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NUCLEAR-SPIN DIFFUSION IN ELECTRON-NUCLEAR DOUBLE RESONANCE

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Electron-nuclear double resonance in a system with hyperfine interaction is considered. Spin diffusion is assumed to be the mechanism of transfer of excitation from remote nuclei to the paramagnetic centers. The correlation function of the nuclear system is calculated for this relaxation mechanism. The corrections to the relaxation times of the electron system due to spin diffusion are found. The susceptibility of the electron system is calculated.

1. STATEMENT OF THE PROBLEM

IN the method of electron-nuclear double resonance (ENDOR), one subjects the electron spin system to the action of a microwave field and at the same time the nuclear spin system to a radiofrequency field.[1] As a consequence of the interaction between the electrons and the nuclei, absorption in the electron system can vary when the nuclear system is in resonance. An example of such a system is a crystal having nuclei with spin $I = \frac{1}{2}$ arranged on its sites and containing an impurity that possesses an uncompensated electron spin. The electron spin can interact strongly only with the nuclei that are nearest to it. In addition, it changes significantly the local magnetic field for nuclei situated in a volume of a certain radius[2] near this impurity compared to the local fields of distant nuclei. Experimentally, there has been observed[3] an effect on the absorption in the electronic system due to resonance in both the nearest and the distant nuclei. This can be explained if it is assumed that there is a mechanism by which the energy received by the remote nuclear spins from the rf field is transferred to the paramagnetic impurity. Spin diffusion[3] is such a mechanism.

In the present paper we calculate the dispersion and absorption of the electron system in the presence of nuclear-spin diffusion.

Consider a system of electron spins $\hat{\mathbf{S}}^{\mathrm{i}}$ and nuclear spins $\hat{\mathbf{I}}^{\mathrm{i}}$ in an applied constant magnetic field $\mathbf{H}_0 \equiv \{0, 0, \mathrm{H}_0\}$, a microwave field

$$\mathbf{h}^s(t) = \{h_{+1}{}^s = h^s e^{-i\omega_s t},\ h^s_{-1} = h^s{}_0 = 0\}$$

and an rf field

$$\mathbf{h}^I(t) \equiv \{h_{+1}{}^I = 0,\ h_{-1}{}^I = h^I e^{-i\omega_I t},\ h_0{}^I = 0\}.$$

The general form for the electron-nuclear magnetic interaction operator is:

$$\hat{H}' = {}^{16}/_3\, \pi\mu_s\mu_I\delta(\mathbf{r})(\hat{\mathbf{I}}\hat{\mathrm{S}}) + 2\mu_s\mu_I[3(\hat{\mathrm{S}}\mathbf{r})(\hat{\mathbf{I}}\mathbf{r}) - \mathbf{r}^2(\hat{\mathrm{S}}\hat{\mathbf{I}})]\mathbf{r}^{-5}.$$

Here the first term describes the contact interaction; it is proportional to $|\psi(0)|^2$ and is non-zero only for an s-state electron (when the wave function does not have a node at the point $\mathbf{r} = 0$). The second term describes the dipole-dipole interaction and is zero in an s state by virtue of the spherical symmetry of the wave function.

The electron state can be a superposition of states with different orbital quantum numbers ($\psi = \alpha_{\mathrm{S}}\psi_{\mathrm{S}} + \alpha_{\mathrm{p}}\psi_{\mathrm{p}} + \ldots$), and then both types of magnetic hyperfine interaction are present. If α_{S} is not small, i.e., $|\psi(0)|^2$ is rather large, then, as a rule, the contact term is much larger than the dipole-dipole term, and the latter may be neglected.[4] The validity of this assumption has been confirmed for many substances investigated by the double resonance method.[4]

Hence we make the assumption that there is a contact interaction between the electrons and nuclei of the form

$$\hat{H}' = \sum_i a_i (\hat{\mathrm{S}}^i \hat{\mathbf{I}}^i). \tag{1}$$

We remark that even if we did take the dipole-dipole term into account, there would be no important changes in the results of the calculation. The Hamiltonian of the system has the form

$$\hat{\mathscr{H}} = -\gamma^s\hbar \sum_k \hat{\mathrm{S}}^k \mathbf{H} - \gamma^I\hbar \sum_k \hat{\mathbf{I}}^k \mathbf{H} + \hat{H}' + \hat{\mathrm{S}}\hat{\mathbf{F}}$$

$$+ \hat{\mathbf{I}}\hat{\mathbf{F}} + \hat{H}_F \equiv \hat{H}_0 + \hat{H}' + \hat{\mathrm{S}}\hat{\mathbf{F}},$$

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{h}^s(t) + \mathbf{h}^I(t), \tag{3}$$

where γ^{I} and γ^{S} are the gyromagnetic ratios for the nuclei and the electrons, the operators $\hat{\mathbf{S}}\hat{\mathbf{F}}$ and $\hat{\mathbf{I}}\hat{\mathbf{F}}$ describe the interactions of the electrons with the lattice and of the nuclei with the lattice, respectively, and $\hat{H}_F$ is the lattice energy operator.

We shall assume that the system of nuclear spins, electronic spins, and lattice can be described by density operators $\hat{\sigma}'$, $\hat{\sigma}$, and $\hat{\rho}'$, respectively, and that the total density operator $\hat{\rho}$ is

$$\hat{\rho} = \hat{\sigma}' \hat{\sigma} \hat{\rho}', \tag{4}$$

i.e., the energy of the interaction between the individual subsystems is small in comparison with the Zeeman energy of the electrons and nuclei and the lattice energy. With these assumptions, the equations of motion for the magnetization **M** of the electronic system were obtained in [5]:

$$\begin{aligned}\frac{d}{dt}\langle \hat{\mathbf{M}}^T\rangle_\sigma &= \frac{i}{\hbar}\langle[\hat{\mathbf{M}}^T, \hat{H}_0{}^T]\rangle_\sigma \\ &- \frac{i}{\hbar}\sum_\nu a_{0\nu}(\vartheta_s)(\Phi_0 \pm \Psi_0)\langle[\hat{\mathbf{M}}^T, \hat{S}_\nu]\rangle_\sigma \\ &- \sum_{\mu\nu\nu'} a_{\mu\nu}(\vartheta_s)\, a_{-\mu\nu'}(\vartheta_s)\{(\Phi_{\mu\nu'} \pm \Psi_{-\mu\nu'})\langle[\hat{\mathbf{M}}^T, \hat{S}_\nu]\rangle_\sigma \\ &- (\Phi_{\mu\nu'} \pm \Psi_{\mu\nu'})\langle \hat{S}_{\nu'}[\hat{\mathbf{M}}^T, \hat{S}_\nu]\rangle_\sigma,\end{aligned} \tag{5}$$

where

$$\hat{Q}^T = \exp(i\omega_s\hat{S}_0 t)\,\hat{Q}\exp(-i\omega_s\hat{S}_0 t), \tag{6}$$

S_ν ($\nu = \pm 1, 0$) are the circular projections of the electron spin, and the matrix $a_{\mu\nu}(\vartheta_S)$ has the elements

$$a_{\mu\nu}(\vartheta_s) = \begin{pmatrix} {}^1/_2(\cos\vartheta_s + 1) & 2^{-1/2}\sin\vartheta_s & {}^1/_2(\cos\vartheta_s - 1) \\ -2^{-1/2}\sin\vartheta_s & \cos\vartheta_s & -2^{-1/2}\sin\vartheta_s \\ {}^1/_2(\cos\vartheta_s - 1) & 2^{-1/2}\sin\vartheta_s & {}^1/_2(\cos\vartheta_s + 1) \end{pmatrix}, \tag{7}$$

$$\sin\vartheta_s = h^s[(H_0 + \omega_s/\gamma_s)^2 + (h^s)^2]^{-1/2} \equiv h^s/H_{eff}{}^s. \tag{8}$$

In (5) we have introduced the symbols:

$$\Phi_{\mp\mu\nu'}(t) \equiv \int_0^t d\tau \exp(i\mu\omega_s\tau + i\nu'\Omega_s\tau)\left\langle \hat{F}^*_{\mp\mu}\begin{pmatrix}\tau\\0\end{pmatrix}\hat{F}^*_{\pm\mu}\begin{pmatrix}0\\\tau\end{pmatrix}\right\rangle_\rho,$$

$$\Phi_0 \equiv h^{-1}\langle \hat{F}_0{}^*(0)\rangle_\rho; \tag{9}$$

$$\Psi_{\mp\mu\nu'}(t) \equiv \sum_l a_l{}^2\int_0^t d\tau\exp(i\mu\omega_s\tau + i\nu'\Omega_s\tau)$$

$$\times\left\langle \hat{I}^{l*}_{\mp\mu}\begin{pmatrix}\tau\\0\end{pmatrix}\hat{I}^{l*}_{\pm\mu}\begin{pmatrix}0\\\tau\end{pmatrix}\right\rangle_{\sigma'},$$

$$\Psi_0 \equiv \sum_l a_l\langle \hat{I}_0{}^{l*}(0)\rangle_{\sigma'}, \tag{10}$$

where $\Omega_S = \gamma^S H^S_{eff}$, and $\hat{F}^*_{\mp\mu}(\tau)$ are the circular projections of the lattice operators in the interaction representation, and

$$\hat{I}^{l*}_{\mp\mu}(\tau) = \exp\left(i\frac{\hat{H}_1 + \hat{V}}{\hbar}\tau\right)\hat{I}^l_{\mp\mu}\exp\left(-i\frac{\hat{H}_1 + \hat{V}}{\hbar}\tau\right), \tag{11}$$

$$\hat{H}_1 = \sum_i(-\gamma^I\hbar)\,\hat{\mathbf{I}}^i(\mathbf{H}_0 + \mathbf{h}^I(\tau)), \quad \hat{V} = \hat{\mathbf{I}}\hat{F}. \tag{12}$$

The functions $\Phi_{\pm\mu\nu'}$ describe the relaxation processes in the electronic system and were introduced by Tomita.[6] The functions (10) are characteristic for the present problem. They have appeared as a consequence of including the contact interaction and show the effect of correlations within the nuclear system on the electronic magnetization.

2. CALCULATION OF THE CORRELATION FUNCTIONS OF THE NUCLEAR SYSTEM

Thus, the problem is reduced to a calculation of the correlation functions

$$\left\langle \hat{I}^{l*}_{\mp\mu}\begin{pmatrix}\tau\\0\end{pmatrix}\hat{I}^{l*}_{\pm\mu}\begin{pmatrix}0\\\tau\end{pmatrix}\right\rangle.$$

When $\mu \neq 0$, Eq. (10) contains the rapidly oscillating factor $\exp(i\mu\omega_S\tau)$; hence we may set

$$\Psi_{\pm 1,\,\nu'} \approx 0, \qquad \Psi_{0\nu'} \neq 0.$$

The satellite lines are neglected. Now it is necessary to calculate the correlation function

$$G^l(\tau) \equiv \langle \hat{I}_0{}^{l*}(\tau)\,\hat{I}_0{}^l\rangle_{\sigma'}. \tag{13}$$

We make the assumption that

$$[\hat{H}_1, \hat{V}] = 0. \tag{14}$$

This is valid, for example,[7] if $\hat{V}$ is understood to be the dipole-dipole interaction of the nuclei and the non-secular terms that lead to satellite lines are neglected. Then (13) can be written as:

$$G^l(\tau) = \left\langle \exp\left(\frac{i}{\hbar}\hat{V}\tau\right)\hat{I}^l_0\exp\left(-\frac{i}{\hbar}\hat{V}\tau\right)\exp\left(-\frac{i}{\hbar}\hat{H}_1\tau\right)\hat{I}_0{}^l\right.$$

$$\left.\times\exp\left(\frac{i}{\hbar}\hat{H}_1\tau\right)\right\rangle_{\sigma'} \equiv \langle \check{I}_0{}^l(\tau)\,\hat{I}_0{}^l(\tau)\rangle_{\sigma'}. \tag{15}$$

For the calculation of $I^l_0(\tau)$, we note that

$$\hat{I}_0{}^l(\tau) = \exp\left(-\frac{i}{\hbar}\hat{H}_1{}^l\tau\right)\hat{I}_0{}^l\exp\left(\frac{i}{\hbar}\hat{H}_1{}^l\tau\right),$$

$$\hat{H}^l_1 = -\gamma^I\hbar\,(H_0\hat{I}_0{}^l + h^I\hat{I}_-{}^l e^{i\omega_I\tau}), \qquad \hat{H}_1 = \sum_l \hat{H}_1{}^l. \tag{16}$$

We transform to a rotating coordinate system:

$$\begin{aligned}\hat{I}_0{}^{lT}(\tau) &= \exp(i\omega_I\hat{I}_0\tau)\,\hat{I}_0{}^l(\tau)\exp(-i\omega_I\hat{I}_0\tau) \\ &= \exp\left(-\frac{i}{\hbar}\hat{H}_1{}^{lT}\tau\right)\hat{I}_0{}^l\exp\left(\frac{i}{\hbar}\hat{H}_1{}^{lT}\tau\right),\end{aligned}$$

$$\hat{H}_1{}^{lT} = -\gamma^I\hbar\,(H_0\hat{I}_0{}^l + \hbar^I\hat{I}_-{}^l). \tag{17}$$

Then

$$i\hbar\frac{\partial\hat{I}^{lT}(\tau)}{\partial\tau}=[\hat{H}_1^{lT},\ \hat{I}_0^{lT}(\tau)]=$$

$$=-\gamma^I\hbar h^I\exp\left(-\frac{i}{\hbar}\hat{H}_1^{lT}\tau\right)\hat{I}_-^{l}\exp\left(\frac{i}{\hbar}\hat{H}_1^{lT}\tau\right). \quad (18)$$

Using the definition of the exponential

$$\exp\left(-\frac{i}{\hbar}\hat{H}_1^{lT}\tau\right)=\lim_{n\to\infty}\left(1-\frac{t\tau}{n\hbar}\hat{H}_1^{lT}\right)^n$$

and the commutation rule for the spin components, it is easily found that

$$\exp\left(-\frac{i}{\hbar}\hat{H}_1^{lT}\tau\right)\hat{I}_-^{l}$$

$$=\hat{I}_-^{l}\exp\left(-\frac{i}{\hbar}\hat{H}_1^{lT}\tau\right)\exp(-i\omega_0^I\tau), \quad (19)$$

where $\omega_0^I=\gamma^I H_0$.

Substituting (19) into (18) and integrating the expression obtained, we find

$$\hat{I}_0^{lT}(\tau)=\hat{I}_0^{l}+\hat{I}_-^{l}\frac{h^I}{H_0}[1-\exp(-i\omega_0^I\tau)]$$

or, reverting to the initial coordinate system,

$$\hat{I}_0^{l}(\tau)=\hat{I}_0^{l}+\hat{I}_-\frac{h^I}{H_0}[\exp(i\omega_I\tau)-\exp(i(\omega_I-\omega_0^I)\tau)]. \quad (20)$$

Considering (20), we may write (15) in the form

$$G^l(\tau)=\langle\check{I}_0^{l}(\tau)\hat{I}_0^{l}\rangle_{\sigma'}+\frac{h^I}{H_0}\langle\check{I}_0^{l}(\tau)\hat{I}_-^{l}\rangle_{\sigma'}$$

$$\times[\exp(i\omega_I\tau)-\exp(i(\omega_I-\omega_0^I)\tau)]. \quad (21)$$

The implicit time dependence remaining in $G^l(\tau)$ is due only to the form of the interaction of the nuclei among themselves and can in principle be calculated to any approximation. However, for the present purpose—the calculation of the effect of spin diffusion—it is not necessary to give $\hat{V}$ a concrete form. Spin diffusion can be taken into account if it is assumed that there exists a local equilibrium, characterized by a local value of the spin temperature $T_S(\mathbf{r},t)$ within volume elements dv that are macroscopically small but sufficiently large microscopically. The time and volume distribution of the spin temperature is determined by the spin-diffusion equation. More precisely, this equation determines the distribution of the quantity

$$p(\mathbf{r},\ t)\equiv(N^+-N^-)_{(dv)}$$

$$=-(E^+-E^-)_{(dv)}/kT_s(\mathbf{r},\ t) \quad (22)$$

in the approximation

$$h\omega/kT\ll 1, \quad (23)$$

where N^+, E^+ and N^-, E^- are the populations and energies respectively of the upper and lower levels in each element dv.

In order to calculate the averages remaining in (21), we go to a new coordinate system by means of the transformation

$$\hat{\tilde{Q}}_\mu^T=\exp(i\omega_I\hat{I}_0t)\left(\sum_\nu a_{\mu\nu}(\vartheta_I)\hat{Q}_\nu\right)\exp(-i\omega_I\hat{I}_0t), \quad (24)$$

where $a_{\mu\nu}(\vartheta_I)$ is a matrix of the type (7), and

$$\sin\vartheta_I=h^I/H_{eff}^I,\quad H_{eff}^I=\left[\left(H_0+\frac{\omega_I}{\gamma_I}\right)^2+(h^I)^2\right]^{1/2}. \quad (25)$$

In this coordinate system the equilibrium density matrix in the approximation (23) locally has the form

$$\hat{\sigma}'\sim 1-[\hbar\Omega_I\hat{I}_0/kT_s(\mathbf{r},\ t)]=1+p(\mathbf{r},\ t)\hat{I}_0. \quad (26)$$

In addition

$$\hat{\tilde{I}}_0^{lT}=\hat{\tilde{I}}_0^{l},\qquad \tilde{I}_-^{lT}=\hat{\tilde{I}}_-^{l}e^{-i\omega_I t}. \quad (27)$$

Now the averages in (21) can be calculated as

$$\langle\check{I}_0^{l}(\tau)\hat{I}_0^{l}\rangle_{\sigma'}=\mathrm{Sp}\,(\check{\tilde{I}}_0^{lT}(\tau)\hat{\tilde{I}}_0^{l})$$

$$+\sum_{dv}p(\mathbf{r},\ t)\,\mathrm{Sp}_{dv}\,(\hat{I}_0\check{\tilde{I}}_0^{lT}(\tau)\hat{\tilde{I}}_0^{l}),$$

where summation over dv means summation over all elements dv after equilibrium averaging in each of them.

We shall assume that the implicit nuclear spin-spin interaction provides within the limits of each element dv a relaxation according to the law $\exp(-\tau/\tau_c)$ and write

$$\mathrm{Sp}_{(dv)}\,(\hat{I}_0\check{\tilde{I}}_0^{lT}(\tau)\hat{\tilde{I}}_0^{l})=e^{-\tau/\tau_c}B_1^l dv, \quad (28)$$

where B_1^l is some constant, which can be calculated explicitly if $\hat{V}$ is given. Similarly, we introduce

$$\mathrm{Sp}\,(\check{\tilde{I}}_0^{lT}(\tau)\hat{\tilde{I}}_0^{l})=C_1^l e^{-\tau/\tau_c}. \quad (29)$$

Then we have

$$\langle\check{I}_0^{l}(\tau)\hat{I}_0^{l}\rangle_{\sigma'}=C_1^l e^{-\tau/\tau_c}+B_1^l e^{-\tau/\tau_c}\int_V p(\mathbf{r},\ \tau)\,dv. \quad (30)$$

In completely analogous fashion we find

$$\langle\check{I}_0^{l}(\tau)\hat{I}_-^{l}\rangle_{\sigma'}=C_2^l e^{-\tau/\tau_c}\exp(-i\omega_0^I\tau)$$

$$+B_2^l e^{-\tau/\tau_c}\exp(-i\omega_0^I\tau)\int_V p(\mathbf{r},\ \tau)\,dv; \quad (31)$$

$$\mathrm{Sp}\,(\check{\tilde{I}}_0^{lT}(\tau)\hat{\tilde{I}}_-^{l})=C_2^l e^{-\tau/\tau_c},$$

$$\mathrm{Sp}_{(dv)}\,(\hat{I}_0\check{\tilde{I}}_0^{lT}(\tau)\hat{\tilde{I}}_-^{l})=B_2^l e^{-\tau/\tau_c}dv. \quad (32)$$

Now we obtain (21) in the form

$$G^l(\tau) = e^{-\tau/\tau_c}\Big\{C_1^l + B_1^l \int p(\mathbf{r}, \tau)\, dv$$

$$+ \frac{h^I}{H_0}\Big[C_2^l + B_2^l \int p(\mathbf{r}, \tau)\, dv\Big](1 - \exp(-i\omega_0{}^I\tau))\Big\}. \qquad (33)$$

We shall simplify this general expression by assuming that $h^I/H_0 \ll 1$. Using the symbols

$$\int (\mathbf{r}, \tau)\, dv \equiv q(\tau), \qquad B_1^l \equiv B^l, \qquad C_1^l \equiv C^l, \qquad (34)$$

we obtain

$$G^l(\tau) \cong e^{-\tau/\tau_c}[C^l + B^l q(\tau)]. \qquad (35)$$

To calculate $q(\tau)$ we make use of the spin-diffusion equation[7]:

$$\frac{\partial p}{\partial t} = D\Delta p - CF(\mathbf{r}, t) - 2Ap. \qquad (36)$$

Here D is the spin-diffusion coefficient; the term proportional to C takes into account the direct interaction of the paramagnetic impurity with the surrounding nuclei (e.g., in calculating the dipole-dipole interaction it has the form[7]

$$F(\mathbf{r}, t) = \sum_n \frac{p - p_0}{|\mathbf{r} - \mathbf{r}_n|^6},$$

where the $\mathbf{r}_n$ are the radius vectors of the sites occupied by impurities); A is the probability that a nuclear spin is flipped by the radio-frequency field.

However, Eq. (36) was proposed as the equation describing the mechanism by which information about the lattice temperature produced by the electronic spins is conveyed to remote nuclear spins. The second term on the right-hand side then describes the direct relaxation preceding the nuclear spin-diffusion process and is an effective source for the change of nuclear polarization with time.

We shall not make direct use of Eq. (36), since we have stated the problem in reverse: to consider the mechanism by which information about the nuclear spin temperature is conveyed to the electronic spins. The rf field excites nuclei that are far away from the impurity (the nearest nuclei are not excited, since they are far from resonance because of the strong local field of the impurity); then the excitation is "relayed" on to the nuclei closest to the electron spin and because of the contact interaction (as we assumed in the very beginning) is transferred to the spin of the paramagnetic impurity.

In this way the electron-nucleus interaction does not now precede the spin-diffusion process but is a consequence of it. Hence the corresponding source for the change in nuclear polarization with time cannot be present in Eq. (36). Consequently, we use Eq. (36) without its second term. Then (36) takes the form

$$\partial p / \partial t = D\Delta p - 2Ap. \qquad (37)$$

This equation may be considered as the analog of the equation of continuity if we write

$$D\,\Delta p \equiv -\operatorname{div}(\mathbf{v}p), \qquad \mathbf{v} = -p^{-1}D \operatorname{grad} p$$

and assume that the quantity 2A characterizes the power of the internal sources. Integrating (37) over volume and using the Ostrogradskiĭ-Gauss theorem, we have

$$\frac{\partial}{\partial t} q(t) = DP - 2Aq(t), \qquad (38)$$

$$P = \oint_S \operatorname{grad} p\, d\mathbf{S}. \qquad (39)$$

The quantity DP characterizes the "flow of spin density" through the surface of the sample due to the change in spin polarization on the boundary. In steady state this quantity (and consequently P as well) is independent of time and is proportional to the difference

$$W - \Delta Q, \qquad (40)$$

where W is the surface power absorbed by the sample from the rf field, and ΔQ is the power lost in heating the sample as a consequence of relaxation processes.

Integrating (38), we find

$$q(\tau) = M_0 e^{-2A\tau} + \frac{DP}{2A}(1 - e^{-2A\tau}), \qquad (41)$$

where M_0 is the initial equilibrium magnetization of the nuclear spins.

Substituting (41) into (35) and turning to (10), we obtain

$$\Psi_{0\nu'}(t) = \sum_l a_l^2 \Big[K_1^l(t) + \frac{D}{2A} K_2^l(t)\Big]; \qquad (42)$$

$$K_1^l(t) = C^l \frac{\exp[(i\nu'\Omega_s - \tau_c^{-1})t] - 1}{i\nu'\Omega_s - \tau_c^{-1}}$$

$$+ M_0 B^l \frac{\exp[(i\nu'\Omega_s - 2A - \tau_c^{-1})t] - 1}{i\nu'\Omega_s - \tau_c^{-1} - 2A}.$$

$$K_2^l(t) = PB^l \Big\{ \frac{\exp[(i\nu'\Omega_s - \tau_c^{-1})t] - 1}{i\nu'\Omega_s - \tau_c^{-1}}$$

$$- \frac{\exp[(i\nu'\Omega_s - \tau_c^{-1} - 2A)t] - 1}{i\nu'\Omega_s - \tau_c^{-1} - 2A}\Big\} \qquad (43)$$

3. EFFECT OF SPIN DIFFUSION ON THE SUSCEPTIBILITY AND RELAXATION TIME OF THE ELECTRONIC SYSTEM

If the system is studied at a time t that is considerably greater than the relaxation time, it is possible to set

$$\Psi_{0,\pm1}(t) \approx \Psi_{0,\pm1}(\infty) \equiv \Psi_{0,\pm1}.$$

Then, according to (42) and (43), we obtain

$$\Psi_{0,\mp1} = \Psi' \pm i\Psi'' = \sum_l a_l^2\left(K_1^{l'} + \frac{D}{2A}K_2^{l'}\right) \pm i\sum_l a_l^2\left(K_1^{l''} + \frac{D}{2A}K_2^{l''}\right); \tag{44}$$

$$K_1^{l'} = C^l\tau_c^{-1}(\Omega_s^2+\tau_c^{-2})^{-1} + M_0B^l(\tau_c^{-1}+2A)[\Omega_s^2+(\tau_c^{-1}+2A)^2]^{-1}, \tag{45}$$

$$K_2^{l'} = PB^l\{\tau_c(\Omega_s^2+\tau_c^{-2})^{-1} - (\tau_c^{-1}+2A)[\Omega_s^2+(\tau_c^{-1}+2A)^2]^{-1}\},$$

$$K_1^{l''} = \Omega_s\{C^l(\Omega_s^2+\tau_c^{-2})^{-1} + M_0B^l[\Omega_s^2+(\tau_c^{-1}+2A)^2]^{-1}\}, \tag{46}$$

$$K_2^{l''} = \Omega_sPB^l\{(\Omega_s^2+\tau_c^{-2})^{-1} - [\Omega_s^2+(\tau_c^{-1}+2A)^2]^{-1}\}.$$

For the final transformation of the equations of motion (6) it is necessary to know the explicit form of the functions $\Phi_{\mu\nu'}$. Considering the presence in (9) of a rapidly oscillating factor, we may set

$$\Phi_{0\nu'} \neq 0, \qquad \Phi_{\pm1,\nu'} = 0.$$

Further, if the concentration of the paramagnetic impurity is small, then the local fields created at the site of a given impurity by the electron spins of other impurities can be considered to be vanishingly small. In this case the functions $\Phi_{0\nu'}$ have the form[6]

$$\Phi_{0,\pm1} = \Phi' \pm i\Phi'' = \sigma_0^2\frac{\Phi_0 \pm i\Omega_s}{\Omega_s^2+\Phi_0^2}. \tag{47}$$

Then, as was shown in [5], Eq. (6) leads to equations of the Bloch type (the electronic system is exactly at resonance):

$$\frac{dM_x^T}{dt} + \left(\frac{1}{T_2} \mp \frac{1}{T'}\right)M_x^T = \chi_0\frac{h^s}{T_2},$$

$$\frac{dM_y^T}{dt} + \left(\frac{1}{T_2} \mp \frac{1}{T'}\right)M_y^T = \gamma^sh^sM_z^T,$$

$$\frac{dM_z^T}{dt} + \gamma^sh^sM_y^T + \frac{M_z^T}{T_1} = \chi_0\frac{H_0}{T_1}. \tag{48}$$

Here T_1 and T_2 are the usual longitudinal and transverse relaxation times calculated in [6], and χ_0 is the static susceptibility of the electron system. The addition of T' is due to the electron-nuclear interaction via the spin-diffusion mechanism:

$$\frac{1}{T'} = \Psi' = \sum_l a_l^2\left(K_1^{l'} + \frac{D}{2A}K_2^{l'}\right), \tag{49}$$

where $K_1^{l'}$ and $K_2^{l'}$ are given by the relations (45).

Solving the system of equations (48) for the stationary case, we obtain the following expression for the complex susceptibility of the electron system ($\chi_S' = M_X^T/h^S$, $\chi_S'' = M_y^T/h^S$):

$$\chi_s' = \chi_0\left[1 \mp T_2\sum_l a_l^2\left(K_1^{l'} + \frac{D}{2A}K_2^{l'}\right)\right]^{-1}, \tag{50}$$

$$\chi_s'' = \chi_0T_2\gamma^sH_0\left[1 + (\gamma^sh^s)^2T_1T_2 \mp T_2\sum_l a_l^2\left(K_1^{l'} + \frac{D}{2A}K_2^{l'}\right)\right]^{-1} \tag{51}$$

It is seen from (51) that when the electron system is saturated, the absorption of energy from the microwave field may be changed as a consequence of resonant transitions in the nuclear system, since $K_1^{l'}$ and $K_2^{l'}$ increase as the difference $(\omega_0^I - \omega_I)$ approaches zero (since $K_1^{l'}$ and $K_2^{l'}$ contain elements of the matrix $a_{\mu\nu}(\vartheta_I)$, which depend in resonant fashion on this difference). In the absence of spin diffusion ($D = 0$) such a change can be evoked only by nuclei in direct interaction with the electron of the paramagnetic center and in resonance. Spin diffusion leads to the resonant excitation of distant nuclei being transferred to nuclei in direct interaction with electrons and thus enhances the effect of nuclear resonance on the electronic resonance.

Since the local fields of the remote and the directly interacting nuclei are different, appropriate matching of the frequency of the rf field ω_I can produce resonance only at the remote nuclei. Then, for fixed values of the other parameters, χ_S'' will change only by virtue of spin diffusion. This effect can be observed most distinctly if a crystal with two kinds of nuclei with markedly different gyromagnetic ratios is used.[3]

Depending on which of the pairs of hyperfine sublevels is involved in the induced nuclear transitions, it is necessary to choose the plus or minus sign in (6) and (51) ($m_S = 1/2$, $\Delta m_I = 1$ or $m_S = -1/2$, $\Delta m_I = -1$). The dependence of $(\chi_S'')^{-1}$ on D for these two cases has the form

$$(\chi_{s\pm}'')^{-1} = b \mp 1/2\,\Delta(D),$$

$$b = (\chi_0T_2\gamma^sH_0)^{-1}(1 + (\gamma^sh^s)^2T_1T_2), \quad \Delta(D) = 2(\chi_0\gamma^sH_0T')^{-1}.$$

Thus, by measuring in a given sample (i.e., for a fixed value of D) the difference $(\chi''_{S-})^{-1} - (\chi''_{S+})^{-1} = \Delta(D)$, one can find the correction to the relaxation time due to spin diffusion, and then from Eq. (49) the spin-diffusion coefficient D as well, if the correlation time τ_c is known.

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