dynamics* (North-Holland, Amsterdam–New York, 1985) [Russ. transl., Mir, Moscow, 1988].
[15]N. P. Fokina, K. O. Khutsishvili, and S. G. Chkhaidze, Zh. Éksp. Teor. Fiz. **102**, 1013 (1992) [Sov. Phys. JETP **75**, 552 (1992)].

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