ON THE THEORY OF DOUBLE ELECTRON AND NUCLEAR RESONANCE IN SYSTEMS WITH HYPERFINE INTERACTION

T. G. IZYUMOVA and G. V. SKROTSKIĬ

Ural Polytechnic Institute

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The complex susceptibility of electron spins interacting with a nuclear system is calculated on the basis of the statistical perturbation theory. The dependence of the conditions for the saturation of the electron system on the resonance conditions of the nuclear system is obtained.

1. INTRODUCTION

THE method of double magnetic resonance is applied to systems containing two different kinds of magnetic moments. The sample to be investigated is placed in a constant magnetic field $H_0 = H_Z$ and in two periodic fields of frequencies close to the Larmor precession frequencies for both kinds of magnetic moments. The existence of an interaction between the magnetic moments of the two systems (for example, hyperfine interaction) leads to the result that resonance in one of the systems has an effect on the nature of the resonance in the other system. In systems exhibiting both nuclear and electronic paramagnetism the existence of hyperfine interaction results in a number of effects which may be divided into two groups.

To the first group belong the effects associated with the influence of the electron paramagnetic resonance on the nuclear resonance. As the electron system approaches saturation an increase in the polarization of the nuclear magnetic moments (the Overhauser effect) may be achieved. The Overhauser effect[1] can be observed in substances with a "rapidly fluctuating lattice": in this case the method of double resonance is ordinarily used in order to intensify the nuclear magnetic resonance signal.

To the second group belong the effects associated with the influence of the nuclear resonance on the electron resonance. The first to observe this phenomenon experimentally and to give it a qualitative explanation was Feher.[2] The saturation of the nuclear system does not result in any appreciable polarization of the electron spins. However, it alters the conditions for the saturation of the electron system and, consequently, leads to a change in the absorption of energy from the radio frequency field by the electron system.

In order to explain this phenomenon Feher[2] considers a simple system consisting of electrons ($s = \frac{1}{2}$) and nuclei ($I = \frac{1}{2}$). In strong constant magnetic fields the energy level spectrum of such a system is of the form shown in the diagram. Transitions induced by a microwave field of frequency ω_S obey the selection rules $\Delta m_S = 1$ and $\Delta m_I = 0$. The amplitude of the signal due to these transitions is proportional to the difference in the populations of the levels E_1 and E_2'. If we partially saturate the electron system, then the signal due to the absorption of microwave power will be decreased. If at the same time we induce nuclear transitions of frequency ω_I, then the possibility arises of equalizing the populations of levels E_1 and E_2', as a result the difference in the populations of the levels E_2 and E_2' will increase, and this will in turn lead to an increase in the electron resonance signal. By inducing the nuclear transitions $E_1' \rightarrow E_1$, we can observe a sharp decrease in the electron resonance signal.

With such a formulation of the problem the method of double resonance turns out to be a sensitive means for studying the phenomenon of nuclear resonance. It enables us to determine, in particular, the value of the nuclear factor g_I. The method may be successfully applied in the case when the value of the hyperfine interaction $A(\mathbf{s}\cdot\mathbf{I})$ is small compared to the width of the electron resonance line, and therefore the hyperfine structure can not be resolved by the usual method of observing the absorption signal due to the electron system.[3] However, this turns out to be possible if the observations are made by the double resonance method, because of the small width of the nuclear resonance line.

The method enables us to resolve the hyperfine structure of a line due to an unpaired electron present in a complicated chemical compound arising from the interaction of this electron with the surrounding nuclei. Among such compounds we can include organic free radicals, irradiated crystals, and structures with displaced atoms or ruptured bonds. In this case we can obtain information with regard to the distribution of the electron density in molecules, crystals, F centers, etc.[4] Thus, the method of double resonance is of great practical interest.

In this paper we present a quantum-mechanical analysis of the phenomenon of the effect of nuclear magnetic resonance on the electron paramagnetic resonance in systems with hyperfine interaction. Such an analysis can not be carried through within the framework of the linear theory of magnetic resonance, since the very formulation of the problem assumes the possibility of applying strong radio frequency and microwave fields sufficient for the saturation both of electron and of nuclear resonance.

In this paper we have used the method of the statistical perturbation theory developed by Tomita[5] for the case of circularly-polarized radiation of arbitrary amplitude.

2. FORMULATION OF THE PROBLEM

We consider a system consisting of uncompensated electron spins $\mathbf{s}^k$, surrounded by several nuclei with different angular momenta $\mathbf{I}^l$. We assume the existence of a scalar interaction between the electrons and the nuclei, and also of an interaction of the electrons with the lattice. We place the sample in the magnetic field

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{h}_s(t) + \mathbf{h}_I(t), \tag{1}$$

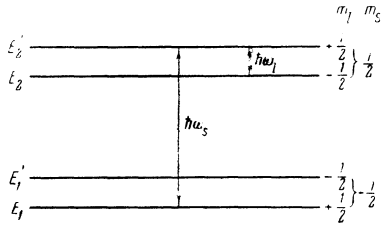
where $\mathbf{h}_S$ and $\mathbf{h}_I$ are respectively the intensities of the microwave and of the radio-frequency fields. These fields are circularly polarized in the plane perpendicular to $\mathbf{H}_0$.

We write the Hamiltonian for the system of electrons and nuclei in the following form

$$\hat{\mathcal{H}} = -g_s\mu_s\sum_k \hat{\mathbf{s}}^k\mathbf{H} - \sum_l g_l^I\mu_l^I\hat{\mathbf{I}}^l\mathbf{H} + \sum_{l,k} A_l\hat{\mathbf{s}}^k\hat{\mathbf{I}}^l + \hat{\mathbf{s}}\hat{\mathbf{F}} + \hat{\mathcal{H}}_F, \tag{2}$$

where μ_S and μ_I are the electron and the nuclear magnetons, while A_l is the hyperfine interaction constant. The term $\hat{\mathbf{s}}\cdot\hat{\mathbf{F}}$ where $\mathbf{s} = \Sigma\mathbf{s}^k$ takes into account the interaction of the electrons with the lattice, while $\hat{\mathcal{H}}_F$ is the operator for the energy of the "lattice".

For subsequent discussion it will be convenient to go over to the circular variables



$$\hat{s}_{\pm1} = \frac{1}{\sqrt{2}}(\hat{s}_x \pm i\hat{s}_y), \quad \hat{s}_0 = \hat{s}_z,$$

$$\hat{I}_{\pm1} = \frac{1}{\sqrt{2}}(\hat{I}_x \pm i\hat{I}_y), \quad \hat{I}_0 = \hat{I}_z, \tag{3}$$

in terms of which the microwave and the radio frequency fields assume the form

$$h^s_{+1} = h^s e^{-i\omega_s t}, \qquad h^s_0 = h^s_{-1} = 0;$$
$$h^I_{+1} = h^I_0 = 0, \qquad h^I_{-1} = h^I_0 e^{i\omega_I t}, \tag{4}$$

while the Hamiltonian (2) may be written in the following form:

$$\hat{\mathcal{H}} = -g_s\mu_s\sum_k \hat{s}^k_0 H_0 - g_s\mu_s\sum_{k,\mu\neq0}\hat{s}^k_\mu h^s_{-\mu} - g_s\mu_s\sum_{k,\mu\neq0}\hat{s}^k_\mu h^I_{-\mu}$$
$$-\sum_l g^I_l\mu^I_l\hat{I}^l_0 H_0 - \sum_{l,\mu\neq0} g^I_l\mu^I_l\hat{I}^l_\mu h^s_{-\mu} - \sum_{k,\mu\neq0} g^I_l\mu^I_l\hat{I}^l_\mu h^I_{-\mu}$$
$$+\sum_\mu \hat{s}_\mu\hat{F}_{-\mu} + \sum_{lk} A_l\hat{s}^k_\mu\hat{I}^l_{-\mu} + \hat{\mathcal{H}}_F. \tag{5}$$

In future we shall assume that the energy of the hyperfine interaction is small compared to the Zeeman energy of the electrons. In this case the electron and the nuclear spins precess about the strong constant field H_0 independently of each other. The hyperfine interaction introduces only a perturbation of this motion. This latter circumstance enables us to pose the problem of finding the complex susceptibility of the electron spin system by itself. The hyperfine interaction will lead to the "inhomogeneous broadening"[6] of the electron paramagnetic resonance line.

"Inhomogeneous broadening" occurs when in the spin system under consideration interactions are possible not only with spins of the same kind ("homogeneous broadening"), but also with other kinds of spins not belonging to this system. Interactions giving rise to "inhomogeneous broadening" do not leave the spin system in equilibrium. They may vary slowly with time. In the case under consideration the second last term in (5) depends on the time, since the nuclear system is also in a state of magnetic resonance.

3. EQUATIONS OF MOTION FOR THE MAGNETIZATION VECTOR OF THE ELECTRON SYSTEM

The density matrix for the whole system in the case under consideration may be written in the form

$$\hat{\rho} \sim e^{-\beta\hat{\mathcal{H}}}, \qquad \hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1, \qquad \beta = 1/kT, \quad (6)$$

$$\hat{\mathcal{H}}_1 = \sum_{lk} A_l \hat{s}_\mu^k \hat{I}_{-\mu}^l + \sum_\mu \hat{s}_\mu \hat{F}_{-\mu}. \quad (7)$$

In accordance with (5) $\hat{\mathcal{H}}_0$ consists of three parts corresponding to the energy of the electrons and of the nuclei in the external field, and also to the lattice energy $\hat{\mathcal{H}}_F$.

On utilizing the operator identity

$$\exp(-\beta(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1)) = \exp(-\beta\hat{\mathcal{H}}_0)\left\{1 - \int_0^\beta d\lambda \exp(\lambda\hat{\mathcal{H}}_0) \times \hat{\mathcal{H}}_1 \exp(-\lambda\hat{\mathcal{H}}_0) + \int_0^\beta d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \exp(\lambda_1\hat{\mathcal{H}}_0)\hat{\mathcal{H}}_1 \exp[-(\lambda_1 - \lambda_2)\hat{\mathcal{H}}_0]\hat{\mathcal{H}}_1 \exp(-\lambda_2\hat{\mathcal{H}}_0) + \ldots\right\} \quad (8)$$

and on taking into account that the energy of the hyperfine interaction $\hbar\omega_{int}$ is small compared to the Zeeman energy, while at the same time $\delta = \hbar\omega_{int}/kT \ll 1$, we shall write the density matrix (6) in the form of a product of three independent factors

$$\hat{\rho} = \hat{\sigma}\hat{\sigma}'\hat{\rho}'. \quad (9)$$

Here $\hat{\sigma}$ is the density matrix for the electron spin system, $\hat{\sigma}'$ is the density matrix for the nuclear spin system and $\hat{\rho}'$ is the density matrix for the lattice.

The magnetization for the electron system is, evidently, determined in the following manner:

$$\langle \hat{M}_s \rangle = \mathrm{Sp}(\hat{\sigma}\mu_s\hat{s}) = \mu_s \mathrm{Sp}(\hat{\sigma}_+\hat{s}) - \mu_s \mathrm{Sp}(\hat{\sigma}_-\hat{s}). \quad (10a)$$

Here $\hat{\sigma}_+$ describes the ensemble of electrons whose spins are opposite to the field, while $\hat{\sigma}_-$ describes those whose spins are parallel to the field.

Similarly, for the nuclear system we have

$$\langle \hat{M}_I \rangle = \mathrm{Sp}(\hat{\sigma}'\mu_I\hat{I}) = \mu_I \mathrm{Sp}(\hat{\sigma}'_-\hat{I}) - \mu_I \mathrm{Sp}(\hat{\sigma}'_+\hat{I}). \quad (10b)$$

On taking (10a) and (10b) into account we can rewrite (9) in the form

$$\hat{\rho} = (\hat{\sigma}_+ - \hat{\sigma}_-)(\hat{\sigma}'_+ - \hat{\sigma}'_-)\hat{\rho}' = (\hat{\sigma}_+\hat{\sigma}'_+ + \hat{\sigma}_-\hat{\sigma}'_- - \hat{\sigma}_+\hat{\sigma}'_- - \hat{\sigma}_-\hat{\sigma}'_+)\hat{\rho}'. \quad (10c)$$

It is necessary to carry out such a decomposition because in the problem under consideration when energy is absorbed from the microwave field transitions occur not from both hyperfine sublevels of the ground state, but only from the one which, for example, corresponds to the value of the nuclear magnetic quantum number $m_I = +\frac{1}{2}$. The transition may occur to the upper level $m_S = \frac{1}{2}$ which also corresponds to $m_I = \frac{1}{2}$.

The variation of $\hat{\rho}$ with time is determined by the equation of motion

$$-i\hbar\,\partial\hat{\rho}/\partial t = [\hat{\rho}\hat{\mathcal{H}}]. \quad (11)$$

If we do not restrict ourselves to the case of small amplitudes of the microwave field h_S, then we cannot assume that the system of electron spins is in a state of thermodynamic equilibrium, since it is acted upon by a large secular time-dependent perturbation. In a system of coordinates rotating about the direction of the constant magnetic field with frequency ω_S, the system of electron spins will be acted upon by an effective magnetic field which is independent of the time. Now only those terms will depend on the time which describe a weak interaction of the electrons with the nuclei and with the lattice. In this system of coordinates there exists an equilibrium distribution of electron spins determined by the Boltzmann factor. The effective field H_{eff} is inclined to the z axis at an angle ϑ:

$$\sin\vartheta = h^s[(H_0 + \omega_s/\gamma_s)^2 + h^{s2}]^{-1/2}, \quad \cos\vartheta = (H_0 + \omega_s/\gamma_s)[(H_0 + \omega_s/\gamma_s)^2 + h^{s2}]^{-1/2}, \quad (12)$$

$$H_{eff} = [(H_0 + \omega_s/\gamma_s)^2 + h^{s2}]^{1/2}. \quad (13)$$

The transition to the coordinate system rotating about the effective field is accomplished by means of the canonical transformation

$$\hat{s}_\mu^T = \exp(i\omega_s\hat{s}_0 t)\left(\sum_\nu a_{\mu\nu}(\vartheta)\hat{s}_\nu\right)\exp(-i\omega_s\hat{s}_0 t). \quad (14)$$

The matrix $a_{\mu\nu}(\vartheta)$ has the form

$$a_{\mu\nu}(\vartheta) = \begin{vmatrix} \frac{1}{2}(\cos\vartheta + 1) & 2^{-1/2}\sin\vartheta & \frac{1}{2}(\cos\vartheta - 1) \\ -2^{-1/2}\sin\vartheta & \cos\vartheta & -2^{-1/2}\sin\vartheta \\ \frac{1}{2}(\cos\vartheta - 1) & 2^{-1/2}\sin\vartheta & \frac{1}{2}(\cos\vartheta + 1) \end{vmatrix}. \quad (15)$$

Here μ and ν take on in turn the values 1, 0, − 1.

Upon application of the transformation (14), Eq. (11) is written in the following form:

$$-i\hbar\,d\hat{\rho}^T/dt = [\hat{\rho}^T\hat{\mathcal{H}}^T]. \quad (16)$$

Here

$$\hat{\mathcal{H}}^T = \hat{\mathcal{H}}_0^T + \hat{\mathcal{H}}_1^T(t), \quad (17)$$

$$\hat{\mathcal{H}}_0^T = -\sum_k \gamma^s\hbar\hat{s}_0^k\left(H_0 + \frac{\omega_s}{\gamma_s}\right) - \sum_{k,\mu\neq 0}\gamma^s\hbar\hat{s}_\mu^k h_{-\mu}^s + \hat{\mathcal{H}}_F - \sum_l g_l^l\mu_l^l\hat{I}_0^l H_0 \quad (18)$$

$$\hat{\mathcal{H}}_1^T(t) = \sum_{l,k,\mu} A_l\hat{s}_\mu^k I_{-\mu}^l e^{i\mu\omega_s t} + \sum_{k,\mu}\hat{s}_\mu^k F_{-\mu}e^{i\mu\omega_s t}, \quad \hbar\gamma^s = g_s\mu_s \quad (19)$$

On assuming that the time interval t defined by the inequality $\epsilon = \mathcal{H}_1^T t/\hbar \ll 1$ is greater than the relaxation time for the electron spin system we can utilize time-dependent perturbation theory. In order to do this it is convenient to go over to the interaction representation, and to expand the density matrix in powers of the parameter ϵ retaining second order terms:

$$\hat{\rho}^{T*}(t) = \hat{\rho}^{T*}(0) - \frac{i}{\hbar}\int_0^t [\hat{\rho}^{*T}(0)\,\hat{\mathcal{H}}_1^{*T}(t_1)]\,dt_1$$

$$-\frac{1}{\hbar^2}\int_0^t\int_0^{t_1} dt_1 dt_2\,[[\hat{\rho}^{*T}(0)\,\hat{\mathcal{H}}_1^{*T}(t_1)]\hat{\mathcal{H}}_1^{T*}(t_2)]. \qquad (20)$$

We note that ϵ^2 always remains greater than δ, and, therefore, the neglect of terms linear in δ in (8) is quite legitimate.

It is necessary to average expression (20) over the canonical ensemble of the nuclei and the "lattice." After averaging and differentiation with respect to time we shall obtain the approximate equation for the density matrix of the electron system in the interaction representation:

$$\frac{\partial\hat{\sigma}^{T*}(t)}{\partial t} = -\frac{i}{\hbar}\frac{\partial}{\partial t}\int_0^t \langle[\hat{\rho}^{*T}(0)\,\hat{\mathcal{H}}_1^{*T}(t_1)]\rangle_{\sigma',\rho'}dt_1$$

$$-\frac{1}{\hbar^2}\frac{\partial}{\partial t}\int_0^t\int_0^{t_1} dt_1 dt_2\,\langle[[\hat{\rho}^{*T}(0)\,\hat{\mathcal{H}}_1^{*T}(t_1)]\,\hat{\mathcal{H}}_1^{*T}(t_2)]\rangle_{\sigma',\rho'}. \qquad (21)$$

In averaging over the ensemble of the nuclei we must distinguish two cases, depending on what type of nuclear transitions are induced. In the transitions $E_1' \rightarrow E_1$ it is necessary to take into account only the nuclei coupled to the electrons parallel to the field, and the averaging is taken only over the part of the density martix $\sigma_+(\sigma_+' - \sigma_-')$ from (10c). If the transitions $E_2 \rightarrow E_2'$ are being induced, then it is necessary to average over the other part of (10c) $\sigma_-(\sigma_+' - \sigma_-')$, since in this case we consider only the nuclei coupled to the electrons whose spins are directed oppositely to the field. In these two cases the averages of the terms including the hyperfine interaction will differ only in their sign.

It is necessary to substitute expression (19) into equation (21), and in doing so it is necessary to keep in mind that in the problem under consideration we neglect the satellite absorption lines of the electron system (their frequencies lie far from the main line). Therefore, in the term linear in $\hat{\mathcal{H}}_1$ it is necessary to set $\mu = 0$, and in the quadratic term to set $\mu = -\mu'$. Then after a straightforward calculation we obtain:

$$\frac{\partial\hat{\sigma}^{*T}(t)}{\partial t} = -\frac{i}{\hbar}e^{-i\nu\Omega_1 t}\sum_{k\nu} a_{0\nu}(\vartheta)\left\{\langle\hat{F}_0^*(t_1)\rangle \mp \sum_i A_i\langle\hat{I}_{i0}^*(t_1)\rangle\right\}$$

$$\times[\hat{\sigma}^{*T}(0)\,\hat{s}_{k\nu}] - \frac{1}{\hbar^2}\sum_{k\mu\nu\nu'} a_{\mu\nu}(\vartheta)\,a_{-\mu\nu}(\vartheta)\exp(-i\nu\Omega_1 t$$

$$-i\nu'\Omega_1 t)\int_0^t d\tau\exp(i\mu\omega_1\tau + i\nu'\Omega_1\tau)\left\{\left(\langle\hat{F}_{-\mu}^*(\tau)\,\hat{F}_\mu^*(0)\rangle\right.\right.$$

$$\left.\mp\sum_l A_l^2\langle\hat{I}_{-\mu}^*(\tau)\hat{I}_\mu^*(0)\rangle\right)[\hat{s}_\nu\hat{s}_{\nu'}\hat{\sigma}^{*T} - \hat{s}_{\nu'}\hat{\sigma}^{*T}\hat{s}_\nu]$$

$$+\left(\langle\hat{F}_\mu^*(0)\,\hat{F}_{-\mu}^*(\tau)\rangle \mp \sum_l A_l^2\langle\hat{I}_\mu^*(0)\,\hat{I}_{-\mu}^*(\tau)\rangle\right)[\hat{\sigma}^{*T}\hat{s}_{\nu'}\hat{s}_\nu$$

$$\left.-\hat{s}_\nu\hat{\sigma}^{*T}\hat{s}_{\nu'}]\right\}. \qquad (22)$$

The left hand side of (22) can be written in the form

$$\frac{\partial}{\partial t}\hat{\sigma}^{*T} = \frac{\partial}{\partial t}\left\{\exp\left(-i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right)\hat{\sigma}^T\exp\left(i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right)\right\}$$

$$= \exp\left(-i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right)\left\{\frac{\partial\hat{\sigma}^T}{\partial t} + i\left[\hat{\sigma}^T,\ \frac{\hat{\mathcal{H}}_0^T}{\hbar}\right]\right\}\exp\left(i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right). \qquad (23)$$

On multiplying both parts of (22) on the left by $\exp(i\hat{\mathcal{H}}_0 t/\hbar)$ and on the right by $\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$, and on noting that in the energy representation ($\hat{\mathcal{H}}_0^T$ diagonal) we have

$$\exp\left\{i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right\}\hat{s}_\nu\exp\left\{-i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right\} = \hat{s}_\nu e^{i\nu\Omega_1 t},$$

we go over in (22) from the interaction representation again to the rotating coordinate system:

$$\frac{\partial\hat{\sigma}^T}{\partial t} = -i\left[\hat{\sigma}^T,\ \frac{\hat{\mathcal{H}}_0^T}{\hbar}\right] - \frac{i}{\hbar}\sum_{k\mu\nu} a_{\mu\nu}(\vartheta)\left\{\sum_l\langle\hat{F}_0^*(0)\rangle_{\rho'}\right.$$

$$\left.\mp A_l\langle\hat{I}_0^{l*}(0)\rangle_{\sigma'}\right\}[\hat{\sigma}^T, \hat{s}_\nu^k]$$

$$-\frac{i}{\hbar^2}\sum_{k\mu\nu\nu'} a_{\mu\nu}(\vartheta)\,a_{-\mu\nu'}(\vartheta)\int_0^t d\tau\exp(i\mu\omega_1\tau + i\nu'\Omega_1\tau)$$

$$\times\left\{\left[\langle\hat{F}_{-\mu}^*(\tau)\,\hat{F}_\mu^*(0)\rangle_{\rho'} \mp \sum_l A_l^2\langle\hat{I}_{-\mu}^{l*}(\tau)\hat{I}_\mu^{l*}(0)\rangle_{\sigma'}\right][\hat{s}_\nu\hat{s}_{\nu'}\hat{\sigma}^T\right.$$

$$\left.-\hat{s}_{\nu'}\hat{\sigma}^T\hat{s}_\nu] + \left[\langle\hat{F}_\mu^*(0)\,\hat{F}_{-\mu}^*(\tau)\rangle_{\rho'}\right.\right.$$

$$\left.\left.\mp\sum_l A_l^2\langle\hat{I}_\mu^{l*}(0)\,\hat{I}_{-\mu}^{l*}(\tau)\rangle_{\sigma'}\right][\hat{\sigma}^T\hat{s}_{\nu'}\hat{s}_\nu - \hat{s}_\nu\hat{\sigma}^T s_{\nu'}]\right\}. \qquad (24)$$

Here $\langle\ \rangle_{\sigma'}$ and $\langle\ \rangle_{\rho'}$ denote averages over σ' and ρ', while

$$\hat{I}^{*T}(t) = \exp\left\{i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right\}\hat{I}\exp\left\{-i\frac{\hat{\mathcal{H}}_0^T}{\hbar}t\right\},$$

$$\hat{F}^{*T}(t) = \exp\left\{i\frac{\hat{\mathcal{H}}_F}{\hbar}t\right\}\hat{F}\exp\left\{-i\frac{\hat{\mathcal{H}}_F}{\hbar}t\right\} \qquad (25)$$

are the operators for the nuclear spin and for the "lattice" in the interaction representation.

In order to obtain the equations of motion for the magnetization of the spin system we multiply (24) on the left by $\mu_S \cdot \mathbf{s}$ and sum over the states of the electron system. As a result of this we obtain

$$\frac{d}{dt}\langle\hat{\mathbf{M}}^T\rangle = \frac{i}{\hbar}\langle[\hat{\mathbf{M}}^T,\ \hat{\mathcal{H}}_0^T]\rangle - \frac{i}{\hbar}\sum_\nu a_{0\nu}(\vartheta)(\Phi_0 \mp \Psi_0)\langle[\hat{\mathbf{M}}^T,\ \hat{s}_\nu]\rangle$$

$$-\sum_{\mu\nu\nu'} a_{\mu\nu}(\vartheta)\,a_{-\mu\nu'}(\vartheta)\{(\Phi_{\mu\nu'} \mp \Psi_{-\mu\nu'})\langle[\hat{\mathbf{M}}^T,\ \hat{s}_\nu]s_{\nu'}\rangle$$

$$-(\Phi_{\mu\nu'} \mp \Psi_{\mu\nu'})\langle\hat{s}_{\nu'}[\hat{\mathbf{M}}^T,\ \hat{s}_\nu]\rangle\}. \qquad (26)$$

Here we have introduced the notation

$$\frac{1}{\hbar^2}\int_0^t d\tau\exp(i\mu\omega_s\tau + i\nu'\Omega_s\tau)\left\langle\hat{F}_{\mp\mu}^*\begin{pmatrix}\tau\\0\end{pmatrix}\hat{F}_{\pm\mu}^*\begin{pmatrix}0\\\tau\end{pmatrix}\right\rangle$$

$$\equiv \Phi_{\mp\mu\nu'}(t),$$

$$\frac{1}{\hbar}\langle\hat{F}_0^*(0)\rangle \equiv \Phi_0; \qquad (27)$$

$$\sum_l a_l^2 \int_0^t d\tau \exp(i\mu\omega_s\tau + i\nu'\Omega_s\tau) \left\langle \hat{I}^{l*}_{\mp\mu}\begin{pmatrix}\tau\\0\end{pmatrix} \hat{I}^{l*}_{\pm\mu}\begin{pmatrix}0\\\tau\end{pmatrix}\right\rangle_0,$$

$$\equiv \Psi_{\mp\mu\nu'}(t), \qquad \sum a_l \left\langle \hat{I}^{l*}_0(0)\right\rangle \equiv \Psi_0, \tag{28}$$

where $a_l = A_l/\hbar$. The functions $\Phi_{\mu\nu}$ determine the nature of the relaxation processes due to the interaction of the electron spins with the lattice, and, in general, with one another. The expressions for these functions agree with those introduced in Tomita's paper.[5]

The functions $\Psi_{\mu\nu}$ are characteristic for the problem under consideration. They are due to the hyperfine interaction and lead to "inhomogeneous" broadening of the electron line. As will be seen from the following discussion, they depend in an essential manner on the resonance conditions for the system of nuclear spins.

In order to obtain the final form of the functions $\Psi_{\mu\nu}$ it is necessary to evaluate the average values appearing in (28). As we have already mentioned, $I^{l*}_{-\mu}(\tau)$ — the operator for the nuclear spin in the interaction representation — is the solution of the equation

$$i\hbar\, d\hat{I}^{l*}/dt = [\hat{I}^{l*}\hat{\mathcal{H}}^*_{\text{int}}]. \tag{29}$$

$\hat{\mathcal{H}}^*_{\text{int}}$ contains all the interactions within the nuclear system which we do not introduce explicitly. In order to utilize in subsequent calculations the representation in which $\mathcal{H}_{0\,\text{nucl}}$ (the Zeeman energy of the nuclei) is diagonal, it is necessary, just as in the case of the electron system, to go over to the system of coordinates in which we can speak of an equilibrium ensemble. This is the system of coordinates rotating about the effective field

$$H^l_{eff} = [\{(H_0 \pm a_l s_0) - \omega_l/\gamma_l\}^2 + h'^2]^{1/2} \tag{30}$$

with frequency ω_I. The field H^l_{eff} is inclined to the z axis at an angle θ_l determined by the expressions

$$\cos\theta_l = [(H_0 \pm a_l s_0) - \omega_l/\gamma_l]/H^l_{eff}, \quad \sin\theta_l = h'/H^l_{eff}. \tag{31}$$

In this case the old operators will be expressed in terms of the new ones in the following manner:

$$\hat{I}^{l*}_\mu(\tau) = \sum_\lambda a_{\mu\lambda}(\theta_l)\, e^{i\mu\omega_l\tau} \hat{I}^{l*}_\lambda(\tau). \tag{32}$$

The matrix $a_{\mu\lambda}(\theta_l)$ is of the same form as (15). On taking (32) into account we obtain

$$\left\langle \hat{I}^{l*}_{-\mu}(\tau)\hat{I}^{l*}_\mu(0)\right\rangle = \sum_{\lambda\lambda'} a_{-\mu\lambda}(\theta_l)\, a_{\mu\lambda'}(\theta_l)\, e^{i\mu\omega_l\tau} \left\langle \hat{I}^{l*}_\lambda(\tau)\hat{I}^{l}_{\lambda'}(0)\right\rangle$$

$$= \sum_{\lambda\lambda'} a_{-\mu\lambda}(\theta_l)\, a_{\mu\lambda}(\theta_l) \exp(i\lambda\Omega_l\tau + i\mu\omega_l\tau) \left\langle \hat{I}^{l}_\lambda \hat{I}^{l}_{\lambda'}\right\rangle.$$

However,

$$\left\langle \hat{I}^{l}_\lambda \hat{I}^{l}_{\lambda'}\right\rangle = \exp(-\hbar\Omega_l/kT)\left\langle \hat{I}^{l}_{\lambda'}\hat{I}^{l}_\lambda\right\rangle, \tag{33}$$

and, therefore, we have

$$\Psi_{-\mu\nu'} = \Psi_{\mu\nu'}. \tag{34}$$

Thus, we have

$$\Psi_{\mu\nu}(t) = \sum_l \sum_{\lambda\lambda'} a_l^2 \int_0^t d\tau \exp(-i\nu\Omega_s\tau + i\mu\omega_s\tau$$

$$+ i\mu\omega_l\tau)\, a_{-\mu\lambda}(\theta_l)\, a_{\mu\lambda'}(\theta_l) \left\langle \hat{I}^{l*}_\lambda(\tau)\hat{I}^{l*}_{\lambda'}(0)\right\rangle. \tag{35}$$

It may be seen from (35) that for $\mu \neq 0$ these functions vanish, since they contain a factor oscillating rapidly with frequency ω_S. On taking into account the fact that

$$\left\langle \hat{I}_x\hat{I}_z\right\rangle = \left\langle \hat{I}_y\hat{I}_z\right\rangle = \left\langle \hat{I}_x\hat{I}_y\right\rangle = 0,$$

we obtain for $\Psi_{0\nu}$ the expression

$$\Psi_{0\nu} = \sum_l a_l^2 \int_0^t d\tau e^{-i\nu\Omega_s\tau} \left\{\cos^2\theta_l \left\langle \hat{I}^*_0(\tau)\hat{I}^*_0(0)\right\rangle\right.$$

$$\left. + \sin^2\theta_l \left\langle \hat{I}^{l*}_x(\tau)\hat{I}^{l*}_x(0)\right\rangle\right\}. \tag{36}$$

The quantity $\langle \hat{I}^{l*}_x(\tau)\hat{I}^{l*}_x(0)\rangle$ is the usual relaxation function for the nuclear system introduced in the linear theory of Kubo and Tomita.[7] On substituting in place of $\hat{I}^{l*}_x(\tau)$ the solution of (29) up to quantities of the second order in $\mathcal{H}^*_{\text{int}}\tau/\hbar$, we obtain:

$$\left\langle \hat{I}^{l*}_x(\tau)\hat{I}^{l*}_x(0)\right\rangle = \frac{1}{2}\left\langle \hat{I}^{l}_x\hat{I}^{l}_x\right\rangle \left\{\exp(-i\Omega_l - \Phi_l)\tau\right.$$

$$\left. + \exp(i\Omega_l - \Phi_l)\tau\right\}. \tag{37}$$

The parameter Φ_l has the meaning of an inverse relaxation time determined by the interactions within the nuclear system. For t greater than the time of occurrence of the relaxation processes in the electron system the value of the integral (27) will not be altered if t is allowed to go to infinity, while

$$\Psi_{0,\pm1} = \sum_l \frac{a_l^2}{3} \frac{\Phi_l I^l(I^l+1)}{\Omega_s^2} \sin^2\theta_l$$

$$\pm i \sum_l \frac{a_l^2}{3} \frac{I^l(I^l+1)}{\Omega_s} = \Psi' + i\Psi''. \tag{38}$$

Formula (38) has been obtained in the approximation $(\Omega_I/\Omega_S)^2 \ll 1$, which holds practically always.

On utilizing (34), and on taking into account the fact[5] that

$$\Phi_{\mu\nu'} = \exp(-\hbar\Omega_F/KT)\,\Phi_{-\mu\nu'}, \tag{39}$$

we obtain in the approximation linear with respect to $\hbar\Omega_F/kT$ the desired equation of motion for the magnetization of the electron system:

$$\frac{d}{dt}\left\langle \hat{\mathbf{M}}^T\right\rangle = \frac{i}{\hbar}\left\langle [\hat{\mathbf{M}}^T,\ \mathcal{H}_0^T]\right\rangle - i\sum_{\nu} a_{0\nu}(\vartheta)(\Phi_0 \mp \Psi_0)\left\langle [\hat{\mathbf{M}}^T,\ \hat{s}_\nu]\right\rangle - \sum_{\mu\nu\nu'} a_{\mu\nu}(\vartheta)\, a_{-\mu\nu'}(\vartheta)\left\{(\Phi_{-\mu\nu'} \mp \Psi_{-\mu\nu'})\left\langle [[\hat{\mathbf{M}}^T\hat{s}_\nu]\hat{s}_{\nu'}]\right\rangle\right\} + \sum_{\mu\nu\nu'} a_{\mu\nu}(\vartheta)\, a_{-\mu\nu'}(\vartheta)\frac{\hbar\Omega_P}{kT}\Phi_{-\mu\nu'}\left\langle \hat{s}_{\nu'}[\hat{\mathbf{M}}^T,\ \hat{s}_\nu]\right\rangle. \quad (40)$$

If the hyperfine interaction is absent then equations (40) agree with the equations obtained by Tomita.[5] As was shown in that paper, in the case of a rapidly fluctuating lattice they reduce to equations of the Bloch type.

4. COMPLEX SUSCEPTIBILITY OF THE ELECTRON SYSTEM

As the nuclear system approaches resonance, a change in the absorption of energy from the microwave field by the electrons occurs which is described by the system of equations (40). In experiments this change is observed under the condition of resonance of the electron system $\omega_S = |\gamma_S| H_0$. In this case after simple but awkward operations of commutation and summation Eqs. (40) assume the form

$$\frac{d}{dt}\begin{bmatrix} M_x^T \\ M_y^T \\ M_z^T \end{bmatrix} + \begin{bmatrix} \Phi_x \mp \Psi' & 0 & 0 \\ 0 & \Phi_y \mp \Psi' & -\gamma_s h^s \\ 0 & \gamma_s h^s & \Phi_z \end{bmatrix}\begin{bmatrix} M_x^T \\ M_y^T \\ M_z^T \end{bmatrix} = \chi_0 \begin{bmatrix} \Phi_x h^s \\ 0 \\ \Phi_z H_0 \end{bmatrix}, \quad (41)$$

where $\chi_0 = \mu_S^2 s(s+1)/3kT$ is the static electron susceptibility. In the derivation of (41) we have neglected second-order perturbation-theory terms which lead to shifts of the resonance frequency.

In the case under consideration[5] $\Phi_X = \Phi_y$. On introducing the notation

$$\Phi_x = \Phi_y = 1/T_2, \qquad \Phi_z = 1/T_1, \qquad \Psi' = 1/T', \quad (42)$$

we obtain

$$\begin{aligned} &\frac{dM_x^T}{dt} + \left(\frac{1}{T_2} \mp \frac{1}{T'}\right) M_x^T = \chi_0 \frac{h^s}{T_2}, \\ &\frac{dM_y^T}{dt} + \left(\frac{1}{T_2} \mp \frac{1}{T'}\right) M_y^T - \gamma_s h^s M_z^T = 0, \\ &\frac{dM_z^T}{dt} + \gamma_s h^s M_y^T + \frac{M_z^T}{T_1} = \chi_0 \frac{H_0}{T_1}. \end{aligned} \quad (43)$$

Equations (43) differ from the Bloch equations in the rotating coordinate system under the conditions of resonance by terms containing T'. The expressions for T_1 and T_2 determine the usual-longitudinal and transverse-relaxation times, and have been evaluated by Tomita.[5] The time T' is due to the presence of the hyperfine interaction.

In the stationary state ($\dot{M}_X^T = \dot{M}_y^T = \dot{M}_Z^T = 0$) we have

$$M_x^T = \chi_s' h^s, \quad M_y^T = \chi_s'' h^s, \quad M_z^T = \chi_0 H_0 Z_s^{\mp}, \quad (44)$$

where

$$\chi_s' = \chi_0/(1 \mp T_2/T') \quad (45)$$

is the real, and

$$\chi_s'' = \chi_0 T_2 \gamma_s H_0/(1 + (\gamma_s h^s)^2 T_1 T_2 \mp T_2/T') \quad (46)$$

is the imaginary part of the complex susceptibility of the electron system, and

$$Z_s^{\mp} = \{1 + T_1 T_2 (\gamma_s h^s)^2/(1 \mp T_2/T')\}^{-1} \quad (47)$$

is the saturation factor. The minus sign corresponds to the transitions between the sublevels of the hyperfine structure corresponding to $m_S = \frac{1}{2}$, while the plus sign corresponds to the transitions with $m_S = -\frac{1}{2}$ (cf. diagram). In accordance with (30), (31), (38) we have

$$\frac{1}{T'} = \frac{1}{3}\sum_l a_l^2 \frac{I^l(I^l+1)}{T_2^l}\frac{(\gamma_I^l h^l)^2}{(\gamma_s h^s)^2}\frac{1}{[(\gamma_s H_0 \pm a_l s_0) - \omega_I]^2 + \gamma_I^{l2} h^{l2}}, \quad (48)$$

where $1/T_2^l = \Phi^l$ is the transverse relaxation time for the nuclear system.

The expression for 1/T' has a resonance character, and attains a maximum when the frequency of the radio frequency field

$$\omega_I = |\gamma_I| H_0 \pm a_l s_0 \quad (49)$$

corresponds to the interaction energy of the uncompensated electron with one of the neighboring nuclei (I^l). The number of maxima and the distances between them are determined by the specific configuration of the system.

Thus, as the frequency ω_I is varied the saturation parameters $Z_S^{\mp}$ will vary in a resonance fashion, diminishing (plus), or increasing (minus) the signal. By observing the absorption of energy from the microwave field, it is possible to find a number of maxima corresponding to the resonance values (49) of the frequency ω_I.

The variation of χ'' depends on a_l^2 and on the value of the ratio of the relaxation time of the electron system T_2 to the relaxation time of the nuclear system T_2^l. The longer is the time T_2, the more slowly will be upset the changes produced in the electron system by the hyperfine interactions.

Therefore, double resonance experiments of such a kind are carried out at low temperatures.[4]

The theory developed for $I = \frac{1}{2}$ exhibits the main features of the phenomenon observed experimentally and can be generalized to the case $I > \frac{1}{2}$.

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