SOVIET PHYSICS JETP VOLUME 14, NUMBER 5 MAY, 1962

THEORY OF NUCLEAR RESONANCE IN PARAMAGNETIC MEDIA

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Submitted to JETP editor May 22, 1961; resubmitted October 15, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 1566-1575 (November, 1961)

A general theory is presented of the shape and width of nuclear magnetic resonance lines in paramagnetic media. The interaction between nuclear and electron spins in the system is due to dipole-dipole and contact forces. Precession, relaxation and exchange motions in the electron spin system and thermal motion of the particles of the medium were taken into account. Formulas have been obtained for the half-width $\Delta\omega_{1/2}$ and for the shift δ of the nuclear resonance line in the limiting cases of fast and slow thermal motion in the medium.

1. INTRODUCTION

THE influence of paramagnetic atoms of a substance on nuclear resonance manifests itself in the decrease in the relaxation times $T_{\parallel}$ and $T_{\perp}$ of the longitudinal and the transverse components (with respect to the external field) of the nuclear magnetization **M**, and also in the shift δ of the nuclear resonance frequency ω_I. These effects are due to the action of the magnetic field of the paramagnetic atoms on the nuclear moments, an action that varies in time (as a result of free precession, electron-spin relaxation processes, and exchange and thermal motions). In a number of theoretical papers[1-3] these effects were studied in the case of substances with a low concentration of paramagnetic ions and without taking the interaction between them into account; a consequence of this was the derivation of the theory of additivity of effects of paramagnetic atoms on the relaxation times $T_{\parallel}$ and $T_{\perp}$: $T_{\parallel}^{-1}, T_{\perp}^{-1} \sim N_S$ (N_S is the concentration of the paramagnetic atoms). Experiments carried out at low concentrations of the paramagnetic substance have confirmed this conclusion.[4,5]

At a high concentration of paramagnetic atoms exchange interactions between them can arise which result in exchange of electron spin orientations; this process will give rise to changes in the internal fields simultaneous with changes due to precession, electron spin relaxation and thermal motion. As a result of this, the internal fields must average out to a greater degree than in the absence of exchange, and this must manifest itself in a decrease in the effectiveness of the influence on the relaxation times $T_{\parallel}$ and $T_{\perp}$ of additional paramagnetic atoms newly added to the substance. Under these conditions the relation $T_{\parallel}^{-1}, T_{\perp}^{-1} \sim N_S$ must break down.

The present paper contains a theory of the shape and of the width (of the relaxation time $T_{\perp}^{-1}$) of the resonance line due to nuclei in paramagnetic media, with account of the exchange interactions between the paramagnetic atoms, which are in turn modulated by the thermal motion in the system. The last circumstance is particularly important in the discussion of this phenomenon in liquids. The results of this paper show that changes in the line width and in the shift δ of the resonance frequency of nuclei in paramagnetic media can turn out to be a direct method for studying exchange interactions which are important in the physics of magnetic phenomena. The calculations are carried out utilizing the method of Kubo and Tomita.[6]

We note here in addition to [1-5] some theoretical papers preceding the present paper and close to it in content. Moriya has considered the effect of exchange on nuclear relaxation both of diamagnetic[7] and of paramagnetic[8] atoms in antiferromagnetic crystals. The relaxation studied by Moriya consists of the transfer of energy from nuclear spins to spin waves (at low temperatures) and to the exchange system (at high temperatures). On the other hand, one of the present authors[9] has made a study of the relaxation of nuclei of paramagnetic atoms in magnetically dilute crystals due to the hyperfine interaction between nuclear and electron spins; in this case the dominant process is the lattice relaxation of electron spin. The object of these papers was to investigate the possibility of observing nuclear resonance for nuclei of paramagnetic atoms. Some of the conclusions reached in [7-9] and also in [1-5] are contained in the present paper as special cases.

In Sec. 2 we evaluate the autocorrelation function for the component M_X of the nuclear magnetization; in Secs. 3 and 4 we have calculated the half-width and the shift of the resonance line due to nuclei in a liquid and a solid paramagnetic medium respectively.

2. THE AUTOCORRELATION FUNCTION FOR THE NUCLEAR MAGNETIZATION

We consider a substance which contains per unit volume N_I identical magnetic nuclei whose resonance is being studied, and N_S paramagnetic atoms. The shape of the absorption line $I(\omega)$ is given by the Fourier transform of the autocorrelation function $G(t)$ of the component of the magnetic moment parallel to the direction (x) of the variable magnetic field[6]:

$$I(\omega) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} G(t)\, e^{-i\omega t}\,dt, \tag{1}$$

$$G(t) = \langle\{\hat{M}_x(t)\,\hat{M}_x(0)\}\rangle. \tag{2}$$

The angle brackets in (2) denote averaging of the symmetrized product $\{\dot{M}_X(t)\,\dot{M}_X(0)\}$ utilizing the density matrix $\hat{\rho}$; since the gaps between the magnetic sublevels are small ($\hbar\omega \ll kT$), we can assume

$$\rho = 1/(2I+1)^{N_I}(2S+1)^{N_S}; \tag{2a}$$

and finally obtain

$$\hat{M}_x(t) = \exp(it\hat{\mathscr{H}}/\hbar)\,\hat{M}_x \exp(-it\hat{\mathscr{H}}/\hbar), \tag{3}$$

where $\hat{\mathscr{H}}$ is the Hamiltonian for the system without the variable field which includes in our case the Zeeman energies

$$\hat{\mathscr{H}}_z^I = \gamma_I H_0 \sum_k \hat{I}_k^z, \qquad \hat{\mathscr{H}}_z^S = \gamma_S H_0 \sum_l \hat{S}_l^z$$

of the nuclear and the electronic moments in a constant magnetic field H_0 ($H_0 \parallel z$, $\gamma_I = g_I\beta_N$, $\gamma_S = g\beta$), the energy of interaction of nuclear and electronic moments

$$\hat{\mathscr{H}}_{IS} = \gamma_I\gamma_S \sum_{k>l} r_{kl}^{-3}\,[\hat{\mathbf{I}}_k\hat{\mathbf{S}}_l - 3r_{kl}^{-2}(\hat{\mathbf{I}}_k\mathbf{r}_{kl})(\hat{\mathbf{S}}_l\mathbf{r}_{kl})] + \hbar\sum_{k>l} A_{kl}\hat{\mathbf{I}}_k\hat{\mathbf{S}}_l,$$

the energy of the exchange interaction of electron spins among themselves

$$\hat{\mathscr{H}}_e = \hbar\sum_{i>j} J_{ij}(r_{ij})\,\hat{\mathbf{S}}_i\hat{\mathbf{S}}_j,$$

the kinetic energy of the system $\hat{\mathscr{H}}_K$ and the energy $\hat{\mathscr{H}}_{SK}$ of interaction of the electron spin system with $\hat{\mathscr{H}}_K$.

We separate the Hamiltonian $\hat{\mathscr{H}}$ into three parts:

$$\hat{\mathscr{H}}_1 = \hat{\mathscr{H}}_z^I, \qquad \hat{\mathscr{H}}_2 = \hat{\mathscr{H}}_z^S + \hat{\mathscr{H}}_{SK} + \hat{\mathscr{H}}_K + \hat{\mathscr{H}}_e, \qquad \hat{\mathscr{H}}' = \hat{\mathscr{H}}_{IS} \tag{4}$$

($\hat{\mathscr{H}}'$ is the perturbation), which satisfy the commutation relations

$$[\hat{\mathscr{H}}_1, \hat{\mathscr{H}}_2] = [\hat{\mathscr{H}}_2, \hat{M}_x] = 0. \tag{5}$$

On substituting into (2) the solution of the Heisenberg equation

$$i\hbar\dot{\hat{M}}_x = [\hat{M}_x(t), \quad \hat{\mathscr{H}}_1 + \hat{\mathscr{H}}_2 + \hat{\mathscr{H}}'], \tag{6}$$

we obtain the first terms of the series $G(t) = \Sigma G_n(t)$ $\quad (G_1(t) = 0)$:

$$G_0(t) = \tfrac{1}{6}N_I\gamma_I^2 I(I+1)\,[e^{i\omega_I t} + \text{c.c.}], \tag{7}$$

$$G_2(t) = -\tfrac{1}{6}N_I\gamma_I^2 I(I+1)\Big[e^{i\omega_I t} \times \sum_\gamma \sigma_\gamma^2 \int\limits_0^t d\tau\,(t-\tau)\,e^{i\omega_\gamma\tau} f_\gamma(\tau) + \text{c.c.}\Big], \tag{8}$$

where

$$\sigma_\gamma^2 = \hbar^{-2}\langle|[\hat{M}_+^{(0)}, \hat{\mathscr{H}}_\gamma'(0)]|^2\rangle / \langle|\hat{M}_+^{(0)}|^2\rangle, \tag{9}$$

$$\hat{M}_\pm^{(0)} = \gamma_I \sum_k (\hat{I}_k^x \pm i\hat{I}_k^y),$$

$$f_\gamma(\tau) = \hat{N}\langle[\hat{M}_+^{(0)}, \hat{\mathscr{H}}_\gamma'(\tau)]\,[\hat{\mathscr{H}}_{-\gamma}'(0), \hat{M}_-^{(0)}]\rangle, \tag{10}$$

$$\hat{\mathscr{H}}'(\tau) = \sum_\gamma e^{i\omega_\gamma\tau}\hat{\mathscr{H}}_\gamma'(\tau) = \sum_\gamma e^{i\omega_\gamma\tau}\exp(i\tau\hat{\mathscr{H}}_2/\hbar)\,\hat{\mathscr{H}}_\gamma'\exp(-i\tau\hat{\mathscr{H}}_2/\hbar). \tag{11}$$

Here σ_γ^2 is the contribution to the second moment of the resonance line (in frequency units) due to $\hat{\mathscr{H}}_\gamma'$ (the contributions of the individual terms in the perturbation $\hat{\mathscr{H}}_{IS}$ to the second moment are additive); $f_\gamma(\tau)$ is the correlation function for the quantities $\hat{\mathscr{H}}_\gamma'(\tau)$ which vary in time under the influence of $\hat{\mathscr{H}}_2$ [modulation of the perturbation by "motion" (in the broad sense of this word)]; $\hat{N}$ is a formal operator defined by the relation

$$\hat{N}A(t) = A(t)/A(0).$$

We note that $G_0(t)$ describes the unperturbed motion of the nuclear magnetization—the free precession.

In order to obtain $f_\gamma(\tau)$ of the form (10) we have to evaluate

$$\hat{\mathscr{H}}_\gamma'(\tau) = \exp[i\hbar^{-1}\tau(\hat{\mathscr{H}}_z^S + \hat{\mathscr{H}}_{SK} + \hat{\mathscr{H}}_K + \hat{\mathscr{H}}_e)] \times \hat{\mathscr{H}}_\gamma'\exp[-i\hbar^{-1}\tau(\hat{\mathscr{H}}_z^S + \hat{\mathscr{H}}_{SK} + \hat{\mathscr{H}}_K + \hat{\mathscr{H}}_e)]. \tag{12}$$

The presence of $\hat{\mathscr{H}}_Z^S$ gives in (12) time factors of the form $\exp(i\beta\omega_S\tau)$, $\beta = 0, \pm 1$. $\hat{\mathscr{H}}_{SK}$ describes relaxation processes for the components of the electron spin, so that in them we can take[1] for $f_\gamma(\tau)$

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[1] A review of papers on the relaxation of electron spins in liquids is available in the book by S. A. Al'tshuler and B. M. Kozyrev[10]; c.f., also[11].

$$\hat{N}\langle\hat{S}_\beta(\tau)\,\hat{S}_{-\beta}(0)\rangle = \exp(-|\tau|/T_\beta), \qquad T_\beta = \begin{cases} T_1, & \beta = 0 \\ T_2, & \beta = \pm 1 \end{cases} \tag{13}$$

Further, we assume that the time variations of the exchange energy

$$\hat{\mathscr{H}}_e(\tau) = \exp(i\tau\hat{\mathscr{H}}_K/\hbar)\,\hat{\mathscr{H}}_e \exp(-i\tau\mathscr{H}_K/\hbar)$$

under the influence of thermal motion in the system $\hat{\mathscr{H}}_K$ are characterized by the correlation time τ_e:

$$\hat{N}\langle\hat{\mathscr{H}}_e(\tau)\,\hat{\mathscr{H}}_e(0)\rangle = \exp(-|\tau|/\tau_e). \tag{14}$$

On taking into account the fact that usually $<|\hat{\mathscr{H}}_e|^2> \ll <|\mathscr{H}_K|^2>$, we expand (12) into a series in powers of $\hat{\mathscr{H}}_e$; in this case it turns out that the effect of $\mathscr{H}_e$ on the correlation function for the perturbation $f_\gamma(\tau)$ will manifest itself in the term in the expansion quadratic in $\hat{\mathscr{H}}_e$ (the term linear in $\hat{\mathscr{H}}_e$ gives zero on averaging).

Taking into account what we have just said with respect to $\hat{\mathscr{H}}'_\gamma(\tau)$ and $f_\gamma(\tau)$, and after simple but fairly lengthy calculations we can obtain

$$\begin{aligned} &\langle|[\hat{M}_+^{(0)}, \hat{\mathscr{H}}'_\gamma(0)]|^2\rangle f_\gamma(\tau) \\ &= \sum_\beta \sum_{\alpha=1,2} e^{i\beta\omega_S\tau} \langle|[\hat{M}_+^{(0)}, \hat{\mathscr{H}}^{IS}_{\gamma\beta,\alpha}(0)]|^2\rangle f_{\gamma\beta,\alpha}(\tau) \\ &\times (1 - \omega^2_{e\gamma\beta,\alpha} F(\tau)) \exp(-|\tau|/T_\beta); \end{aligned} \tag{15}$$

$$\begin{aligned} f_{\gamma\beta,1}(\tau) &= \hat{N}\sum_{k>l}\langle\exp(i\hbar^{-1}\tau\hat{\mathscr{H}}_K)\,\Phi^{\gamma\beta}_{kl} \\ &\times \exp(-i\hbar^{-1}\tau\hat{\mathscr{H}}_K)\,\Phi^{-\gamma,-\beta}_{kl}\rangle \\ &= \hat{N}\sum_{k>l}\langle\Phi^{\gamma\beta}_{kl}(\tau)\,\Phi^{-\gamma,-\beta}_{kl}(0)\rangle, \end{aligned} \tag{16}$$

$$\begin{aligned} f_{\gamma\beta,2}(\tau) &= \hat{N}\sum_{k,l}\langle\exp(i\hbar^{-1}\tau\hat{\mathscr{H}}_K)\,A^{\gamma\beta}_{kl}(r_{kl}) \\ &\times \exp(-i\hbar^{-1}\tau\hat{\mathscr{H}}_K)\,A^{-\gamma,-\beta}_{kl}(r_{kl})\rangle \\ &= \hat{N}\sum_{k,l}\langle A^{\gamma\beta}_{kl}(\tau)\,A^{-\gamma,-\beta}_{kl}(0)\rangle; \end{aligned}$$

$$F(\tau) = \int_0^\tau (\tau - \tau')\,d\tau' \exp(-|\tau|/\tau_e), \tag{17}$$

$$\omega^2_{e\gamma\beta,\alpha} = \langle|[\hat{\mathscr{H}}_e, [\hat{M}_+^{(0)}, \hat{\mathscr{H}}^{IS}_{\gamma\beta,\alpha}]]|^2\rangle / \hbar^2 \langle|[\hat{M}_+^{(0)}, \hat{\mathscr{H}}^{IS}_{\gamma\beta,\alpha}]|^2\rangle. \tag{18}$$

Here $\hat{\mathscr{H}}^{IS}_{\gamma\beta,\alpha}$ are the terms in the expansion of the energy of interaction between nuclear and electron spins in terms of the Zeeman frequencies of nuclear and electron spins (cf. the table):

$$\begin{aligned} \hat{\mathscr{H}}' = \hat{\mathscr{H}}_{IS} &= \sum_{\gamma,\beta}(\hat{\mathscr{H}}^{IS}_{\gamma\beta,1} + \hat{\mathscr{H}}^{IS}_{\gamma\beta,2}) \\ &= \sum_{\gamma,\beta}\Big[\sum_{k>l}\{kl\}_{\gamma\beta,1}\,\Phi^{\gamma\beta}_{kl} + \sum_{k,l}\{kl\}_{\gamma\beta,2}\,A^{\gamma\beta}_{kl}\Big]. \end{aligned}$$

The subscript α distinguishes quantities which refer to the dipole ($\alpha = 1$) and the hyperfine ($\alpha = 2$) interactions.

We shall be interested in the shape of the resonance line out to distances from the center of the line of the order of its width. Information with respect to this part of the line will be obtained if we carry out the integration in (8) up to $t \sim T^0_\perp$, where $T^0_\perp$ is the transverse relaxation time of the nuclei in the absence of motion.[6] It can be easily shown that $F(\tau) = \tau^2/2$ for $T^0_\perp \ll \tau_e$ and $F(\tau) = |\tau|\tau_e$ for $T^0_\perp \gg \tau_e$. Then, following [6] and denoting $\omega^2_{e\gamma\beta,\alpha} = \omega^2_e$ (cf. the table), we can write

$$1 - \omega^2_{e\gamma\beta,\alpha}F(\tau) \approx \exp[-\omega^2_e F(\tau)]$$

$$= \begin{cases} \exp(-\tau^2\omega^2_e/2), & T^0_\perp \ll \tau_e \qquad (19.1) \\ \exp(-|\tau|\tau_e\omega^2_e), & T^0_\perp \gg \tau_e \qquad (19.2) \end{cases}$$

The quantity $\omega^2_{e\gamma\beta}$ (18) has the meaning and the dimensions of the square of the exchange frequency.

For the correlation function (16) for the coordinate part of the perturbation $\mathscr{H}^{IS}_{\gamma\beta,1}$ which varies under the influence of the thermal classical motion of $\hat{\mathscr{H}}_K$ we can take as usual[1]

$$f_{\gamma\beta,1}(\tau) = \exp(-|\tau|/\tau_1). \tag{20.1}$$

With respect to the hyperfine interaction energy two cases must be distinguished. If we have in mind the interaction of the electron and nuclear spins belonging to different particles moving independently then we can set

$$f_{\gamma\beta,2}(\tau) = \exp(-|\tau|/\tau_2), \tag{20.2}$$

where τ_2 stands for the lifetime of the diamagnetic particle in the solvate shell of the paramagnetic ion. Obviously in a solid we shall have $\tau_2^{-1} = 0$. But if we consider the isotropic interaction of the nuclear moment of the ion with its own electron moment (the anisotropic part is usually not very great and its effect is negligible), then we have $\tau_2^{-1} = 0$, and

$$f_{\gamma\beta,2} = 1, \tag{20.3}$$

since this interaction is not modulated by thermal motion.

Now on substituting (15) into (8) and taking into account (19) and (20) we obtain for $G_0(t) + G_2(t)$ the expression (omitting a constant factor)

$$\begin{aligned} &e^{i\omega_I t}\Big\{1 - \sum_{\alpha=1,2}\sum_{\gamma,\beta}\sigma^2_{\gamma\beta,\alpha}\int_0^t d\tau\,(t-\tau)\,e^{i(\gamma\omega_I+\beta\omega_S)\tau} \\ &\times \exp[-|\tau|\tau_\alpha^{-1} - |\tau|T_\beta^{-1} - \omega^2_e F(\tau)]\Big\} + \text{c.c.}, \end{aligned} \tag{21}$$

which can be approximately represented in the form

$$\begin{aligned} &\exp\Big\{i\omega_I t - \sum_{\alpha=1,2}\sum_{\gamma,\beta}\sigma^2_{\gamma\beta,\alpha}\int_0^t d\tau\,(t-\tau)e^{i(\gamma\omega_I+\beta\omega_S)\tau} \\ &\times \exp[-|\tau|\tau_\alpha^{-1} - |\tau|T_\beta^{-1} - \omega^2_e F(\tau)]\Big\} + \text{c.c.} \end{aligned} \tag{22}$$

$\gamma\beta$	$\{kl\}_{\gamma\beta,1}$	$\Phi^{\gamma\beta}_{kl}/\gamma_I\gamma_S r^{-3}_{kl}$	$\{kl\}_{\gamma\beta,2}$	$A^{\gamma\beta}_{kl}$	$\sigma^2_{\gamma\beta,1}$	$\sigma^2_{\gamma\beta,2}$
00	$\hat{I}^z_k\hat{S}^z_l$	$1-3\cos^2\vartheta_{kl}$	$\hat{I}^z_k\hat{S}^z_l$	A_{kl}	$\frac{1}{3}S(S+1)\sigma^2_{IS}$	$\frac{1}{3}S(S+1)\langle A^2\rangle$
01	$\hat{I}^z_k\hat{S}^-_l$	$-\frac{3}{2}\sin\vartheta_{kl}\cos\vartheta_{kl}\exp(i\varphi_{kl})$	0	0	$\frac{1}{4}S(S+1)\sigma^2_{IS}$	0
0—1	$\hat{I}^z_k\hat{S}^+_l$	$-\frac{3}{2}\sin\vartheta_{kl}\cos\vartheta_{kl}\exp(-i\varphi_{kl})$	0	0	$\frac{1}{4}S(S+1)\sigma^2_{IS}$	0
10	$\hat{I}^-_k\hat{S}^z_l$	$-\frac{3}{2}\sin\vartheta_{kl}\cos\vartheta_{kl}\exp(i\varphi_{kl})$	0	0	$\frac{1}{4}S(S+1)\sigma^2_{IS}$	0
11	$\hat{I}^-_k\hat{S}^-_l$	$-\frac{3}{4}\sin^2\vartheta_{kl}\exp(2i\varphi_{kl})$	0	0	$\frac{1}{2}S(S+1)\sigma^2_{IS}$	0
1—1	$-\frac{1}{4}\hat{I}^-_k\hat{S}^+_l$	$1-3\cos^2\vartheta_{kl}$	$\frac{1}{2}\hat{I}^-_k\hat{S}^+_l$	A_{kl}	$\frac{1}{12}S(S+1)\sigma^2_{IS}$	$\frac{1}{3}S(S+1)\langle A^2\rangle$
—10	$\hat{I}^+_k\hat{S}^z_l$	$-\frac{3}{2}\sin\vartheta_{kl}\cos\vartheta_{kl}\exp(-i\varphi_{kl})$	0	0	0	0
—11	$-\frac{1}{4}\hat{I}^+_k\hat{S}^-_l$	$1-3\cos^2\vartheta_{kl}$	$\frac{1}{2}\hat{I}^+_k\hat{S}^-_l$	A_{kl}	0	0
—1—1	$\hat{I}^+_k\hat{S}^+_l$	$-\frac{3}{4}\sin^2\vartheta_{kl}\exp(-2i\varphi_{kl})$			0	0

Here

$$\hbar^2\sigma^2_{IS} = N_I^{-1}\sum_{k>l}|\Phi^{00}_{kl}|^2 = \frac{8}{3}N_I^{-1}\sum_{k>l}|\Phi^{01}_{kl}|^2 = \frac{8}{3}N_I^{-1}\sum_{k>l}|\Phi^{11}_{kl}|^2 = \frac{4}{5}\gamma_I^2\gamma_S^2\sum_l\langle r_{kl}^{-6}\rangle$$

for an isotropic distribution (powders, glasses and liquids);

$$\langle A^2\rangle = N_I^{-1}\sum_{k,l}|A^{\gamma\beta}_{kl}|^2;$$

with $A^{\gamma\beta}_{k,l} = A_{k,l}$ $\quad \omega^2_{e\gamma\beta,\alpha} = \omega^2_e = \frac{2}{3}\langle J^2\rangle S(S+1) = \frac{2}{3}N_S^{-1}\sum_{i\neq j}J^2_{ij}S(S+1).$

We now carry out calculations of the line shape for two limiting cases—fast motion (liquids) and slow motion (viscous liquids, solids) of the molecules of the system.

3. FAST THERMAL MOTION: $T^0_\perp \gg \tau_e$

In order to find the line shape I (ω) near its maximum one should in the case $T^0_\perp \gg \tau_e$ evaluate the Fourier transform (1) of the autocorrelation function (22) making use of (19.2); in this case we obtain a Lorentz line of half-width $\Delta\omega_{1/2}$ and with its center at the frequency[2)] $\omega_I + \delta$:

$$\Delta\omega_{1/2} = S(S+1)\sigma^2_{IS}\left\{\frac{1}{3}K_{01} + \frac{1}{2}\frac{K_{11}^{-1}}{K_{11}^{-2}+\omega_S^2} + \frac{1}{4}\frac{K_{01}^{-1}}{K_{01}^{-2}+\omega_I^2} + \frac{1}{2}\frac{K_{11}^{-1}}{K_{11}^{-2}+(\omega_S+\omega_I)^2} + \frac{1}{12}\frac{K_{11}^{-1}}{K_{11}^{-2}+(\omega_I-\omega_S)^2}\right\} + \frac{1}{3}S(S+1)\langle A^2\rangle\left\{K_{02} + \frac{K_{12}^{-1}}{K_{12}^{-2}+(\omega_I-\omega_S)^2}\right\}, \tag{23}$$

$$-\delta = S(S+1)\sigma^2_{IS}\left\{\frac{1}{2}\frac{\omega_I}{K_{01}^{-2}+\omega_I^2} + \frac{1}{2}\frac{\omega_I+\omega_S}{K_{11}^{2}+(\omega_I+\omega_S)^2} + \frac{1}{12}\frac{\omega_I-\omega_S}{K_{11}^{-2}+(\omega_I-\omega_S)^2}\right\} + \frac{1}{3}S(S+1)\langle A^2\rangle\frac{\omega_I-\omega_S}{K_{12}^{-2}+(\omega_I-\omega_S)^2}; \tag{24}$$

$$K^{-1}_{0,\alpha} = \tau_\alpha^{-1} + T_1^{-1} + \tau_e\omega_e^2, \qquad K^{-1}_{1,\alpha} = \tau_\alpha^{-1} + T_2^{-1} + \tau_e\omega_e^2. \tag{25}$$

We discuss formulas (23) — (25) briefly. First, it follows from the definition of $K^{-1}_{0,\alpha}$, $K^{-1}_{1,\alpha}$ in (25) that the half-width and the shift of the resonance line due to nuclear spins are determined by the velocities of thermal motion, by the electron relaxation or by the electron exchange motion depending on which process proceeds at the greatest rate: τ_α^{-1}, T_β^{-1} or $\tau_e\omega_e^2$. For paramagnetic ions of the type Cu^{2+}, VO^{2+} etc. T_1^{-1}, $T_2^{-1} \sim 10^8$ sec^{-1}; for other paramagnetic ions (Ti^{3+}, Fe^{2+}, Co^{2+} from the iron group, the rare earth ions) the relaxation times are very short, and, apparently, one can take[10] $T_1^{-1} > 10^{10}$ sec^{-1}.

In nonviscous liquids $\tau_1^{-1} \sim 10^{11}$ sec^{-1}. One can suppose that the values of τ_e^{-1} will be somewhat greater than the values of τ_1^{-1} in view of the greater sensitivity of the exchange energy to the

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[2)] The shift δ must be measured from the frequency $\omega_I + \Delta$, where Δ is a line shift of the Knight type (cf.[5]) which is proportional to the magnetization of the system in the field H_0. In the approximation for the density matrix ρ utilized by us [Eq. (2a)] the constant magnetization of the system, and consequently also Δ, are both equal to zero ($\rho = (2I+1)^{-N_I} \times (2S+1)^{-N_S}$ presupposes all the magnetic energy sublevels to be equally populated).

variations in the distances between the paramagnetic atoms. For rough calculations one can assume that $\tau_e^{-1} \sim \tau_1^{-1}$. The lifetime of a particle in the solvate shell of the ion τ_2, as a rule, will be greater than the relaxation times T_1 and T_2; in these cases the effect of thermal motion on the hyperfine interaction will become unobservable. Moreover, in concentrated solutions, $\sigma_{IS}^2 \gg \langle A^2 \rangle$, since the internal field amounts to $\sim 10^3$ oe, while $|A| \sim 10 - 10^2$ oe. In concentrated solutions ω_e can attain values of $10^{10} - 10^{11}$ sec^{-1}.

These estimates show that very different situations can be realized in practice. The case appears to be of interest when the dominant terms in $K_{\beta,\alpha}^{-1}$ are the terms $\omega_e^2 \tau_e + \tau_\alpha^{-1}$. It is realized in solutions of relatively high concentrations of paramagnetic particles with not too short relaxation times T_1, T_2. Then

$$K_{\beta,\alpha} = \tau_\alpha/(1 + \tau_\alpha \tau_e \omega_e^2)$$

and for $K_{\beta,\alpha}^{-1} \gg \omega_I, \omega_S$ we obtain from (23) the following expression for the half-width

$$\Delta\omega_{1/2} = \tfrac{20}{12} S(S+1)\sigma_{IS}^2 \tau_1/(1 + \tau_1 \tau_e \omega_e^2) + \tfrac{2}{3} S(S+1)\langle A^2 \rangle \tau_2/(1 + \tau_2 \tau_e \omega_e^2). \tag{26}$$

For large values of ω_e^2 we obtain on neglecting in the denominators of (26) unity in comparison with $\tau_\alpha \tau_e \omega_e^2$

$$\Delta\omega_{1/2} = S(S+1)\left[\tfrac{20}{12}\sigma_{IS}^2 + \tfrac{2}{3}\langle A^2 \rangle\right]/\tau_e \omega_e^2. \tag{26.1}$$

Since σ_{IS}^2, ω_e^2, $\langle A^2 \rangle \sim N_S$ (we are considering the hyperfine interaction with an electron spin belonging to a different ion), then it follows from (26.1) that in this range the dependence of $\Delta\omega_{1/2}$ on concentration will be due to the variations in τ_e which increases as the concentration is increased; therefore, $\Delta\omega_{1/2}$ will decrease. Further, in accordance with (23), the line width will gradually diminish as the external field increases. In weak fields ($K_{\beta,\alpha}^2 \omega_S^2 \ll 1$) the observed width is given by (26). In strong fields $K_{\beta,\alpha}^2 \omega_S^2 \gg 1$ (but $K_{\beta,\alpha}^2 \omega_I^2 \ll 1$) we have

$$(\Delta\omega_{1/2}) = \tfrac{7}{12} S(S+1)\sigma_{IS}^2 K_{\beta,1} + \tfrac{1}{3} S(S+1)\langle A^2 \rangle K_{\beta,2}.$$

In the absence of exchange (low concentration of paramagnetic ions), (23) together with (25) become similar to the well known formulas from [3,12].

Of some interest are the investigations of the line shift $-\delta$ [formula (24) gives the shift in units of rad/sec]. In order of magnitude the value of $-\delta$ is close to the line width. As can be seen from (24), $-\delta$ passes through a maximum (as the external field is varied) at $\omega_I = K_{0I}^{-1}$ and $\omega_S + \omega_I = K_{1I}^{-1}$. At the same time the shift diminishes as the velocity of the motion $K_{\beta,\alpha}^{-1}$ increases.

4. SLOW THERMAL MOTION: $T_\perp^0 \ll \tau_e$

The condition $T_\perp^0 \ll \tau_e, \tau_1, \tau_2$ corresponds to a slow modulation of the exchange, hyperfine and dipole interactions with the thermal motion. The nature of the phenomenon is in this case determined by the exchange and the relaxation motions in the electron spin system. The nuclear absorption line near its maximum has a Lorentz shape, since the approximate autocorrelation function assumes the following form for $T_\perp^0 \ll \tau_e$ [cf. (19.1)]:

$$\exp\left\{i\omega_I t - t\sum_{\gamma,\beta} \sigma_{\gamma\beta}^2 \int_0^\infty \exp\left[-\tau\left[T_\beta^{-1} - i(\gamma\omega_I + \beta\omega_S)\right] - \tau^2\omega_e^2/2\right] d\tau\right\} + \text{c.c.},$$

$$\sigma_{\gamma\beta}^2 = \sigma_{\gamma\beta,1}^2 + \sigma_{\gamma\beta,2}^2. \tag{27}$$

The factor multiplying it in the exponent of the exponential determines the position of maximum intensity $\omega_I + \delta$ (cf. footnote 2)), while the factor multiplying $-t$ determines the half width $\Delta\omega_{1/2}$:

$$\Delta\omega_{1/2} = \sqrt{\frac{\pi}{2}}\frac{1}{\omega_e}\sum_{\gamma=0}^{1}\sum_{\beta=-1}^{1}\sigma_{\gamma\beta}^2 \operatorname{Re} L(z_{\gamma\beta}), \tag{28}$$

$$\omega_I + \delta = \omega_I - \sqrt{\frac{\pi}{2}}\frac{1}{\omega_e}\sum_{\substack{\gamma=0 \\ |\gamma|+|\beta|\neq 0}}^{1}\sum_{\beta=-1}^{1}\sigma_{\gamma\beta}^2 \operatorname{Im} L(z_{\gamma\beta}); \tag{29}$$

$$z_{\gamma\beta} = (\gamma\omega_I + \beta\omega_S - iT_\beta^{-1})/\omega_e\sqrt{2}, \tag{30}$$

$$L(z) = e^{-z^2} - i2W(z)/\sqrt{\pi}, \qquad W(z) = e^{-z^2}\int_0^z e^{x^2}dx. \tag{31}$$

We present a brief analysis of formulas (28) — (31). In a number of cases (Mn^{2+}, Cr^{3+}, VO^{2+}) the electron relaxation times $T_\beta = T_1, T_2$ are comparatively long, $\sim 10^{-7} - 10^{-8}$ sec (cf., the discussion in Sec. 3), so that $T_\beta^{-1} \ll \omega_S \neq 0$; therefore in $z_{\gamma\beta}$ the imaginary part can be neglected if $\beta \neq 0$. Moreover, let $T_\beta \omega_e \gg 1$. Then the formula for the half width of the line (28) assumes the following form:

$$\Delta\omega_{1/2} = \sqrt{\frac{\pi}{2}}\,\omega_e^{-1}\left[\sigma_{00}^2 + \sigma_{10}^2 + \sum_{\gamma=0,1}\sum_{\beta=\pm1}\sigma_{\gamma\beta}^2 \exp\left[-\frac{(\gamma\omega_I + \beta\omega_S)^2}{2\omega_e^2}\right]\right], \tag{32}$$

analogous to the well known formulas for the half-width of the electron resonance line.[6] For the line shift δ we obtain in the present case ($T_\beta^{-1} \ll |\beta\omega_S|$, $\beta \neq 0$)

$$-\delta = \sqrt{2}\,\omega_e \sum_{\gamma=0,1}\sum_{\beta=\pm1}\sigma_{\gamma\beta}^2 W\left(\frac{\gamma\omega_I + \beta\omega_S}{\sqrt{2}\,\omega_e}\right). \tag{33}$$

On taking into account the fact that $\gamma\omega_I + \beta\omega_S \approx \beta\omega_S$, we obtain from (33) the expression

$$-\delta = \sqrt{2}\omega_e^{-1} S(S+1)\left[\tfrac{5}{12}\sigma_{IS}^2 - \tfrac{1}{3}\langle A^2\rangle\right] e^{-y^2}\int_0^y e^{x^2}dx, \quad (34)$$

which reaches a maximum[13] at $y \equiv \omega_S/\sqrt{2}\omega_e = 0.925$.

Thus, by measuring the width (32) and the shift of the resonance frequency (34) one can find the exchange frequency ω_e.

In the opposite case $T_\beta^{-1} \gg |\gamma\omega_I + \beta\omega_S|$ (weak fields) one can set $z_{\gamma\beta}$ equal to $-i/\sqrt{2}\omega_e T_\beta$. Then the shift $\delta = 0$, since in such an approximation $L(z_{\gamma\beta})$ is real, while the half width of the line $\Delta\omega_{1/2}$ does not depend on the constant magnetic field, but will vary strongly as the concentration of the paramagnetic atoms is varied:

$$\Delta\omega_{1/2} = \sqrt{\frac{\pi}{2}}\frac{1}{\omega_e} S(S+1)\left\{\left(\frac{7}{12}\sigma_{IS}^2 + \frac{1}{3}\langle A^2\rangle\right)e^{u^2}\right.$$
$$\times\left(1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-x^2}dx\right) + \left(\frac{13}{12}\sigma_{IS}^2 + \frac{1}{3}\langle A^2\rangle\right)e^{v^2}$$
$$\left.\times\left[1 - \frac{2}{\sqrt{\pi}}\int_0^v e^{-x^2}dx\right]\right\},$$
$$u = 1/\sqrt{2}\,T_1\omega_e, \qquad v = 1/\sqrt{2}\,T_2\omega_e. \quad (35)$$

In the case of very strong exchange T_1^{-1}, $T_2^{-1} \ll \omega_e$ expression (35) reduces to

$$\Delta\omega_{1/2} = \sqrt{\frac{\pi}{2}}\frac{1}{\omega_e} S(S+1)\left[\frac{5}{3}\sigma_{IS}^2 + \frac{2}{3}\langle A^2\rangle\right]. \quad (J)$$

In the case of weak exchange, when the exchange motion in the electron spin system is slower than the relaxation motions (T_1^{-1}, $T_2^{-1} \gg \omega_e$), formula (35) is inapplicable and we must repeat the calculation, neglecting in (27) the quantity $\omega_e^2\tau^2/2$ in comparison with τ/T_β; we do not reproduce here the formulas obtained in this case, since they coincide exactly with (23) and (24) with $K_{\beta,\alpha}^{-1} = T_\beta^{-1}$. In the case $\omega_e \approx T_\beta^{-1}$ one should utilize formula (35) and tables of functions[13] for estimating the line width.

In conclusion we wish to make some remarks. As can be seen from a detailed discussion of the formulas obtained, systematic measurements of the width and the shift of nuclear magnetic resonance lines in paramagnetic media can serve as an important means of studying exchange and relaxation motions in an electron spin system and thermal motion of the molecules of the medium. Preliminary measurements carried out in the laboratory of the Kazan' Pedagogic Institute have demonstrated agreement between the conclusions of the present theory and experiment.

Note added in proof (October 15, 1961). In solids with a low concentration of paramagnetic particles (in the absence of exchange) the phenomenon of spin diffusion can exert an essential influence on the nonsecular part $(\Delta\omega_{1/2})_{nS}$ of the line width (the terms in the formulas for $\Delta\omega_{1/2}$ containing the frequency ω_I). In these cases $(\Delta\omega_{1/2})_{nS}$ should be replaced by the expression $(1/2T_1)$, where T_1 has been evaluated taking spin diffusion[14] into account.

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Translated by G. Volkoff
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