Dynamic polarization and NMR of nuclei in the immediate vicinity of paramagnetic impurity centers

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We investigate the dynamic polarization mechanisms and calculate the polarization amplification factors and the absorption signals of the NMR 04 nuclei in the immediate vicinity of paramagnetic impurity centers in solid dielectrics under conditions of pulsed and steady saturation of allowed and forbidden EPR transitions of the impurity, with account taken of the electron dipole reservoir. In contrast to the impurity nuclei proper and the remote nuclei of the host lattice, the nearby nuclei are polarized even under pulsed saturation of allowed transitions. It is known that the preliminary polarization of the nearby nuclei by microwave pumping can increase the sensitivity of NMR-signal measurements by two or three orders of magnitude.

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1. INTRODUCTION

Methods of dynamic polarization of nuclei (DPN) have assumed a leading position in modern physics following the development of highly polarized nuclear targets based on solid dielectrics diluted with paramagnetic ions of transition-group elements.[1-3] At present these materials are most promising for research and applications[4,5]

The large amount of information obtainable by DPN studies of the dynamics of electron-nuclear spin systems and various relaxation processes can be fully utilized only with a thorough understanding of the details of the DPN phenomenon, and not only of its basic laws. From this point of view, undisputed importance attaches to the dynamic polarization of nuclei in the immediate vicinity of the paramagnetic impurity ions, whose hyperfine interaction (HFI) with the impurity is of the order of their Zeeman energy.[1)]

Up to now, principal attention was paid to "remote" nuclei,[2)] whose polarization has made it possible to produce targets with high density of oriented nuclei. We know, on the other hand, how important a role is played by the DPN of the impurity themselves ($A \gg \hbar\omega_I$) their low density notwithstanding, when it comes to comparing various relaxation processes of impurity ions,[6] as well as in the investigation of the anisotropy of γ and β rays and in high-precision measurements of nuclear spins and magnetic moments in the case when the nuclei themselves are radioactive.[1,7]

The role of nearby nuclei in spin dynamics of dilute paramagnetic crystals is extremely important and more varied than the role of the nuclei themselves and of remote nuclei. Nearby nuclei are responsible for the unresolved hyperfine structure of the EPR spectra, and cause the so-called inhomogeneous broadening of the EPR lines. They are the intermediate link between the impurity ions and the remote nuclei, and undoubtedly influence the relaxation and polarization of the bulk of the sample nuclei. In addition, the nearby nuclei form the spectra and determine the mechanisms of the electron-nuclear double resonance (ENDOR), and the degree of their polarization prior to application of the radiofrequency field governs the ENDOR signal.

Upon saturation of the allowed and forbidden impurity EPR transitions, "islands" of increased nuclear polarization which duplicate the distribution of the paramagnetic ions, are produced in the sample. The polarization is then transferred to the remote nuclei via nuclear spin diffusion in which the lattice[8] or the dipole reservoir (DR) of the impurity electron spins[9] takes part. It appears that this mechanism can explain the singularities of the Larmor EDNOR.[10]

Interest in nearby nuclei arose after it became clear that it is precisely the forbidden EPR transitions, in conjunction with the nearby nuclei, which are responsible for the discrete[11,12] and the rf discrete[13] saturation of the EPR; these transitions have uncovered new possibilities of investigating the HFI in solids. The most important, in our opinion, stimulus for the investigation of the dynamics of nearby nuclei, and particularly of their dynamic polarization, is undoubtedly the possibility of direct observation of NMR signals from nuclei in individual coordination spheres.[14] Preliminary polarization of the nearby nuclei by microwave pumping can increase the sensitivity of the measurements of the NMR signals from these nuclei by several orders of magnitude. This, in conjunction with EDNOR, can provide more abundant and direct information on the nature of the paramagnetic center and of the HFI.

The present paper is devoted to a theoretical investigation of the mechanisms of dynamic polarization and NMR of nearby nuclei with allowance for the dipole reservoir of the impurity electron spins. We calculate the enchancement coefficients of the polarization signals and the NMR absorption signals of the nearby nuclei under conditions of pulsed and stationary saturation of the allowed and forbidden EPR transitions of the impurity. Samples with which the appropriate experiments can be performed are indicated.

2. BASIC EQUATIONS

We represent a dilute paramagnetic signal as an aggregate of N equivalent electron + nucleus pairs with spins $S = I = 1/2$, and with account taken of the anisotropic HFI

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inside the pair and of the dipole-dipole interaction between the electron spins.[15,16]

In the limit of strong constant magnetic fields $\mathbf{H}_0\uparrow\uparrow z$, when the electron Zeeman energy greatly exceeds the HFI energy, the electron spins are quantized along $\mathbf{H}_0$ if the impurity g factor is isotropic, or else if $\mathbf{H}_0$ is parallel to one of the principal axes of the g tensor. At the same time, the nuclear spins are quantized along the direction of the effective field $\mathbf{H}_M$, which is the sum of $\mathbf{H}_0$ and the field due to the anisotropic-HFI part that is diagonal in the electron spin.[17,11] The magnitude and the direction of the effective field depend on the projection $M = S_{nz} = \pm\frac{1}{2}$ of the electron spin on the $\mathbf{H}_0$ direction. The angle θ_M between the field $\mathbf{H}_M$ and the z axis is defined by the relation

$$\cos\theta_M = \frac{\omega_I - MA/\hbar}{\omega_I^M}, \quad \sin\theta_M = \frac{|B|}{2\hbar\omega_I^M},$$

$$\omega_I^M \equiv \gamma_I H_M = \left[\left(\omega_I - M\frac{A}{\hbar}\right)^2 + \frac{|B|^2}{4\hbar^2}\right]^{1/2}, \tag{1}$$

where A and B are the constants of the anisotropic HFI, and $\omega_I = \gamma_I H_0$.

The energy spectrum of the pair contains four nonequidistant levels with energies $E_{Mm} = \hbar\omega_s M - \hbar\omega_I^M m$. The EPR line consists accordingly of four components (we assume that the hyperfine structure is resolved): two correspond to allowed transitions at frequencies $\omega_s^m = \omega_s + m(\omega_I^- - \omega_I^+)$, and the other two to forbidden transitions at frequencies $\omega_{sI}^\nu = \omega_s + \nu\bar{\omega}_I$. Here $\omega_s = \gamma_s H_0$ is the electron Zeeman frequency

$$\bar{\omega}_I = {}^1/_2(\omega_I^- + \omega_I^+), \quad \omega_I^\pm \equiv \omega_I^{\pm 1/2}, \quad \omega_s^\pm = \omega_s^{\pm 1/2},$$

$\nu = \pm 1$, and $m = \pm\frac{1}{2}$ is the projection of the nuclear spin on $\mathbf{H}_M$. In NMR, two lines at frequencies ω_I^M are observed.

If the microwave field (or the lattice) produce in the electronic transition $M \leftrightarrow M+1$ a substantial change in the direction of $\mathbf{H}_M$, i.e., if the orientation of the quantization axis of the nuclear spins is changed, the probability of the forbidden transition $(M,m) \leftrightarrow (M+1, m\pm 1)$, which takes place with simultaneous change of M and m, turns out to be of the same order of the allowed transition $(M,m) \leftrightarrow (M+1,m)$ (Refs. 18 and 11) (it suffices for this purpose, e.g., to satisfy the inequalities $|A/2 - \hbar\omega_I| \ll |B|/2 \ll \hbar\omega_I$).

Assume that the small time scale τ_0 in the considered spin system is due to the secular part $\mathscr{H}_d$ of the electron dipole-dipole interaction, which commutes with the Hamiltonian

$$\sum_n \mathscr{H}_{0n} = \sum_m \mathscr{H}_s^m + \mathscr{H}_I,$$

where $\mathscr{H}_{0n}$ is the Hamiltonian of the n-th pair and $\mathscr{H}_s^{\pm m}$ are the electron Zeeman subsystems with frequencies $\omega_s^{\pm m}$, and $\mathscr{H}_I$ is the averaged nuclear Zeeman subsystems with frequency $\bar{\omega}_I$ (Ref. 15). For times $t \gg \tau_0$ the quasiequilibrium state of the system can be described by an abbreviated set of macroscopic parameters, $\beta_s^{\pm m}$, β_I, β_d, and β_L, which are the reciprocal temperatures of the subsystems $\mathscr{H}_s^{\pm m}$, $\mathscr{H}_I$, $\mathscr{H}_d$ and of the lattice, respectively.

Taking into account for simplicity only the direct spin-lattice relaxation of the dipole reservoir and neglecting the direct thermal contact between the nuclei and the lattice, we obtain the following system of equations for the reciprocal temperatures[15,16]:

$$\frac{d\beta_s^m}{dt} = -\frac{\beta_s^m - \beta_L}{T_s^m} - \frac{1}{2\omega_s^m}\sum_\nu \omega_{sI}^\nu \frac{\beta_{sI}^\nu - \beta_L}{T_x^\nu} - 2W_s^m\left(\beta_s^m + \frac{\Delta_s^m}{\omega_s^m}\beta_d\right) - \frac{1}{\omega_s^m}\sum_\nu W_{sI}^\nu X^\nu + \frac{4m}{\omega_s^m}\sum_M M W_I^M Y^M,$$

$$\frac{d\beta_d}{dt} = -\frac{\beta_d - \beta_L}{T_{dL}} - \sum_m \frac{\omega_s^m \Delta_s^m}{\omega_d^2} W_s^m\left(\beta_s^m + \frac{\Delta_s^m}{\omega_s^m}\beta_d\right) - \sum_\nu \frac{\Delta_{sI}^\nu}{\omega_d^2} W_{sI}^\nu X^\nu - \frac{1}{\omega_d^2}\sum_M \Delta_I^M W_I^M Y^M, \tag{2}$$

$$\frac{d\beta_I}{dt} = -\frac{1}{2\bar{\omega}_I}\sum_\nu \nu\omega_{sI}^\nu \frac{\beta_{sI}^\nu - \beta_L}{T_x^\nu} - \frac{1}{\bar{\omega}_I}\sum_\nu \nu W_{sI}^\nu X^\nu - \frac{1}{\bar{\omega}_I}\sum_M W_I^M Y^M,$$

$$X^\nu \equiv \omega_{sI}^\nu\left(\beta_{sI}^\nu + \frac{\Delta_{sI}^\nu}{\omega_{sI}^\nu}\beta_d\right),$$

$$Y^M \equiv \omega_I^M \beta_I^M + \Delta_I^M \beta_d, \quad \Delta_s^m = \Omega_s - \omega_s^m, \quad \Delta_I^M = \Omega_I - \omega_I^M,$$

$$W_s^m = p\frac{\pi\omega_{1s}^2}{2}\varphi_s^m(\Delta_s^m),$$

$$W_{sI}^\nu = q\frac{\pi\omega_{1s}^2}{2}\varphi_{sI}^\nu(\Delta_{sI}^\nu), \quad \Delta_{sI}^\nu = \Omega_s - \omega_{sI}^\nu, \quad \omega_{1s} = \gamma_s H_{1s}.$$

For the sake of brevity we have introduced in (2) the reciprocal temperatures β_I^M and β_{sI}^ν of the nuclear transition at the frequency ω_I^M and of the forbidden transition at the frequency ω_{sI}^ν:

$$\beta_I^M = \frac{1}{\omega_I^M}\left(\bar{\omega}_I\beta_I - M\sum_m 2m\omega_s^m\beta_s^m\right),$$

$$\beta_{sI}^\nu = \frac{1}{2\omega_{sI}^\nu}\left(\sum_m \omega_s^m\beta_s^m + 2\nu\bar{\omega}_I\beta_I\right), \tag{3}$$

W_s^m and W_{sI}^ν are the probabilities of the allowed and forbidden transitions and are governed by the transverse microwave field of frequency Ω_s and amplitude H_{1s}; $\omega_d = \hbar^{-1}(\mathrm{Sp}\mathscr{H}_d^2/\mathrm{Sp}S_z^2)^{1/2}$ is the average dipole-reservoir quantum; $\varphi_s^m(\Delta_s^m)$ and $\varphi_{sI}^\nu(\Delta_{sI}^\nu)$ describe the forms of the allowed and forbidden transitions, p and q are the relative probabilities of the allowed and forbidden transitions, respectivley:

$$p = \cos^2\frac{\theta_M + \theta_{-M}}{2}, \quad q = \sin^2\frac{\theta_M + \theta_{-M}}{2}, \tag{4}$$

where θ_M is taken from (1). The probability W_I^M of the nuclear spin flip under the influence of the an rf field of frequency H_{1I}, where $H_{1I} \equiv \omega_{1I}/\gamma_I$ was calculated in Ref. 16:

$$W_I^M = \alpha_M \frac{\pi\omega_{1I}^2}{2} f_I^M(\Delta_I^M), \quad \alpha_M = \begin{cases} 1 + \cos^2\theta_M, & H_{1I} \perp z \\ \sin^2\theta_M, & H_{1I} \parallel z \end{cases}, \tag{5}$$

where $f_I^M(\Delta_I^M)$ is the form of the nuclear transition at the frequency ω_I^M.

The times T_s^m and T_x^ν characterize the "direct" and "indirect" relaxation transitions at the frequencies ω_s^m and ω_{sI}^ν, respectively. The appearance of the T_x^ν processes is due, in particular, to forbidden electronic transitions induced by the lattice.

We note that in Ref. 15 it was assumed that $T_s^+ = T_s^- \equiv T_s$ and $T_x^+ = T_x^- \equiv T_x$

3. GENERAL EXPRESSIONS FOR THE POLARIZATION ENHANCEMENT COEFFICIENTS AND FOR THE NMR ABSORPTION SIGNALS OF THE NEARBY NUCLEI

The enhancement coefficient of the polarization of the nuclei is defined as the quantity $E = P/P_0$, where P and P_0 are the equilibrium and nonequilibrium polarizations of the nuclei along the $\mathbf{H}_0$ direction:

$$P_0=\frac{1}{I}\,\mathrm{Sp}(\rho_0 I_{nz}),\quad P=\frac{1}{I}\,\mathrm{Sp}(\rho_q I_{nz}).$$

Here I_{nz} is the operator of the z-projection of the n-th nuclear spin, and ρ_q and ρ_0 are respectively the quasiequilibrium and equilibrium statistical operators. In the high-temperature approximation we have

$$\rho_q=(\mathrm{Sp}\,1)^{-1}\Big(1-\sum_m \beta_s^m\mathcal{H}_s^m-\beta_I\mathcal{H}_I-\beta_d\mathcal{H}_d\Big),$$

$$\rho_0=(\mathrm{Sp}\,1)^{-1}\Big\{1-\beta_L\Big(\sum_m \mathcal{H}_s^m+\mathcal{H}_I+\mathcal{H}_d\Big)\Big\}.$$

Using the explicit forms of the Hamiltonians $\mathcal{H}_s^m$, $\mathcal{H}_I$, and $\mathcal{H}_d$ (Ref. 15) and performing simple calculations, we obtain for the case $I=\frac{1}{2}$

$$P_0={}^1/_2\hbar\omega_I\beta_L,\quad P={}^1/_4\hbar\sum_M\cos\theta_M\Big(\overline{\omega}_I\beta_I-M\sum_m 2m\omega_s^m\beta_s^m\Big).$$

The expression for the nuclear-polarization enhancement takes the form

$$E=(2\omega_I\beta_L)^{-1}\sum_M\cos\theta_M\Big(\overline{\omega}_I\beta_I-M\sum_M 2m\omega_s^m\beta_s^m\Big).\qquad(6)$$

Using (3), we can express E in terms of the nuclear parameters β_I^M:

$$E=(2\omega_I\beta_L)^{-1}\sum_M\omega_I^M\beta_I^M\cos\theta_M.\qquad(7)$$

The power Q_I absorbed by the spin system from the rf field source is

$$Q_I=2\Omega_I H_{1I}^2\chi_I''^M=\frac{d}{dt}\,\mathrm{Sp}\Big\{\rho_q\Big(\sum_m\mathcal{H}_s^m+\mathcal{H}_I+\mathcal{H}_d\Big)\Big\},\qquad(8)$$

where d/dt denotes the change of the corresponding quantity under the influence of the rf field and $\chi_I''^M$ is the imaginary part of the complex susceptibility, called hereafter the NMR absorption signal at the frequency ω_I^M.

Using the explicit form of ρ_q and the system of equations (2) and (8), we can derive the following expression for the NMR absorption signal of the nearby nuclei:

$$\chi_I''^M=\chi_{I0}''^M(\Delta_I^M)(\omega_I^M\beta_I^M+\Delta_I^M\beta_d)/\Omega_I\beta_L,\qquad(9)$$

$$\chi_{I0}''^M(\Delta_I^M)={}^1/_8\pi\alpha_M\chi_{0I}\Omega_I f_I^M(\Delta_I^M),\quad \chi_{0I}=N\hbar^2\gamma_I^2\beta_L/4,\qquad(10)$$

χ_{0I} is the static nuclear susceptibility and $\chi_{I0}''^M(\Delta_I^M)$ is the equilibrium absorption signal. The quantity $(\omega_I^M\beta_I^M+\Delta_I^M\beta_d)/\Omega_I\beta_L$ describes the effects of saturation in a nuclear transition of frequency ω_I^M and is equal to unity at equilibrium.

4. DISCRETE SATURATION OF ALLOWED AND FORBIDDEN EPR TRANSITIONS

We assume that the spin system at equilibrium is subject to the action of a saturating microwave pulse of frequency $\Omega_s\approx\omega_s^m$, whose duration is much shorter than all the relaxation times. Neglecting in (2) the relaxation processes, putting $W_s^{-m}=W_I^{\pm M}=W_{sI}^{\pm\nu}=0$, and solving the obtained equations under the initial conditions $\beta_s^m(0)=\beta_s^{-m}(0)=\beta_I(0)=\beta_d(0)=\beta_L$, we obtain for the time of action of the pulse

$$t>\tau_s^m=\{2W_s^m[1+(\Delta_s^m)^2/2\omega_d^2]\}^{-1},$$

i.e., after the completion of the saturation we obtain quasistationary values of the reciprocal temperatures:

$$\beta_d=-\frac{\omega_s^m}{\Delta_s^m}\beta_s^m=\beta_L\frac{2\omega_d^2-\omega_s^m\Delta_s^m}{2\omega_d^2+(\Delta_s^m)^2},\quad \beta_s^{-m}=\beta_I=\beta_L.\qquad(11)$$

Similarly, in the case of a short microwave pulse at the forbidden transition $\Omega_s\approx\omega_{sI}^\nu$, at a pulse action time

$$t>\tau_{sI}^\nu=\{2W_{sI}^\nu[1+(\Delta_{sI}^\nu)^2/2\omega_d^2]\}^{-1}$$

we obtain

$$\beta_s^{\pm m}=\beta_L\Big\{1-\frac{\Omega_s}{\omega_s^{\pm m}}\frac{\omega_d^2}{2\omega_d^2+(\Delta_{sI}^\nu)^2}\Big\},\quad \beta_d=\beta_L\frac{2\omega_d^2-\omega_{sI}^\nu\Delta_{sI}^\nu}{2\omega_d^2+(\Delta_{sI}^\nu)^2},$$
$$\beta_I=\beta_L\Big\{1-\frac{\nu\Omega_s}{\overline{\omega}_I}\frac{\omega_d^2}{2\omega_d^2+(\Delta_{sI}^\nu)^2}\Big\}.\qquad(12)$$

Substitution of (11) and (12) in (6) leads to the following values of the nuclear-polarization amplification coefficient:

$$E_p^m=1+2m\frac{\Omega_s}{\omega_I}\frac{\omega_d^2}{2\omega_d^2+(\Delta_s^m)^2}\sum_M M\cos\theta_M,\qquad(13)$$

$$E_q^\nu=1-\nu\frac{\Omega_s}{2\omega_I}\frac{\omega_d^2}{2\omega_d^2+(\Delta_{sI}^\nu)^2}\sum_M\cos\theta_M.\qquad(14)$$

According to (13) and (14) the polarization of nearby nuclei of opposite sign is obtained following discrete saturation by a transverse microwave field not only for forbidden but also for allowed transitions. We emphasize that in the case of allowed-transition pulsed saturation that overtakes all the relaxation processes in the system, neither the nuclei of the impurity proper nor the remote nuclei of the host lattice are polarized at all. Since the anisotropic HFI mixes the states of a pair with identical values of M, a longitudinal microwave field does not polarize the nearby nuclei, in contrast to the impurity nuclei themselves.[1,19]

Allowance for the dipole reservoir decreases the polarization, which is maximal at the centers of the lines $\Delta_s^m=0$ or $\Delta_{sI}^\nu=0$:

$$(E_p^m)_{max}\approx 2m\frac{\Omega_s}{4\omega_I}\sum_M 2M\cos\theta_M,$$

$$(E_q^\nu)_{max}\approx -\nu\frac{\Omega_s}{4\omega_I}\sum_M\cos\theta_M. \quad (15)$$

The reason is that in discrete saturation with detuning of both the allowed and the forbidden transitions, a strong shift of the dipole temperature β_d^{-1} takes place in accord with (11) and (12), and prevents equalization of the populations of the saturated pair of levels, and E decreases as a result. The situation here is different from the mechanism of dynamic cooling of remote nuclei,[19–21] in which it is precisely the shift of β_d^{-1} upon saturation of the allowed transition with detuning which causes the polarization of the nuclei on account of the thermal I–d contact between the nuclear Zeeman subsystem and the electronic dipole reservior with the Hamiltonian $\mathscr{H}_{ss}I([\mathscr{H}_{ss},\Sigma_n S_{nz}]=0)$. The I–d coupling is effected with a characteristic velocity $1/T_{Id}$ and is most effective at $\omega_I\lesssim\omega_{ss}$,

$$\omega_{ss}=\hbar^{-1}(\mathrm{Sp}\,\mathscr{H}_{ss}^2/\mathrm{Sp}\,S_z^2)^{1/2}.$$

There is no analog of the indicated mechanism in the case of nearby nuclei under the considered conditions of a resolved hyperfine structure of the EPR spectrum, when $\omega_I^\pm\gg\omega_d$. The terms of type $S_{\eta z}I_n^\pm$, responsible for the I–d contact of the remote nuclei with $\mathscr{H}_{ss}$, were taken into account exactly and led to renormalization of the dipole reservoir, as a result of which $\mathscr{H}_d$, unlike $\mathscr{H}_{ss}$, depends on the nuclear-spin operators. To be sure, in the remaining part of the s–s interaction $\mathscr{H}_{ss}-\mathscr{H}_d$ there are forbidden flip-flop transitions of two electron spins, of the type $(-\,+;\,+\,+)\leftrightarrow(+\,-;\,-\,-)$, which takes place at a frequency $\omega_{sI}^+-\omega_{sI}^-=2\bar\omega_I$ and connect β_I and β_d without changing β_s^m, i.e., produce an I–d contact at the frequency $2\bar\omega_I$, but these processes are ineffective because $2\bar\omega_I\gg\omega_d$.

The mechanism of polarization of nearby nuclei on account of saturation of forbidden transitions is similar to the usual "solid effect"[1–5] for remote nuclei. There is, however, also a difference. It is known that in the "solid effect" allowance for the dipole reservoir decreases E_q^ν for two reasons: 1) the I–d contact shortens the nuclear spin-lattice relaxation time T_{IL}, leading to the change

$$T_{IL}\to T_I=(1/T_{IL}+1/T_{Id})^{-1}<T_{IL},$$

which makes it difficult to reach full saturation of the forbidden transition, $W_{sI}^\nu T_I\gg 1$;2) in the presence of overlap of the forbidden and allowed transitions, the saturation of a forbidden transition leads to saturation of the allowed transition with detuning and accordingly to a shift of β_d^{-1}, which decreases E_q^ν. In the considered case of nearby nuclei, as noted above, there is neither I–d coupling nor overlap of the allowed and forbidden transitions. However, owing to the high probability of the forbidden transitions we have $W_{sI}^\nu\gg 1/T_s^\pm$ ($W_{sI}^\nu\ll 1/T_s^\pm$ for the remote nuclei), therefore regardless of the allowed transition, saturation of a forbidden transition with $\Delta_{sI}^\nu\neq 0$ shifts β_d^{-1} and decreases E_q^ν.

According to (13) and (14), if $\theta_M\equiv\theta\neq f(M)$ (this takes place, in particular, at $A/2\ll\hbar\omega_I\sim|B|/2$) we have

$$E_q^\nu\simeq-\nu\frac{\Omega_s}{\omega_I}\frac{\omega_d^2}{2\omega_d^2+(\Delta_{sI}^\nu)^2}\cos\theta,\quad \cos\theta=\frac{\omega_I}{[\omega_I^2+|B|^2/4\hbar^2]^{1/2}}, \quad (16)$$

and $E_p^m=1$. Consequently, the polarization of the nearby nuclei by pulsed saturation of the allowed transition is due entirely to the change of the z-projection of the effective field $\mathbf{H}_M$ in the electronic transition $M\leftrightarrow M+1$.

If $|A/2-\hbar\omega_I|\ll|B|/2\ll\hbar\omega_I$, we have $\cos\theta_+\ll\cos\theta_-\approx 1$ and Eqs. (13) and (14) yield

$$E_p^m\approx-2m\frac{\Omega_s}{2\omega_I}\frac{\omega_d^2}{2\omega_d^2+(\Delta_s^m)^2},\quad E_q^\nu\simeq-\nu\frac{\Omega_s}{2\omega_I}\frac{\omega_d^2}{2\omega_d^2+(\Delta_{sI}^\nu)^2}, \quad (17)$$

whence

$$|E_p^m|_{max}\approx|E_q^\nu|_{max}=\omega_s/4\omega_I,$$

which is half the pulsed value $|E_q^\nu|_{\max}$ for remote nuclei.

Interesting features can be observed when both the allowed and forbidden transitions are discretely saturated simultaneously. We apply to an equilibrium system two short saturating pulses at the frequencies $\Omega_1=\omega_s^m+\Delta_1^m$ and $\Omega_2=\omega_s^{-m}+\Delta_2^{-m}$. Putting $W_I^{\pm M}=W_{sI}^{\pm\nu}=0$, in (2), neglecting the relaxation processes, and solving the resultant system of equations under equilibrium conditions, we can easily show that after the termination of both saturations, i.e. after a time $t>\tau_s^{\pm m}$, a quasistationary state is established in the spin system with reciprocal temperatures

$$\beta_s^m=-\frac{\Delta_1^m}{\omega_s^m}\beta_d^{m,-m},\quad \beta_s^{-m}=-\frac{\Delta_2^{-m}}{\omega_s^{-m}}\beta_d,\quad \beta_I=\beta_L,$$
$$\beta_d^{m,-m}=\frac{2\omega_d^2-\omega_s^m\Delta_1^m-\omega_s^{-m}\Delta_2^{-m}}{2\omega_d^2+(\Delta_1^m)^2+(\Delta_2^{-m})^2}\beta_L. \quad (18)$$

In the case $\Omega_1=\omega_{sI}^\nu+\Delta_1^\nu$, $\Omega_2=\omega_{sI}^{-\nu}+\Delta_2^{-\nu}$ we obtain analogously at a time $t>\tau_{sI}^{\pm\nu}$

$$\beta_s^{\pm m}=\frac{\beta_L}{2\omega_s^{\pm m}}\left\{\pm 2m(\omega_I^--\omega_I^+)-(\Delta_1^\nu+\Delta_2^{-\nu})\frac{\beta_d^{\nu,-\nu}}{\beta_L}\right\},$$
$$\beta_I=\frac{\Delta_2^{-\nu}-\Delta_1^\nu}{2\nu\bar\omega_I}\beta_d^{\nu,-\nu},\quad \beta_d^{\nu,-\nu}=\beta_L\frac{2\omega_d^2-\omega_{sI}^\nu\Delta_1^\nu-\omega_{sI}^{-\nu}\Delta_2^{-\nu}}{2\omega_d^2+(\Delta_1^\nu)^2+(\Delta_2^{-\nu})^2}. \quad (19)$$

Substitution of (18) and (19) in (6) yields

$$E_p^{m,-m}\approx 2m\frac{\Delta_1^m-\Delta_2^{-m}}{2\omega_I}\frac{\beta_d^{m,-m}}{\beta_L}\sum_M M\cos\theta_M,$$
$$E_q^{\nu,-\nu}\approx-\nu\frac{\Delta_1^\nu-\Delta_2^{-\nu}}{4\omega_I}\frac{\beta_d}{\beta_L}\sum_M\cos\theta_M. \quad (20)$$

It follows from (20) that $|E_q^{\nu,-\nu}|\gg 1$ at $|\beta_d^{\nu,-\nu}|\gg\beta_L$ and $|E_p^{m,-m}|\gg 1$ at $|\beta_d^{m,-m}|\gg\beta_L$ only for nearby nuclei with θ_M dependent on M. Thus, in the case of two-pulse saturation of both the allowed and forbidden transitions, the polarization of the nearby nuclei is due entirely to the shift of the dipole-reservoir temperature.

We put $\Delta_2^{-m}=0$ and $\Delta_2^{-\nu}=0$ in (20); then

$$E_p^{m,-m}\approx 2m\frac{\omega_s^m}{4\omega_I}\frac{(\Delta_1^m)^2}{2\omega_d^2+(\Delta_1^m)^2}\sum_M 2M\cos\theta_M,$$
$$E_q^{\nu,-\nu}\approx\nu\frac{\omega_{sI}^\nu}{4\omega_I}\frac{(\Delta_1^\nu)^2}{2\omega_d^2+(\Delta_1^\nu)^2}\sum_M\cos\theta_M. \quad (21)$$

We obtain practically the same polarization as in one-pulse saturation with frequency $\Omega_s \approx \omega_s^m (\Omega_s \approx \omega_{sI}^\nu)$, but with opposite sign. Consequently, two-pulse saturation can reverse the sign of the polarization produced in one-pulse saturation.

We calculate now the NMR absorption signal of the nearby nuclei. Using (3) with (11) and (12) we obtain

$$(\beta_I^M)_m=\beta_L\left\{1+4mM\frac{\Omega_s}{\omega_I^M}\frac{\omega_d^2}{2\omega_d^2+(\Delta_s^m)^2}\right\}, \tag{22}$$

$$(\beta_I^M)_\nu=\beta_L\left\{1-\nu\frac{\Omega_s}{\omega_I^M}\frac{\omega_d^2}{2\omega_d^2+(\Delta_{sI}^\nu)^2}\right\}. \tag{23}$$

Obviously,

$|\beta_I^M|\gg\beta_L$, $(\beta_I^M)_m(\beta_I^{-M})_m<0$, $(\beta_I^M)_\nu(\beta_I^{-M})_\nu>0$, i.e., discrete saturation shifts greatly both nuclear temperatures, with one of the nuclear transitions inverted in the case of the allowed transitions, whereas a microwave pulse of frequency ω_{sI}^+ inverts both nuclear transitions simultaneously in the case of forbidden transitions.

Subsituting (22), (23) and β_d from (11) and (12) in (9), we get

$$\chi_I^{\prime\prime M}|_m=\chi_{I0}^{\prime\prime M}(\Delta_I^M)\left\{1+\frac{\Omega_s}{\Omega_I}\frac{4mM\omega_d^2-\Delta_I^M\Delta_s^m}{2\omega_d^2+(\Delta_s^m)^2}\right\}, \tag{24}$$

$$\chi_I^{\prime\prime M}|_\nu=\chi_{I0}^{\prime\prime M}(\Delta_I^M)\left\{1-\frac{\Omega_s}{\Omega_I}\frac{\nu\omega_d^2+\Delta_I^M\Delta_{sI}^\nu}{2\omega_d^2+(\Delta_{sI}^\nu)^2}\right\}. \tag{25}$$

Consequently, the usually very weak NMR absorption signal from the nearby nuclei is amplified as a result of microwave pumping of the allowed and forbidden transitions by approximately $\Omega_s/\Omega_I\approx\gamma_s/\gamma_I\sim10^3$ times. In pulsed saturation at the frequency $\Omega_s\approx\omega_{sI}^+$ stimulated emission should be observed for both nuclear transitions, whereas for pulsed saturation at the frequency $\Omega_s\approx\omega_s^m$ stimulated emission takes place only for the nuclear transition $M=-m$, $(\chi_I^{\prime\prime M=-m}|_m<0)$.

Allowance for the dipole reservoir decreases $|\chi_I^{\prime\prime M}|$ if the quantities $4mM\omega_d^2$ and $-\Delta_I^M\Delta_s^m$ (or $\nu\omega_d^2$ and $\Delta_I^M\Delta_{sI}^\nu$) are of the same sign, and decreases $|\chi_I^{\prime\prime M}|$ if the signs are opposite. It is interesting to note that by choosing the signs and magnitudes of the detunings $\Delta_s^m,\Delta_{sI}^\nu,\Delta_I^M$ at specified values of m and ν we can change the sign of the absorption signal. For example, if $\Delta_s^m\Delta_I^M<0$ and $|\Delta_s^m\Delta_I^M|>\omega_d^2$, then $\chi_I^{\prime\prime M=-m}|_m>0$.

Under condition of two-pulse saturation of both the forbidden and the allowed transitions we have

$$(\beta_I^M)_{m,-m}=\frac{\beta_L}{\omega_I^M}\left\{\bar\omega_I+2mM(\Delta_1^m-\Delta_2^{-m})\frac{\beta_d^{m,-m}}{\beta_L}\right\}, \tag{26}$$

$$(\beta_I^M)_{\nu,-\nu}=-\frac{\beta_L}{2\omega_I^M}\left\{2M(\omega_I^--\omega_I^+)+\nu(\Delta_1^\nu-\Delta_2^{-\nu})\frac{\beta_d^{\nu,-\nu}}{\beta_L}\right\}, \tag{27}$$

where $\beta_d^{m,-m}$ and $\beta_d^{\nu,-\nu}$ are taken from (18) and (19). The shifts of the nuclear temperatures in this case is due entirely to the shift of the dipole-reservoir temperature. Comparison of (17), (26) with (22), (23) shows that the second resonant microwave pulse ($\Delta_2^{-m}=0$ or $\Delta_2^{-\nu}=0$), without practically changing the values of $(\beta_I^{\pm M})_m$ and $(\beta_I^{\pm M})_\nu$, inverts both nuclear transitions:

$$(\beta_I^{\pm M})_{m,-m}\approx-(\beta_I^{\pm M})_m,\quad(\beta_I^{\pm M})_{\nu,-\nu}\approx-(\beta_I^{\pm M})_\nu.$$

Substitution of (26), (27) and $\beta_d^{m,-m}$,$\beta_d^{\nu,-\nu}$ from (18) and (19) into (9) yields (we assume that $\Delta_2^{-m}=0$,$\Delta_2^{-\nu}=0$ and discard the small terms)

$$\chi_I^{\prime\prime M}|_{m,-m}\approx-\chi_{I0}^{\prime\prime M}(\Delta_I^M)\frac{\omega_s^m}{\Omega_I}\frac{\Delta_1^m(2mM\Delta_1^m+\Delta_I^M)}{2\omega_d^2+(\Delta_1^m)^2}, \tag{28}$$

$$\chi_I^{\prime\prime M}|_{\nu,-\nu}\sim\chi_{I0}^{\prime\prime M}(\Delta_I^M)\frac{\omega_{sI}^\nu}{\Omega_I}\frac{\Delta_1^\nu(\nu\Delta_1^\nu-\Delta_I^M)}{2\omega_d^2+(\Delta_1^\nu)^2}. \tag{29}$$

Consequently the reversal of the signs of the absorption under the influence of the second resonant microwave pulse does indeed take place at $\Delta_I^M=0$. In the general case $\Delta_I^M\neq0$ this sign reversal does not occur if $\Delta_1^m(2mM\Delta_1^m+\Delta_I^m)<0$ or $\Delta_1^\nu(\nu\Delta_1^\nu-\Delta_I^m)<0$, and the absolute values $|\chi_I^{\prime\prime M}|$ can either increase or decrease compared with the case of single-pulse saturation, depending on the relations between the detunings Δ_1^m,Δ_1^ν and Δ_I^M.

5. STATIONARY SATURATION OF ALLOWED AND FORBIDDEN EPR TRANSITIONS

We consider stationary saturation of an allowed transition at a frequency $\Omega_s\approx\omega_s^m$. Assuming in (2)

$$\frac{d\beta_s^m}{dt}=\frac{d\beta_d}{dt}=\frac{d\beta_I}{dt}=0,\quad W_s^{-m}=W_{sI}^{\pm\nu}=W_I^{\pm M}=0,$$

we can obtain stationary reciprocal-temperature values containing the allowed-transition saturation parameter $S_p^m\equiv2W_s^mT_p^m$. The time T_p^m is given by

$$T_p^m=T_s^m(T_s^{-m}+T_x^++T_x^-)/(T_s^++T_s^-+T_x^++T_x^-)$$

and is the effective time of the spin-lattice relaxation for a transition at the frequency ω_s^m. Obviously $T_p^m<T_s^m$ because of the presence of relaxation $T_x^\pm$ processes in the system.

Under saturation conditions $S_p^m\gg1$ the expressions for the stationary reciprocal temperatures take the simpler form

$$\beta_d=\beta_L\frac{2\alpha_p^m\omega_d^2-\omega_s^m\Delta_s^m}{2\alpha_p^m\omega_d^2+(\Delta_s^m)^2},$$

$$\beta_I=\beta_L\left\{1-\frac{\Omega_s}{2\bar\omega_I}\frac{2\alpha_p^m\omega_d^2}{2\alpha_p^m\omega_d^2+(\Delta_s^m)^2}\frac{T_x^+-T_x^-}{T_s^{-m}+T_x^++T_x^-}\right\},$$

$$\beta_s^{-m}=\beta_L\left\{1+\frac{\Omega_s}{\omega_s^{-m}}\frac{2\alpha_p^m\omega_d^2}{2\alpha_p^m\omega_d^2+(\Delta_s^m)^2}\frac{T_s^{-m}}{T_s^{-m}+T_x^++T_x^-}\right\},$$

$$\beta_s^m=-\frac{\Delta_s^m}{\omega_s^m}\beta_d,\quad\alpha_p^m=\frac{T_p^m}{T_{dL}}. \tag{30}$$

Similarly, in the cae of forbidden-transition saturation at a frequency $\Omega_s\approx\omega_{sI}^\nu$ the saturation parameter is $S_q^\nu\equiv2W_{sI}^\nu T_q^\nu$, and the effective spin-lattice relaxation time T_q^ν is given by

$$T_q^\nu=T_x^\nu(T_s^++T_s^-+T_x^{-\nu})/(T_s^++T_s^-+T_x^++T_x^-).$$

Assuming that $S_q^\nu\gg1$, we can obtain the stationary values of the reciprocal temperatures in the form

$$\beta_d=\beta_L\frac{2\alpha_q^\nu\omega_d^2-\Delta_{sI}^\nu\omega_{sI}^\nu}{2\alpha_q^\nu\omega_d^2+(\Delta_{sI}^\nu)^2},$$

$$\beta_s^{\pm m}=\beta_L\left\{1-\frac{\Omega_s}{\omega_s^{\pm m}}\frac{2\alpha_q^\nu\omega_d^2}{2\alpha_q^\nu\omega_d^2+(\Delta_{sI}^\nu)^2}\frac{T_s^{\pm m}}{T_s^++T_s^-+T_x^{-\nu}}\right\},$$

$$\beta_I=\beta_L\left\{1-\nu\frac{\Omega_s}{2\bar\omega_I}\frac{2\alpha_q^\nu\omega_d^2}{2\alpha_q^\nu\omega_d^2+(\Delta_{sI}^\nu)^2}\frac{T_s^++T_s^-+2T_x^{-\nu}}{T_s^++T_s^-+T_x^{-\nu}}\right\}, \tag{31}$$

where $\alpha_q^\nu = T_q^\nu / T_{dL}$.

Substituting (30) and (31) in (6) we obtain after some calculations the stationary values of the amplification coefficient of the polarization of the nearby nuclei:

$$E_p{}^m = 1 + 2m \frac{\Omega_s}{\omega_I} \frac{\alpha_p{}^m \omega_d{}^2}{2\alpha_p{}^m \omega_d{}^2 + (\Delta_s{}^m)^2} \sum_M M a_p(M, m) \cos\theta_M,$$

$$a_p(M, m) = \frac{2T_s{}^{-m} + T_x{}^+(1-4Mm) + T_x{}^-(1+4Mm)}{T_s{}^{-m} + T_x{}^+ + T_x{}^-}, \quad (32)$$

$$E_q{}^\nu = 1 - \nu \frac{\Omega_s}{\omega_I} \frac{\alpha_q{}^\nu \omega_d{}^2}{2\alpha_q{}^\nu \omega_d{}^2 + (\Delta_{sI}{}^\nu)^2} \sum_M a_q(M, \nu) \cos\theta_M,$$

$$a_q(M, \nu) = \frac{2T_x{}^{-\nu} + T_s{}^+(1-2M\nu) + T_s{}^-(1+2M\nu)}{T_s{}^+ + T_s{}^- + T_x{}^{-\nu}}. \quad (33)$$

Obviously, the factors a_p and a_q, which reflect the relative efficiency of the different relaxation processes, vary in the range $0 \leqslant a_{p,q} \leqslant 2$, therefore allowance for the relaxation processes can either increase or decrease the polarization of the nearby nuclei.

According to (32) and (33), just as in the case of discrete saturation, allowance for the dipole reservoir decreases the nuclear polarization; it is maximal upon saturation at the line centers. As follows from (33), the polarization has different signs for different forbidden transitions. This is not always the case for allowed transitions. For example, if the angle θ_M is independent of M, in contrast to the case of discrete saturation of the allowed transition, stationary polarization of the nuclei does take place and is given according to (32) by the expression

$$E_p{}^m \simeq \frac{\Omega_s}{\omega_I} \frac{\alpha_p{}^m \omega_d{}^2}{2\alpha_p{}^m \omega_d{}^2 + (\Delta_s{}^m)^2} \frac{T_x{}^- - T_x{}^+}{T_s{}^{-m} + T_x{}^+ + T_x{}^-} \cos\theta. \quad (34)$$

In this case the stationary polarization is due to T_x^+ or T_x^- processes and does not take place at $T_x^+ = T_x^-$, i.e., we have the analog of the normal Overhauser effect.[9] (The mechanism of polarization of the nuclei proper on account of the $T_x^\pm$ processes upon saturation of an allowed transition was proposed by Abragam.[22])

According to (34), the sign of the polarization is the same for both allowed transitions and is determined by the predominance of the indirect relaxation: $E_p^m \gtrless 0$ at $T_x{}^- \gtrless T_x^+$.

It follows from a comparison of (32) and (33) with (13) and (14) that at zero detunings, if $T_x^\pm \ll T_s^{-m} \approx T_s^m$, i.e., if the $T_x^\pm$ processes are more effective than the $T_s^\pm$ processes, then $(E_{p0}^m)_{st} \approx 2(E_{p0}^m)_{imp}$ and $(E_{q0}^\nu)_{st} \approx (E_{q0}^\nu)_{imp}$. In the other limiting case $T_s^\pm \ll T_x^{-\nu} \approx T_x^\nu$, when the direct relaxation processes are more effective than the indirect ones, the situation is reversed:

$$(E_{q0}{}^\nu)_{st} \approx 2(E_{q0}{}^\nu)_{imp}, \quad (E_{p0}{}^m)_{st} \approx (E_{p0}{}^m)_{imp}.$$

If, however, $T_s^\pm \ll T_x^+ \ll T_x^-$ and $\cos\theta_+ \ll \cos\theta_-$, we have as before

$$(E_{q0}{}^\nu)_{st} \approx 2(E_{q0}{}^\nu)_{imp} \text{ и } (E_{p0}{}^-)_{st} \approx (E_{p0}{}^-)_{imp},$$

but $(E_{p0}^+)_{st} \ll (E_{p0}^+)_{imp}$.

As shown in Ref. 15, for the two-phonon mechanisms of the electronic spin-lattice relaxation, due to modulation of the spin-orbit coupling, we have $T_s^+ = T_s^- \equiv T_s$, $T_x^+ = T_x^- \equiv T_x$ with $T_s/T_{dL} = 2/p$, $T_x/T_{dL} = 2/q$. Then $\alpha_p^m = (p+1)/p$, $\alpha_q^\nu = (q+1)/q$ and in accord with (32) and (33) we obtain

$$E_p{}^m \approx 4m \frac{\Omega_s}{\omega_I} \frac{\omega_d{}^2/p}{2(p+1)\omega_d{}^2/p + (\Delta_s{}^m)^2} \sum_M M \cos\theta_M, \quad (35)$$

$$E_q{}^\nu \approx -\nu \frac{\Omega_s}{\omega_I} \frac{\omega_d{}^2/q}{2(q+1)\omega_d{}^2/q + (\Delta_{sI}{}^\nu)^2} \sum_M \cos\theta_M. \quad (36)$$

Comparing (35) and (36) with (13) and (14) at $\Delta_s^m = \Delta_{sI}^\nu = 0$, we have

$$(E_{p0}{}^m)_{st} = \frac{2}{p+1}(E_{p0}{}^m)_{imp}, \quad (E_{q0}{}^\nu)_{st} = \frac{2}{q+1}(E_{q0}{}^\nu)_{imp}.$$

Thus, measurement of the stationary and pulsed nuclear polarizations allows us to compare the efficiencies of various mechanisms of electronic spin-lattice relaxation, and to estimate in the particular case $T_s^m \equiv T_s$, $T_x^\nu \equiv T_x$ the values of the parameters p and q.

We denote by $\chi_{Ip}''^M$ and $\chi_{Iq}''^M$ the NMR absorption signals in stationary of allowed and forbidden transitions, respectively. Calculating β_I^M with the aid of (3), (30), and (31) and substituting β_I^M and β_d in (9) we easily obtain a genereal expression for $\chi_{Ip,q}''^M$, which we do not write out for the sake of brevity. Under conditions of strictly resonant saturation of the lines ($\Delta_s^m = 0$ or $\Delta_{sI}^\nu = 0$) the stationary and pulsed NMR singals turn out to be proportional to each other

$$\chi_{Ip}''^M \approx a_p(M, m)\chi_I''^M|_m, \quad \chi_{Iq}''^M \approx a_q(M, \nu)\chi_I''^M|_\nu, \quad (37)$$

where $\chi_I''^M|_{m,\nu}$ and $a_{p,q}$ are taken from (24), (25) and (32), (33).

The analysis of Eqs. (37) is analogous in many respects to the foregoing discussion of the stationary polarization of the nuclei, and we therefore note only certain distinguishing features. Relaxation processes, without changing the signs of the NMR signals, increase them or do not change them significantly in certain cases, and suppress them in others. Thus at $T_s^\pm \ll T_x^+ \ll T_x^-$ we have $a_q(M,\nu) \approx 2$, $a_p(M,m) \approx 1$ but $a_p(-M,m) \approx T_\alpha^+ / T_x^- \ll 1$, i.e., $\chi_{Iq}''^M \approx \chi_I''^M|_\nu$, $\chi_{Ip}''^M \approx \chi_I''^M|_m$, and $\chi_{Ip}''^{-m} \ll \chi_I''^{-m}|_m$ (the stationary value of the signal for the nuclear transition $M = -m$), turns out to be much smaller than the pulsed value.

Allowance for the dipole reservoir, just as in discrete saturation, can change the sign of the signals, and also, in contrast to polarization. It can not only decrease the NMR signals but also increase them.

6. CONCLUSION

The investigation of the mechanisms of the polarization and NMR of the nuclei of the nearest environment of impurity paramagnetic centers with allowance for the dipole-reservoir impurities, carried out in this paper, can be generalized to arbitrary values of the pair spins S and I, with allowance for the fine structure and for quadrupole interactions, and also to the case when several equivalent nuclei belong to one center. To realize such a program, however, the appropriate experiments are necessary. We shall therefore dwell once more on the limitations of the employed models and point out samples in which, in our opinion, one could attempt to observe the features of the spin dynamics of nearby nuclei.

The main assumption of the model is expressed by the inequality $\omega_d \ll \omega_I^M$, therefore the results are applicable to samples with a sufficiently well resolved hyperfine structure of the EPR spectra from the spectra of the immediate vicinity of the paramagnetic centers, such as $ZnF_2{:}\,Mn^{2+}$ (Ref. 17) and $CaF_2{:}Cl^{3+}$ (Ref. 23). Each of the hyperfine components was assumed to be homogeneously broadened with a width of the order of ω_d, thus imposing restrictions on the impurity density f: by choosing the optimum density it is necessary to ensure, on the one hand, that the hyperfine structure is not "smeared" (upper bound on f), and on the other, that each component of the EPR spectrum behave as a homogeneously broadened line (lower bound on f).

The most suitable sample may be LiF with low density of F centers, in which $A/\hbar \sim 200$ MHz, $\omega_I \sim 100$ MHz (i.e., $A \sim \hbar\omega_I$), and $\omega_d \sim 1$–10 MHz $\ll \omega_I^M$ (Ref. 24).

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[1)] The condition $A \sim \omega_I$ is usually satisfied for nuclei of the first or second coordination sphere in the vicinity of a paramagnetic ion (A is the HFI constant and ω_I is the nuclear Zeeman frequency).
[2)] Nuclei with $A \ll \hbar\omega_I$ are regarded as remote.

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