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CONTRIBUTION TO THE QUANTUM-STATISTICAL THEORY OF DYNAMIC POLARIZATION OF NUCLEI

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A quantum-statistical analysis of the dynamic polarization of nuclei is carried out by taking into account diffusion of the nuclear spins as well as the dipole interaction of the electron spins. A set of integro-differential equations is obtained for the nuclear Zeeman, electron Zeeman, and dipole-dipole reservoir temperatures. Various particular cases are discussed.

1. WHEN forbidden paramagnetic resonance in a solid becomes saturated by a magnetic field perpendicular to the constant field, the nuclei acquire a large polarization. This phenomenon is called dynamic nuclear polarization (DNP) and is the most powerful method of polarizing nuclei.

DNP has been the subject of several papers.[1-3] In the theoretical analysis[3-5] it is assumed that the line width of the electron resonance is due to dipole-dipole interaction. If the concentration of the paramagnetic impurities is sufficiently large or if the experiments are carried out at low temperatures, then the line width of the electron resonance is indeed due to dipole-dipole interaction. The cited papers treat spatially-homogeneous cases; thus, no account is taken of the inhomogeneity of the thermodynamic quantities. However, in experiments aimed at obtaining DNP, there are many nuclear spins for each paramagnetic spin. The nuclear spins located near the impurity greatly interact with the spin of the ion and become polarized more rapidly than the remote nuclear spins. This creates a gradient of the nuclear spin temperature and spin diffusion takes place in the DNP process.

An equation for DNP with spin diffusion taken into account was derived by Winter[6] on the basis of simple physical considerations. He disregarded the electronic dipole-dipole reservoir.

In the present paper we present a rigorous quantum-statistical analysis with a consistent account of both the electronic dipole-dipole reservoir and of nuclear spin diffusion.

If the amplitude of the external alternating field is so small that the transition probability due to the external field is smaller than the transition probability associated with the interaction within an individual subsystem, then the entire system will be in a quasi-equilibrium state during the process of energy absorption from the external alternating field. Under these conditions we can use the method developed by Zubarev[7] for the construction of the nonequilibrium density matrix. In this method one constructs local integrals of motion with the aid of the conservation laws, and these integrals are used in trying to construct the statistical operator.

2. Neglecting the lattice, our system consists of three subsystems: the nuclear and electronic Zeeman subsystems and the dipole-dipole reservoir of the electronic subsystem. The secular parts of the intranuclear and nuclear-electronic dipole-dipole interaction are not regarded as subsystems, for the sake of simplicity.

The Hamiltonian of the system is written in the form

$$H = \omega_e \sum_n S_n^z - \omega_n \sum_i I_i^z + H_{SS} + H_{II} + \frac{1}{2} \sum_{in} (v^{-z}(in) I_i^+ + v^{+z}(in) I_i^-) S_n^z + \frac{\omega_{e1}}{2} \sum_n (S_n^+ e^{i\omega t} + S_n^- e^{-i\omega t}); \quad (1)$$

the first and second terms are, respectively, the nuclear and electronic Zeeman energies, the third and fourth are the secular parts of the interaction of the intraelectronic and intranuclear subsystems, respectively, the fifth term is the part of the dipole-dipole interaction between the electron and nucleus leading to the effect, and the last term is the interaction between the electronic subsystem and the external alternating field.

For a thermodynamic analysis it is convenient to go over to a rotating coordinate frame in which the Hamiltonian (1) does not depend exclusively on the time.[3] Then the Hamiltonian takes the form

$$H^* = (\omega_e - \omega) \sum_n S_n^z - \omega_n \sum_i I_i^z + H_{SS} + H_{II}$$

$$+\frac{1}{2}\sum_{in}(v^{+z}(in)I_i^- + v^{-z}(in)I_i^+)S_n^z$$

$$+\frac{\omega_{e1}}{2}\sum_n (S_n^+ + S_n^-). \tag{2}$$

To construct a nonequilibrium density matrix we write out, following Zubarev,[7] the integrals of motion. Inasmuch as inhomogeneities can occur only in the intranuclear Zeeman subsystem, we must set up density equations for it. These equations are

$$\frac{\partial H_I(x)}{\partial t} + \operatorname{div} j_I(x) = K_I(x), \qquad \frac{\partial H_S}{\partial t} = K_S,$$

$$\frac{\partial H_{SS}}{\partial t} = -\int K_I(x)\,dx - K_S. \tag{3}$$

The first equation was obtained by Zubarev and the author[8]1) and the last is the result of the energy conservation law, neglecting the change in the energy of interaction between the subsystems

$$H_I(x) = -\omega_n \sum_i I_i^z \delta(x - x_i), \qquad H_S = (\omega_e - \omega)\sum_n S_n^z,$$

$$K_I(x) = -\frac{\omega_n}{2i}\sum_{in} S_n^z (v^{-z}(in) I_i^+ + v^{+z}(in) I_i^-)\delta(x - x_i),$$

$$K_S = \frac{\omega_e - \omega}{2i}\,\omega_{e1}\sum_n (S_n^+ - S_n^-), \tag{4}$$

where $j_I(x)$ is the flux density, an explicit expression for which is given in I.

The integrals of motion take the form[7]

$$A_I(x) = H_I(x) - \int_{-\infty}^{0} e^{\varepsilon t}\{K_I(x, t) - \operatorname{div} j_I(x, t)\}\,dt,$$

$$A_S = H_S - \int_{-\infty}^{0} e^{\varepsilon t} K_S(t)\,dt,$$

$$A_{SS} = H_{SS} + \int_{-\infty}^{0} e^{\varepsilon t}\left[\int dx\, K(x, t) + K_S(t)\right]dt. \tag{5}$$

Therefore, if we assume that a quasiequilibrium state is established in the rotating coordinate system, the density matrix will be of the form

$$\rho = Q^{-1}\exp\Big\{-\int \beta_I(x) H_I(x)\,dx - \beta_S H_S - \beta_d H_{SS}$$
$$+ \int_{-\infty}^{0} e^{\varepsilon t}\,dt\Big\{\int dx\,[j_I(x, t)\nabla\beta_I(x) + K_I(x, t)(\beta_I - \beta_d)]$$
$$+ K_S(t)(\beta_S - \beta_d)\Big\}\Big\}, \tag{6}$$

where β is the reciprocal temperature.

When setting up the density matrix, we have neglected in the integrals the time dependence of the slowly-varying thermodynamic quantities compared with the rapidly-varying correlators. In the linear approximation with respect to the thermodynamic forces we can write with the aid of (6)

$$\langle j_I(x)\rangle = D'\nabla\beta_I(x),$$

$$\langle K_I(x)\rangle = L_{IS}(x)\frac{\beta_S - \beta_d}{\beta_d} + \int L_{II}(xx')\frac{\beta_I(x') - \beta_d}{\beta_d}\,dx',$$

$$\langle K_S\rangle = L_{SS}\frac{\beta_S - \beta_d}{\beta_d} + \int L_{SI}(x')\frac{\beta_I(x') - \beta_d}{\beta_d}\,dx', \tag{7}$$

where

$$L_{\alpha,\beta} = \int_0^{\beta_d} d\lambda \int_{-\infty}^{0} e^{\varepsilon t}\,dt\,\langle K_\alpha K_\beta(t + i\lambda)\rangle,$$

α, β = I, S, and an explicit expression for D′ is given in I.

To calculate the correlators $L_{\alpha,\beta}$ in the expression, we shall use perturbation theory with respect to the last two terms of (2) (denoted by H′). If the remaining part of the Hamiltonian (2) is denoted by H_0, then K_α can be written in the form

$$K_\alpha(t) = K_\alpha^{(0)}(t) + K_\alpha^{(1)}(t) + K_\alpha^{(2)}(t) + \ldots$$

$$K_\alpha^{(0)}(t) = e^{iH_0 t} K_\alpha e^{-iH_0 t}, \qquad K_\alpha^{(n)}(t) = i\int_0 [H', K_\alpha^{(n-1)}(t')]\,dt'. \tag{8}$$

3. Let us consider the case of a strong external field, when the Zeeman energy of the spins is much larger than the energy of interaction between the spins, and let us also assume that $\beta\omega_e < 1$, that is, that the temperature is high.

In this situation, the expression for $L_{\alpha,\beta}$ becomes

$$L_{\alpha,\beta} = \beta_d \int_{-\infty}^{0} e^{\varepsilon t}\langle K_\alpha K_\beta(t)\rangle\,dt. \tag{9}$$

We ultimately obtain

$$L_{IS}(x) = \beta_d \frac{(\omega_e - \omega)\omega_n I(I+1)}{3(2I+1)}(W_x(\omega^+) - W_x(\omega^-))n_I,$$

$$\int L_{II}(xx') f(x')\,dx' = \frac{\omega_n^2 I(I+1) n_I}{3(2I+1)\tau(x)} f(x)$$
$$+ \frac{\omega_n}{3} n_I \frac{I(I+1)}{(2I+1)} f(x)(W_x(\omega^+) + W_x(\omega^-)),$$

$$L_{SS} = \frac{(\omega_e - \omega)^2 S(S+1)}{3(2S+1)} n_S \beta_d W_0(\omega - \omega_e)$$
$$+ \frac{(\omega_e - \omega)^2}{3(2S+1)} I(I+1) n_I \int (W_x(\omega^+) + W_x(\omega^-))\,dx,$$

$$\int L_{IS}(x') f(x')\,dx' = (\omega_e - \omega)\omega_n \beta_d \frac{I(I+1) n_I}{3(2I+1)} \int f(x)$$
$$\times (W_x(\omega^+) - W_x(\omega^-))\,dx, \tag{10}$$

where $\omega t = \omega - \omega_e \pm \omega_n$, n_S and n_I are the num-

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[1] Henceforth cited as I.

bers of the electronic and nuclear spins (it is assumed that the volume is equal to unity),

$$W_x(\omega^\pm) = \frac{\pi\omega_{1e}^2 S(S+1)}{6(2S+1)} \sum_n \frac{|V_{x,n}^{z+}|^2}{\omega_n^2} g(\omega^\pm)$$

is the probability of the forbidden transition,

$$W(\omega-\omega_e) = \pi\omega_{e1}^2 g(\omega-\omega_e)\,/\,2$$

is the probability of the usual allowed transition, $\tau(x)$ is the direct relaxation time, for which an expression is given in I, f(x) is an arbitrary function, and $g(\omega)$ is a function characterizing the shape of the spectral line.

Using the local form of the first law of thermodynamics, we ultimately obtain with the aid of (7) and (10) the sought equations for β_I, β_S and β_d:

$$\frac{\partial\beta_I}{\partial t} = D\Delta\beta_I(x) - \frac{\beta_I(x)-\beta_d}{\tau(x)} - \sum_{k=\pm} W_x(\omega^k)\left(\beta_I(x) + k\beta_d\frac{\omega^k}{\omega_n} + k\beta_S\frac{\omega_e-\omega}{\omega_n}\right), \quad (11a)$$

$$\frac{\partial\beta_S}{\partial t} = -2W_0(\omega-\omega_e)(\beta_S-\beta_d) - C\sum_{k=\pm}\int dx W_x(\omega^k) \times\left(k\beta_I(x) + \frac{\omega_e-\omega}{\omega_n}\beta_S + \beta_d\frac{\omega^k}{\omega_n}\right), \quad (11b)$$

$$\frac{\partial\beta_d}{\partial t} = 2\alpha W(\omega-\omega_e)(\beta_S-\beta_d) + \sum_{k=\pm}\int dx\left\{\delta^k W_x(\omega^k) \times\left(k\beta_I(x) + \frac{\omega_e-\omega}{\omega_n}\beta_S + \beta_d\frac{\omega^k}{\omega_n}\right)\right\} + \gamma\frac{\beta_I(x)-\beta_d}{\tau(x)},$$

$$C = \frac{(2S+1)I(I+1)}{S(S+1)(2I+1)}\frac{\omega_n}{\omega_e-\omega}\frac{n_I}{n_S},$$

$$\alpha = \frac{(\omega_e-\omega)^2 S(S+1)(2S+1)^{n_S}}{3(2S+1)\,\mathrm{Sp}\,H_d^2},$$

$$\gamma = \frac{\omega_n^2 I(I+1)(2S+1)^{n_S}}{3(2I+1)\,\mathrm{Sp}\,H_d^2}, \qquad \delta^\pm = \alpha C \pm \gamma. \quad (11c)$$

When account is taken of the spin-lattice relaxation, certain known terms[3] are added to the first part of (11).

We see that Eq. (11), unlike the results of [3, 6], constitutes a system of integral-differential equations. They can be simplified only if one can neglect in (11b) and (11c) the terms containing the interaction with the nuclear subsystem. We have here two possibilities.

A. When the electron line is so narrow that we can neglect the usual allowed transitions, then β_d and β_S are replaced by β_l (β_l is the reciprocal temperature of the lattice), and the equation for β_I coincides with the equation obtained by Winter,[6] the only difference being that the time of the spin-lattice relaxation of electrons, which enters the expression for the direct relaxation time, is replaced by the spin-spin correlation time.

B. When account must be taken of allowed transitions, β_d and β_S are not replaced by β_l and comprise the solution of the solutions of the following equations:

$$\frac{\partial\beta_S}{\partial t} = -2W(\omega_e-\omega)(\beta_S-\beta_d) - \frac{1}{\tau_S}\left(\beta_S - \frac{\omega_e}{\omega_e-\omega}\beta_l\right),$$

$$\frac{\partial\beta_d}{\partial t} = 2\alpha W(\omega_e-\omega)(\beta_S-\beta_d) - \frac{\gamma_1}{\tau_S}(\beta_d-\beta_l), \quad (12)$$

where τ_S is the spin-lattice relaxation time of the electrons and γ_1 is a numerical factor with an approximate value of two.

Following Winter,[6] we can easily obtain the solution of systems (11a) and (12). We present only the stationary value of the nuclear spin temperature

$$\frac{\beta_I}{\beta_l} = \frac{(\omega_e/\omega_n)(\Gamma^- - \Gamma^+)}{(C_1+\Gamma^-+\Gamma^+)[1+((1+2\alpha^2)/2\alpha^2)W(\omega_e-\omega)\tau_S]} + \frac{\omega_e W(\omega_e-\omega)\tau_S}{(\omega_e-\omega)[2\alpha^2+W(\omega_e-\omega)\tau_S(1+2\alpha^2)]}, \quad (13)$$

where $\Gamma^\pm = W(\omega^\pm)r^6$, $C_1 = \tau^{-1}r^6$, and r is the distance from the nucleus to the paramagnetic center.

The first term of (13) corresponds to the usual DNP effect. The maximum increase in polarization is ω_e/ω_n. The second term is due to the presence of the dipole-dipole reservoir. It is not connected with forbidden transitions, and is governed by allowed transitions and is equal to zero at the resonance point. Physically this is explained by the fact that in ordinary electronic resonance, the dipole-dipole reservoir cools down if $\omega \neq \omega_e$.[9] Since the nuclear spins are in equilibrium with the dipole-dipole reservoir in our analysis, they will also be cooled, of course. The maximum decrease in the temperature is obtained when $\omega = \omega_e - \sqrt{2}\,\Delta\omega$ and is equal to $\sim \omega_e\beta_l/\Delta\omega$, where $\Delta\omega$ is the width of the electron resonance. When $\Delta\omega < \omega_n$, it is clear that the polarization corresponding to the second term will prevail over the effect connected with the first term.

Finally, we note that Abragam and Borghini[3] also investigated in the homogeneous case an effect similar to the second term in (13). However, since they did not take into account the nuclear relaxation via the dipole-dipole reservoir, the effect under consideration is connected with simultaneous saturation of both the allowed and the forbidden resonances. Kozhushner[5] also considered the case of simultaneous saturation of forbidden and allowed resonances.

4. So far we have not considered the case when the expressions containing the interactions with the nuclei are neglected in (11b) and (11c). This neglect is practically always valid in the equation for β_S. As regards (11c), this may not be the case at low temperatures, when the rate of spin-lattice relaxation of the electrons is low. Then, even if we disregard the forbidden transitions and investigate only the relaxation process, we must study, unlike the earlier investigations,[10] a system consisting of two integro-differential equations.

In the present paper we confine ourselves to a study of nuclear relaxation in the homogeneous case.[2)]

If we take exact account of the spin-lattice interaction in the equation for β_I we obtain the following system of equations:

$$\frac{d\beta_I}{dt} = -\frac{\beta_I - \beta_l}{\tau_I} + \frac{\beta_d - \beta_l}{\tau_{Id}},$$

$$\frac{d\beta_d}{dt} = \frac{\beta_I - \beta_l}{\tau_{dI}} - \frac{\beta_d - \beta_l}{\tau_d}, \tag{14}$$

where

$$\frac{1}{\tau_I} = \frac{1}{\tau_{Id}} + \frac{1}{\tau_{Il}}, \qquad \frac{1}{\tau_d} = \frac{1}{\tau_{dl}} + \frac{1}{\tau_{dI}},$$

$$\frac{1}{\tau_{Id}} = -\frac{2I+1}{\mathrm{Sp}(H_I)^2}\beta_l \int\limits_{-\infty}^{0} e^{\varepsilon\tau}\, d\tau\, \langle [H_I, H_{IS}][H_d, H_{IS}](\tau)\rangle,$$

$$\frac{1}{\tau_{Il}} = -\frac{2I+1}{\mathrm{Sp}(H_I)^2}\beta_l \int\limits_{-\infty}^{0} e^{\varepsilon\tau}\, d\tau\, \langle [H_I, H_{IS}][H_l + H_d, H'](\tau)\rangle,$$

$$\tau_{dl}^{-1} = 2\tau_S^{-1}, \qquad \tau_{dI} / \tau_{Id} = E_I / E_d,$$

E_I and E_d are respectively the energy of the nuclear Zeeman and electronic dipole-dipole subsystems.

Equations (14) coincide formally with the equations obtained earlier,[11] where their general solution has been analyzed.

We present only two particular cases:

$$\tau_{Id} < \tau_{Il}, \quad \tau_{dl} < \tau_{dI}, \tau_{Id}, \tag{15}$$

and obtain

$$\partial\beta_I / \partial t = -(\beta_I - \beta_l) / \tau_{Id},$$

which corresponds to the case when the energy is transferred to the lattice via the dipole-dipole reservoir, and β_d does not change in this process, since it had time to relax. τ_{Id} will usually coincide with the expression obtained in [10] for τ, except that the correlators will contain not τ_S, but the spin-spin correlation time.

We note that the analysis carried out by Khutsishvili[12] is valid under the conditions (15).

However, at low temperatures, the condition (15) may be replaced by the following relations

$$\tau_{Id} < \tau_{Il}, \quad \tau_{dI} < \tau_{dl} \text{ and } \tau_{dI} < \tau_{Id}.$$

Then the relaxation will proceed in two steps and the long relaxation time is expressed in the following manner:

$$\frac{1}{T} = \frac{E_d}{E_I}\frac{1}{\tau_{dl}} + \frac{1}{\tau_{Il}} \tag{16}$$

We see that in spite of the fact that the coupling between the nuclear spins and the dipole-dipole reservoir is stronger than the coupling with the lattice, the relaxation of the nuclei will depend on the spin-lattice interaction of the electron spin. If we neglect the second term of (16), then we can state that the "bottleneck" effect exists between the dipole-dipole reservoir and the lattice.

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[2)] This question was considered by the author together with N. Bendiashvili.

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