Theory of multispin and multiquantum effects in electron-nuclear double resonance at distant nuclei

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A formalism based on the method of accelerated convergence is used to consider multispin and multiquantum effects in electron-nuclear double resonance at distant nuclei. Cases of homogeneous and inhomogeneous broadening of the ESR line are considered. Various limiting cases are analyzed. The results are compared with the known experimental data.

A number of recent papers[1–5] report experimental studies of multispin and multiquantum effects in electron nuclear double resonance (ENDOR). These effects were investigated both for distant and close nuclei. Whereas estimates of the corresponding ENDOR transition probabilities were obtained for close nuclei, there are not even qualitative explanations for ENDOR at distant nuclei. Yet effects that call for explanations have been observed in multispin ENDOR at distant nuclei. In particular, in Ref. 4 was studied a system consisting of two species of atoms with different Zeeman frequencies, ω_I and ω_M. Besides the usual ENDOR lines, a line was also observed at a frequency $\omega_I + \omega_M$, and its intensity was approximately the same as at the frequencies ω_I and ω_M. This fact is not obvious, since the probability of the two-spin process is much lower than that of the one-spin one.

An explanation of this phenomenon is one of the tasks of the present paper. We consider also a number of other possible situations in multispin and multiquantum ENDOR at distant nuclei. We deal in particular with the two-quantum transitions observed in Ref. 2 for ENDOR at distant nuclei in sufficiently strong rf fields. Experiment has shown in Ref. 2 that the coupling of the nuclear Zeeman subsystem (NZS) with the electron dipole-dipole reservoir (DDR) is decisive. We shall therefore consider in detail two-quantum and two-spin transitions in ENDOR with account taken of the role of the electron DDR. We shall use[6] a formalism based on the analogy with the method of accelerated convergence and developed in Ref. 7 for the description of multispin processes in magnetic resonance.

In Secs. 1 and 2 we consider multispin processes in ENDOR for a homogeneously and inhomogeneously broadened ESR line. In Sec. 3 we consider two-quantum transitions in ENDOR for the case of quadrupole splitting of the NMR line.

1. MULTISPIN ENDOR IN HOMOGENEOUS BROADENING OF ESR LINE

We consider the spin system experimentally studied in Ref. 4, consisting of paramagnetic impurities of Zeeman frequency ω_0 and two species of nuclei with frequencies ω_I and ω_M. As already noted, besides the usual lines in the ENDOR spectrum at the frequencies ω_I and ω_M an additional line was observed at the frequency $\omega_I + \omega_M$. This line is obviously due to a two-spin resonance process wherein two nuclear spins of different species are simultaneously flipped. Following the method of Ref. 7, we readily obtain a system of equations for the reciprocal temperatures. In the stationary case it takes the form

$$\frac{\beta_S-\beta_L}{T_{SL}}+W_S\left(\beta_S+\frac{\Delta\omega}{\omega_0}\beta_D\right)=0, \tag{1a}$$

$$\frac{\beta_D-\beta_L}{T_{DL}}+\frac{\beta_D-\beta_M}{T_{DM}}+\frac{\beta_D-\beta_I}{T_{DI}}+W_S\frac{\omega_0\Delta\omega}{\omega_D^2}\left(\beta_S+\frac{\Delta\omega}{\omega_0}\beta_D\right)=0, \tag{1b}$$

$$\frac{C_M}{\omega_I}W(\beta_I\omega_I+\beta_M\omega_M)+\frac{\beta_I-\beta_D}{T_{ID}}+\frac{\beta_I-\beta_L}{T_{IL}}=0, \tag{1c}$$

$$\frac{C_I}{\omega_M}W(\beta_I\omega_I+\beta_M\omega_M)+\frac{\beta_M-\beta_D}{T_{MD}}+\frac{\beta_M-\beta_L}{T_{ML}}=0, \tag{1d}$$

where $\beta_S, \beta_D, \beta_I$, and β_M are the reciprocal temperatures of the electron Zeeman subsystem, the DDR, and the nuclear Zeeman subsystems NZS; β_L is the lattice temperature; $W_S = W_S(\Omega - \omega_0)$ is the usual ESR probability due to a microwave field of frequency Ω; $W = W(\omega - \omega_I - \omega_M)$ is the probability of the two-spin nuclear process (we do not present here explicit expressions for W_S and W, since saturation of the ESR and NMR is assumed hereafter); T_{SL}, T_{DL}, etc., are the relaxation times, $\omega_D{}^2 = \mathrm{Sp}(\mathscr{H}_D{}^2)/\mathrm{Sp}(S_z{}^2)$, and $\mathscr{H}_D$ is the DDR Hamiltonian.

We consider first the case when both frequencies ω_I and ω_M are of the order of the homogeneous width of the ESR line (this is apparently the case realized in Ref. 4). The relaxation coupling of the NZS of both species of spins with the DDR will then be strong, so that spin–lattice relaxation can be neglected in the last two equations of the system (1). To calculate the electronic susceptibility we use the formula[8]

$$\chi''=\frac{\pi}{2}\chi_0\omega_0\varphi(\Omega-\omega_0)\frac{1}{\beta_L}\left(\beta_S+\frac{\Delta\omega}{\omega_0}\beta_D\right), \tag{2}$$

where $\chi_0 = \beta_L\gamma^2NS(S+1)/3$ is the static susceptibility, S is the value of the electron spin; γ is the gyromagnetic ratio; $\varphi(\Omega - \omega_0)$ is the profile of the unsaturated ESR line, $\varphi(\Delta\omega) = W_S(\Delta\omega)/\pi\omega_1^2$, and ω_1 is the microwave-field amplitude in frequency units.

Expressing β_S in terms of β_D from Eq. (1a) and substituting in (2), we easily obtain an expression for the absolute change Δ_χ'' of the susceptibility in the presence and in the

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absence of an rf field:

$$\Delta\chi''=\frac{\chi_0}{2S\Delta_S\beta_L}\frac{W_S\Delta\omega}{1/T_{SL}+W_S},\tag{3}$$

where $\Delta\beta_D=\beta_D(W\neq0)-\beta_D(W=0)$, $S=(\omega_1^2/\Delta_S)T_{SL}$ is the ESR saturation parameter, and Δ_S is the ESR line width.

Using (1c) and (1d) to express β_I and β_M in terms of β_D, substituting them in (1b), and assuming that the conditions for the saturation of ESR and NMR are satisfied, we obtain

$$\Delta\chi''=\frac{\chi_0\omega_0}{2S\Delta_S}\left(\frac{\Delta\omega}{\omega_D}\right)^2K\left[\alpha+K+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1}\times\left[\alpha+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1},\tag{4}$$

where $\alpha=T_{SL}/T_{DL}$ and

$$K=\left(\frac{\omega_I}{\omega_M}C_I+\frac{\omega_M}{\omega_I}C_M\right)\frac{1}{C_MT_{ID}+C_IT_{MD}}T_{SL}.\tag{5}$$

Several limiting cases are possible here. We consider first a situation wherein the density of one spin species greatly exceeds that of the other, e.g., $C_I\gg C_M$ (this is realized in the experiment of Ref. 4). In this case

$$K=\frac{\omega_I}{\omega_M}\frac{T_{SL}}{T_{MD}}.$$

Expressing T_{MD} in terms of T_{DM}, T_{SL} in terms of T_{DL}, and recognizing that $\omega_I\sim\omega_M\sim\Delta_S$, we obtain in order of magnitude

$$K\sim\frac{1}{C_M}\frac{T_{DL}}{T_{DM}}.$$

Since $C_M\ll1$, we obtain, if the ratio T_{DL}/T_{DM} is not too small,

$$K\gg1.\tag{6}$$

Consequently (4) takes the form

$$\Delta\chi''=\frac{\chi_0\omega_0}{2S\Delta_S}\left(\frac{\Delta\omega}{\omega_D}\right)^2\left[\alpha+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1}.\tag{7}$$

This expression coincides with the known expression for the susceptibility[9] when there is only one species of nuclei and when the bottleneck case is realized. Obviously, this is indeed the situation in experiment, since the lines have practically equal intensities at the frequencies $\omega_I+\omega_M$ and ω_I.

Thus, the cause of the identical intensity of the lines of the two- and one-spin ENDOR is the saturation of the nuclear spin system and the bottleneck between the NZS and the DDR (as a result of which the change of the spin temperature no longer depends on the intensity of the external field). It is easy to show that in the situation considered above, when there are two species of nuclei and the rf field is applied at the frequency of one of the species of the nuclei under the bottleneck conditions, the result will be the same as for simultaneous saturation of both spin systems.

In the other limiting case, when

$$K=\frac{1}{C_M}\frac{T_{DL}}{T_{DM}}\ll1,$$

Δ_χ'' will be proportional to K and will depend only on the relaxation time of the lesser species of particles. The physical explanation is that absorption of one rf quanta causes flipping of one spin I and of one spin M. Since the heat capacity of spins I is much larger than that of spins M, the NZS of the M spins becomes much more strongly heated and influences the DDR. A similar situation obtains also in dynamic polarization of nuclei.

We consider now the case when one of the frequencies is much higher than the ESR line width, $\omega_I\gg\Delta_S$, $\omega_M\lesssim\Delta_S$. The coupling of spins I with the DDR is then weak and it is necessary to neglect the term $(\beta_I-\beta_D)/T_{ID}$ in Eq. (1c), but to retain the term $(\beta_I-\beta_L)/T_{IL}$. In analogy with the foregoing, it is easy to obtain the following expression for Δ_χ'':

$$\Delta\chi''=\frac{\chi_0\omega_0}{2S\Delta_S}\frac{(\Delta\omega)^2}{\omega_D^2}K'\left[\alpha+K'+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1}\times\left[\alpha+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1},\tag{8}$$

where

$$K'=\frac{\omega_M^2}{\Delta_S^2}\frac{C_MC_I}{T_{IL}C_M+T_{MD}C_I}T_{SL}.$$

If the condition $T_{MD}C_I\gg T_{IL}C_M$ is satisfied, we have

$$K'=\frac{\omega_M^2}{\Delta_S^2}\frac{\alpha C_MT_{DL}}{T_{MD}}\sim\frac{T_{DL}}{T_{DM}}.$$

In the presence of the bottleneck effect we have $K'\gg1$, and consequently expression (8) coincides with (7).

In the other limiting case $T_{MD}C_I\ll T_{IL}C_M$ we have

$$K'=\frac{\omega_M^2}{\Delta_S^2}\frac{C_IT_{SL}}{C_MT_{IL}}.$$

As a rule $T_{SL}\ll T_{IL}$, and consequently $K'\ll1$ and the ENDOR signal is substantially weakened.

The results are physically clear. In the first case, when $T_{MD}C_I\gg T_{IL}C_M$, the spins I relax rapidly to the lattice, so that saturation of the resonance at the frequency $\omega_I+\omega_M$ leads to the equality

$$\beta_M=-\frac{\omega_I}{\omega_M}\beta_I=-\frac{\omega_I}{\omega_M}\beta_L.$$

Under the bottleneck condition we also have $\beta_D=\beta_M$. Without saturation of the NMR we have $\beta_M=\beta_D\sim\beta_L\omega_0/\omega_D$. This reciprocal temperature is much larger than $\beta_L\omega_I/\omega_M$, therefore the ENDOR signal will be the same as when only the M nuclei are saturated ($\beta_M=0$ in this saturation).

At weak coupling of the spins I to the lattice, i.e., when $T_{MD}C_I\ll T_{IL}C_M$, the situation changes. The NMR saturation leads to the equality $\beta_I=-(\omega_M/\omega_I)\beta_M$, and β_M and β_D take on approximately the same values they had prior to the NMR saturation. It is clear therefore that the ENDOR signal will be weak.

2. MULTISPIN ENDOR IN INHOMOGENEOUS BROADENING OF ESR LINE

We shall consider only the case when spectral diffusion can be neglected. [The case of fast spectral diffusion reduces to that of Sec. 1 with the usual DDR replaced by the so-called reservoir of the local fields, $\mathcal{H}_D\rightarrow\mathcal{H}_D+\sum_i\delta\omega_iS_{iz}$ (for details see Ref. 9).] The ESR line can be represented in this situation as an aggregate of independent spin packets. We shall assume that the conditions $\omega_M\sim\Delta$ and $\Delta\ll\omega_I\ll\Delta^*$ are satisfied (Δ is the packet width and Δ^* is the inhomogeneous width of the ESR line).

In the limit of continuous distribution of the Zeeman frequencies ω', the stationary equations for the reciprocal temperatures take the form

$$\frac{\beta(\omega')-\beta_L}{T_{SL}}+W_S^a(\Omega-\omega')\left[\beta(\omega')+\frac{\Omega-\omega'}{\omega'}\beta_D\right]$$
$$+\frac{C_I}{\omega'}W_S^f(\Omega-\omega'+\omega_I)\left[\omega'\beta(\omega')-\omega_I\beta_I-(\omega'-\omega_I-\Omega)\beta_D\right]$$
$$+\frac{C_I}{\omega'}W_S^f(\Omega-\omega'-\omega_I)\left[\omega'\beta(\omega')+\omega_I\beta_I-(\omega'+\omega_I-\Omega)\beta_D\right]=0, \quad (9a)$$
$$\frac{\beta_D-\beta_L}{T_{DL}}+\frac{\beta_D-\beta_M}{T_{DM}}+\frac{1}{\omega_D^2}\int(\Omega-\omega')g(\omega'-\omega_0)W_S^a(\Omega-\omega')$$
$$\times[\omega'\beta(\omega')+(\Omega-\omega')\beta_D]d\omega'$$
$$+\frac{1}{D^2}\int(\Omega-\omega'+\omega_I)g(\omega'-\omega_0)W_S^f(\Omega-\omega'+\omega_I)$$
$$\times[\omega'\beta(\omega')+\omega_I\beta_I-(\omega'+\omega_I-\Omega)\beta_D]d\omega'=0, \quad (9b)$$
$$\frac{\beta_I-\beta_L}{T_{IL}}+\frac{C_M}{\omega_I}W(\beta_I\omega_I+\beta_M\omega_M)-\frac{C_S}{\omega_I}\int g(\omega'-\omega_0)$$
$$\times W_S^f(\Omega-\omega'+\omega_I)[\omega'\beta(\omega')-\omega_I\beta_I-(\omega'-\omega_I-\Omega)\beta_D]d\omega'$$
$$+\frac{C_S}{\omega_I}\int g(\omega'-\omega_0)W_S^f(\Omega-\omega'-\omega_I)$$
$$\times[\omega'\beta(\omega')+\omega_I\beta_I-(\omega'+\omega_I-\Omega)\beta_D]d\omega'=0, \quad (9c)$$
$$\frac{\beta_M-\beta_D}{T_{MD}}+\frac{C_I}{\omega_M}W(\beta_I\omega_I+\beta_M\omega_M)=0. \quad (9d)$$

Here $W_S{}^a(\Omega-\omega')$ is the probability of allowed ESR transitions, $W_S{}^f(\Omega-\omega'\pm\omega_I)$ the probability of forbidden transition with simultaneous electron and nuclear spin flips, and $g(\omega'-\omega_0)$ the inhomogeneous ESR line shape. To calculate the susceptibility we use the equation[9]

$$\chi''=\frac{\pi}{2}\chi_0\frac{1}{\beta_L}\int g(\omega'-\omega_0)\varphi(\Omega-\omega')$$
$$\times[\omega'\beta(\omega')+(\Omega-\omega')\beta_D]d\omega'. \quad (10)$$

Substituting here $\beta(\omega')$ from the first equation of (9) for the change of the susceptibility, we get

$$\Delta\chi''=\frac{\chi_0}{2S\Delta}\frac{1}{\beta_L}\Phi_1(\Omega-\omega_0,S)\Delta\beta_D, \quad (11)$$

where

$$\Phi_k(\Omega-\omega_0,S)=-\pi\Delta S\int\frac{(\Omega-\omega')^k\varphi(\omega'-\Omega)g(\omega'-\omega_0)}{1+\pi\Delta S\varphi(\omega'-\Omega)}d\omega'.$$

Calculating Δ_χ'' to first-order in the small parameter Δ/Δ^* we get

$$\Delta\chi''=\left\{\pi^{1/2}\chi_0\left(\frac{\Delta}{\Delta^*}\right)^2S'g^2(\Omega-\omega_0)\Psi\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta^*}\right)\frac{\Omega(\Omega-\omega_0)\omega_I\omega_M}{\alpha\omega_D^2+\bar{\Delta}^2}\right.$$
$$\left.+\frac{\pi\chi_0}{2}\Delta^3Sg^2(\Omega-\omega_0)\Psi^2\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta^*}\right)\frac{T_{DL}}{T_{IL}}\frac{\Omega\alpha\omega_D^2}{(\alpha\omega_D^2+\bar{\Delta}^2)^2}\right\}$$
$$\times\left(1+\frac{C_IT_{MD}}{C_MT_{IL}}\right)^{-1}, \quad (12)$$

$$\Psi(x)=\int_0^x e^{y^2}dy, \quad \bar{\Delta}=\Delta(1+S)^{1/2}.$$

The first term in the curly brackets corresponds to forbidden transitions, and the second to direct thermal contact of the spins M with the electron DDR. Compared with the case of a homogeneously broadened ESR line, this expression contains the small parameter $(\Delta/\Delta^*)^2$.

It can be seen from (12) that the term corresponding to direct thermal contact vanishes if the spin-lattice relaxation of the I spins is neglected ($T_{IL}\to\infty$). This follows directly from the form of the system (9). Indeed, if we neglect in (9c) the terms corresponding to spin-lattice relaxation and the forbidden transitions, we find that $\beta_I\omega_I+\beta_M\omega_M=0$ and $\beta_M=\beta_D$, i.e., the system of equations will be the same as in the absence of the rf field. This situation is perfectly analogous to that already considered in Sec. 1.

3. TWO-QUANTUM TRANSITIONS IN ENDOR FOR NUCLEI WITH QUADRUPOLE SPLITTING

Resonant transitions due to simultaneous absorption of several rf quanta by one nucleus can occur in a system of nuclei with $I>1/2$ under the influence a strong rf field. These multiquantum effects are diligently studied at present.[1-3,5] We shall consider the simplest case of two-quantum transitions for nuclei with spin $I=1$ and quadrupole splitting, assuming that the quadrupole-splitting constant is not uniform over the sample. We shall also assume that the nuclei are not the "proper" nuclei of the paramagnetic impurities whose resonance is observed (multiquantum transitions on "proper" nuclei are described in Refs. 1 and 3).

The Hamiltonian of a nuclear spin system acted upon by an rf field is

$$\mathcal{H}=\omega_I\sum_j I_{jz}+\sum_j\omega_{Qj}\left[I_{jz}^2-\frac{1}{3}I(I+1)\right]$$
$$+\frac{\omega_1}{2}\sum_j(I_{j+}e^{i\omega t}+I_{j-}e^{-i\omega t})+\mathcal{H}_{II}, \quad (13)$$

where ω_1 is the amplitude of the rf field in frequency units, ω_{Qj} the quadrupole interaction (we consider only the simplest case of hexagonal symmetry), and $\mathcal{H}_{II}$ the dipole-dipole interaction Hamiltonian whose explicit form we do not need. If the condition $\omega_I\gg\bar{\omega}_Q\gg||\mathcal{H}_{II}||$ is satisfied ($||\mathcal{H}_{II}||$ is the "value" of the Hamiltonian in frequency units), two lines at the frequencies $\omega_I\pm\bar{\omega}_Q$ will be observed in the ENDOR spectra. The widths of these lines will be determined mainly by the inhomogeneity of ω_{Qj}. One more line may be observed in this situation, at a frequency ω_I corresponding to the two-quantum transition. To describe this process it is convenient to use the formalism with fictitious spin $-1/2$ (Ref. 10). The eigenfunctions of spin $I=1$, corresponding to the values $m=0,\pm1$ will be designated, following Ref. 10, as $|3\rangle=|-1\rangle$, $|2\rangle=|0\rangle$, and $|2\rangle=|-1\rangle$. We introduce the operators of the fictitious spin I_α^{k-1} ($k,l=1,2,3$; $\alpha=x,y,z$; see Ref. 10 for more detailed properties of these operators). The Hamiltonian (13) can be written as

$$\mathcal{H}=2\omega_I\sum_j I_{jz}^{1-3}+\frac{2}{3}\sum_j\omega_{Qj}(I_{jz}^{1-2}-I_{jz}^{2-3})$$
$$+\frac{\omega_1}{2}\sum_j\{(I_{j+}^{1-2}+I_{j+}^{2-3})e^{i\omega t}+(I_{j-}^{1-2}+I_{j-}^{2-3})e^{-i\omega t}\}+\mathcal{H}_{II}. \quad (13')$$

The first two terms of the Hamiltonian (13′) commute with each other, so that the quasi-equilibrium density matrix can be represented in the form

$$\xi=\frac{1}{\mathrm{Sp}(1)}\left\{1+\beta_I\cdot 2\omega_I\sum_j I_{jz}^{1-3}-\beta\frac{2}{3}\sum_j \omega_{Qj}(I_{jz}^{1-2}-I_{jz}^{2-3})\right\}. \tag{14}$$

To separate in explicit form the perturbation operator corresponding to the two-quantum process, it is convenient to use the formalism developed in Ref. 7. We transform to the interaction representation in terms of the first two operators in the Hamiltonian (13′). The transformed Hamiltonian is written in the form

$$\tilde{\mathscr{H}}(t)=\frac{\omega_1}{2}\sum_j (I_{j+}^{1-2}+I_{j+}^{2-3})\exp(i\Delta\omega t)\exp(-i\omega_{Qj}t)$$

$$\times\exp[4i\omega_{Qj}(I_{jz}^{1-2}+I_{jz}^{2-3})t]+\mathrm{H.c.}+\mathscr{H}_{II}(t), \tag{15}$$

where $\Delta\omega=\omega-\omega_I$.

We assume that the condition $\overline{\omega}_Q\gg\omega 1$ is satisfied. Then, following Ref. 6, the effective Hamiltonian can be represented accurate to second order as

$$\mathscr{H}_{\mathrm{eff}}=\overline{\mathscr{H}}+{}^1/_2\overline{[\tilde{\overline{\mathscr{H}}},\mathscr{H}]},$$

$$\tilde{\mathscr{H}}=i\int^t dt'[\mathscr{H}(t')-\overline{\mathscr{H}}], \tag{16}$$

$$\overline{\mathscr{H}}=\lim_{T\to\infty}\frac{1}{T}\int_0^T dt\,\mathscr{H}(t). \tag{17}$$

The averaging in (17) is only over the "fast" variables. Substituting (15) in (16) and using the equation

$$\exp[4i\omega_{Qj}(I_{jz}^{1-2}+I_{jz}^{2-3})t]=[J_3+4(I_{jz}^{1-2})^2\cos 2\omega_{Qj}t$$

$$+2iI_{jz}^{1-2}\sin 2\omega_{Qj}t][J_1+4(I_{jz}^{2-3})^2\cos 2\omega_{Qj}t+2iI_{jz}^{2-3}\sin 2\omega_{Qj}t]$$

[J_3 and J_1 are 3×3 matrices with unity nonzero matrix elements ($\langle 3|J_3|3\rangle=1$, $\langle 1|J_1|1\rangle=1$)] we obtain for the two-quantum-transition operator:

$$V(t)=\frac{\omega_1^2}{2\overline{\omega}_Q}\left\{\sum_j I_{j+}^{1-3}e^{2i\Delta\omega t}+I_{j-}^{1-3}e^{-2i\Delta\omega t}\right\}. \tag{18}$$

A feature of this expression is that it does not contain an "inhomogeneous" frequency dependence, whereas the perturbation operators corresponding to single-quantum transitions at frequencies $\omega_I+\overline{\omega}_Q$ depend on ω_{Qj}.

Using (18) we can obtain a system of equations that describe the ENDOR. In analogy with (8) we have in the stationary case

$$\frac{\beta_S-\beta_L}{T_{SL}}+W_S\left(\beta_S+\frac{\Omega-\omega_0}{\omega_0}\beta_D\right)=0,$$

$$\frac{\beta_D-\beta_L}{T_{DL}}+\frac{\beta_D-\beta_I}{T_{DI}}+W_S\frac{\omega_0(\Omega-\omega_0)}{\omega_D^2}\left(\beta_S+\frac{\Omega-\omega_0}{\omega_0}\beta_D\right)=0, \tag{19}$$

$$\frac{\beta_I-\beta_D}{T_{ID}}+W^{(2)}\beta_I=0,$$

where

$$W^{(2)}=\frac{2\omega_1^4}{\omega_Q^2}\int\frac{dt\langle I_+^{1-3}(t)I_-^{1-3}\rangle e^{2i\Delta\omega t}}{\langle I_+^{1-3}I_-^{1-3}\rangle}.$$

It is easy to obtain from this an expression for the absolute susceptibility change Δ_χ'' (it is assumed that the ESR saturation condition is met) due to two-quantum transitions:

$$\Delta\chi''=\frac{\chi_0\omega_0}{2S\Delta}\left(\frac{\Delta\omega}{\omega_D}\right)^2K\left[\alpha+K+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1}$$

$$\times\left[\alpha+\left(\frac{\Delta\omega}{\omega_D}\right)^2\right]^{-1}, \tag{20}$$

$$K\equiv\frac{T_{SL}}{T_{DI}}\frac{2W^{(2)}T_{ID}}{1+2W^{(2)}T_{ID}}.$$

At low values of the rf power, when

$$W^{(2)}T_{ID}\ll 1, \tag{21}$$

Δ_χ'' will be proportional to $W^2(\Delta\omega)$. In contrast to one-quantum transitions, $W^2(\Delta\omega)$ does not contain inhomogeneous broadening, so that the resolution of the line is higher. Furthermore, the homogeneous width $W^2(\Delta\omega)$ is approximately half the value in the case of one-quantum transitions, since (19) contains $2\Delta\omega t$ in the exponential. Equation (19), however, contains a small factor $(\omega_1/\omega_Q)^2$, so that under condition (21) the two-quantum ENDOR intensity is lower than the one-quantum one. This is apparently the situation realized in Ref. 2, since the intensity of the two-quantum ENDOR line observed there is much smaller than that of the one-quantum line, and an appreciable line narrowing is observed at the same time.

In the other limiting case $W^2T_{ID}\gg 1$ Eq. (20) coincides with that for the susceptibility change for the usual ENDOR,[9] but the corresponding line width is much smaller.

We note in conclusion that in the case of multispin and multiquantum ENDOR due to the coupling of the nuclear spins with the DDR electrons, the intensity of the double resonance in sufficiently strong alternating fields will be the same as in ordinary ENDOR.

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