SPECTRAL DIFFUSION IN INHOMOGENEOUSLY BROADENED EPR LINES

N. A. EFREMOV and A. M. KOZHUSHNER

Institute of Chemical Physics, U.S.S.R. Academy of Sciences

Submitted February 14, 1969

Zh. Eksp. Teor. Fiz. 57, 534–546 (August 1969)

Spectral diffusion in an inhomogeneously broadened EPR line (unresolved hyperfine structure) is considered. The variation in the spin level populations is due to simultaneous electron and nuclear spin flip induced by spin-lattice interaction. The spin-packet model is not valid in this case. Kinetic equations are presented for the spin-state populations. These equations can be solved exactly for nuclei with spin $\frac{1}{2}$. It is shown that besides the spreading of the "holes" that are burnt out in the EPR line, spikes should be observed at certain frequencies (increase of high-frequency power absorption). The hyperfine coupling constants in forbidden EPR lines can be determined on the basis of the results of the present investigation. The role of independent nuclear spin flips in spectral diffusion is discussed.

1. INTRODUCTION

WHEN a certain section of an inhomogeneously broadened EPR line is saturated, dips appear in definite places on the line (including on the saturation section),[1-4] and vanish gradually after the saturating field is turned off. This process of return to the equilibrium state may be accompanied by distortion of the line sections unaffected by the saturation. Such a propagation of the shape distortion along the line is called spectral diffusion, the concept of which was first introduced by Portis.[5] This phenomenon can occur if there exists some mechanism causing a time variation of the local fields at the electrons, and consequently leads to a time variation of the difference between the spin populations of the electrons with given resonant frequency. In the investigation of EPR in solids it was observed that the shape of a line inhomogeneously broadened by hyperfine interaction of paramagnetic centers with the close nuclear surrounding is strongly influenced by simultaneous reorientation of the electron spin and of the spins of the nuclear surrounding, as well as by the spontaneous flipping of the nuclear spins, due to direct coupling between the nuclei and the lattice. The present paper is devoted mainly to a theoretical investigation of spectral diffusion due to the first of these processes. The influence of the second type of diffusion is considered only qualitatively in a section devoted to a discussion of the results obtained in this paper.

If the time dependence of the EPR line shape is due to the hyperfine interaction (HFI) mechanism considered in the paper, then the law governing this dependence makes it possible, generally speaking, to determine all the constants of the HFI that broaden the EPR line. The determination of the HFI constants, especially in the case of an unresolved hfs, is an important and very timely problem, an unambiguous solution of which is sometimes quite difficult.

2. HAMILTONIAN OF THE SPIN SYSTEM AND JUSTIFICATION OF THE USE OF KINETIC EQUATIONS

We shall assume the concentration of the paramagnetic centers to be low enough to neglect the interaction of the electron spins with one another, and the external magnetic field to be strong enough compared with the local field produced at the electron by the magnetic moments of the nearby nuclei. In addition, the dipole-dipole interaction of the spins of the nuclei close to the electron can be neglected compared with their interaction with the electron spin.

Since the interaction between the electron spins is small at low concentrations, the electrons can be regarded as independent of one another and we can consider a system consisting of one electron coupled by hyperfine interaction with N surrounding nuclei in an external constant magnetic field H_0 directed along the z axis. Then the spin Hamiltonian of such a system can be written in the form

$$\mathscr{H} = \hbar\omega_e S^z - \hbar\omega_n \sum_{i=1}^{N} J_i^z + S^z \sum_{i=1}^{N} A_i J_i^z + S^z \sum_{i=1}^{N} (B_i J_i^+ + B_i^* J_i^-), \quad (1)$$

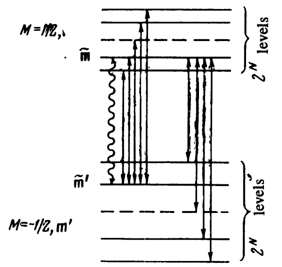
where $\omega_e = \gamma_e H_0$ and $\omega_n = \gamma_n H_0$ are the Zeeman frequencies of the electron and of the nuclei, respectively, S^z and J_i^z are the z-components of the electron spin S and of the spin J_i of the i-th nucleus, and $J_i^\pm = J^x \pm J_i^y$. The third and fourth terms in the right side of (1) cause inhomogeneous broadening of the EPR line. The eigenvalues of the energy of such a system[6] are

$$E_{M, m_1, m_2, \ldots, m_N} = M\hbar\omega_e + \sum_{i=1}^{N} m_i \sqrt{(\hbar\omega_n - MA_i)^2 + |B_i|^2}. \quad (2)$$

Here $M = \pm\frac{1}{2}$ and $m_i = -J_i, -J_i + 1, \ldots, J_i - 1, J_i$—magnetic quantum numbers of the electron and i-th nucleus, respectively.

The figure shows the energy-level scheme (2). Each level is determined by the number M and the combination of numbers $(m_1, m_2, \ldots, m_N) = \{m_i\}$ of all N nuclei. It is convenient to assume that each such combination determines an N-dimensional vector $\mathbf{m} = \{m_i\}$, and we shall denote the levels as follows: $(M = \frac{1}{2}, \mathbf{m})$ and $(M = -\frac{1}{2}, \mathbf{m}')$.

The characteristic scale of the frequency of the system under consideration is the width $\Delta\omega^*$ of the inhomogeneously broadened line. So long as the line broadening due to the spin-lattice interaction $1/T_1$ or the



electron spin-spin interaction $1/T_2$ is much smaller than $\Delta\omega^*$:

$$1/T_1,\ 1/T_2 \ll \Delta\omega^*, \qquad (3)$$

rapidly oscillating terms, containing nondiagonal elements of the density matrix, drop out from the equations for the density-matrix terms that are diagonal in the eigenstates of the Hamiltonian (1).[7] This means that we can describe the system by means of the populations of the spin states $p_M(\mathbf{m})$ which obey the kinetic equations.

The interaction between the electron and the lattice leads to transitions between states with $M = 1/2$ and $M = -1/2$, which establish the equilibrium values of the populations. An important factor here is the absence of limitations on the selection rules with respect to Δm_i, owing to the presence of the last term in (1), which mixes states with different values of m_i. This means that the electron spin, interacting with the lattice, can flip together with the spins of the nuclei surrounding it. The here-considered mechanism of spectral diffusion consists in the following. If the populations of several pairs of levels with $\Delta M = 1$ have assumed values different from the equilibrium values by virtue of some action on the system, for example under the action of a high-frequency field (the wavy arrow in the figure shows only one such pair of levels ($M = 1/2$, $\tilde{\mathbf{m}}$) and ($M = -1/2$, $\mathbf{m}'$), then the return of the system to equilibrium will be accompanied by all possible transitions ($M = 1/2$, $\tilde{\mathbf{m}}$) $\longleftrightarrow$ ($M = -1/2$, $\mathbf{m}'$) and ($M = -1/2$, $\tilde{\mathbf{m}}'$) $\longleftrightarrow$ ($M = 1/2$, $\mathbf{m}$), which lead to a deviation from the equilibrium values of the populations of all the levels of the system, and this in turn leads to a change in all possible population differences $p_{-1/2}(\mathbf{m}') - p_{1/2}(\mathbf{m})$, and consequently to a distortion of the shape of the entire EPR line.

Since the EPR line is formed in this case, generally speaking, by all the possible transitions ($M = 1/2$, $\mathbf{m}$) $\longleftrightarrow$ ($M = -1/2$, $\mathbf{m}'$), it is convenient to describe the inhomogeneously broadened EPR line by the populations of the energy levels of the spin system. The usual description in terms of spin packets, after Portis,[8] presupposes that each packet is determined by a pair (or several pairs) of levels with different values of M, between which transitions occur under the influence of the high-frequency field, and the levels that enter in different packet-pairs are not connected by such transitions. The difference between the populations of the states entering in the packet determines the intensity of absorption of the high-frequency field energy at the frequency corresponding to this packet. In the Portis model, any change of the populations of the states that enter in one packet does not change the populations of the states in other packets (neglecting the interaction between packets). On the other hand, in the case considered by us, this is not so, since the line is formed by transitions between all levels of the system. In our case, therefore, the EPR line cannot be described with the aid of the spin-packet model.[1)]

If the detecting field is sufficiently weak, so that the populations of the spin states practically do not change upon detection, then the observed EPR line shape can be represented in the form of a sum of contributions from different packets. But to describe the spectral diffusion it is necessary to use the spin-level populations.

Since the nuclear spins do not interact with one another, the spin wave function can be written in the form

$$\Psi_{M,\mathbf{m}} = \chi(M) \prod_{i=1}^{N} \varphi_i(M, m_i), \qquad (4)$$

where $\chi(M)$ is the eigenfunction of the operator S^z, and $\varphi_i(M, m_i)$ is the eigenfunction of the Hamiltonian of the i-th nucleus

$$\mathcal{H}_i = (MA_i - \hbar\omega_n)J_i^z + M(B_iJ_i^+ + B_i^*J_i^-). \qquad (5)$$

Then the probability $W_\downarrow$ of the transition from the state ($M = 1/2$, $\mathbf{m}$) to the state ($M = -1/2$, $\mathbf{m}'$) and the probability $W_\uparrow$ of the inverse transition ($M = -1/2$, $\mathbf{m}'$) $\rightarrow$ ($M = 1/2$, $\mathbf{m}$) can be represented in the form

$$W_\downarrow = \frac{1}{\gamma^2+1}\frac{1}{T_1}\prod_{i=1}^{N} F_i(m_i, m_i'), \qquad (6)$$

$$W_\uparrow = \frac{\gamma^2}{\gamma^2+1}\frac{1}{T_1}\prod_{i=1}^{N} F_i(m_i, m_i'),$$

where

$$F_i(m_i, m_i') = |\langle\varphi_i(1/2, m_i),\ \varphi_i(-1/2, m_i')\rangle|^2 \qquad (7)$$

and $1/T_1$ is the average velocity of the electron spin-lattice relaxation, while $\gamma = \exp(-\hbar\omega_e/2kT)$ is the Boltzmann factor. For nuclei with spin $1/2$, the quantity $F_i(m_i, m_i')$ depends only on the modulus of the difference $|m_i - m_i'|$. This circumstance had made it possible to solve exactly a system of $2\exp(N+1)$ kinetic equations for the populations of the states describing the relaxation process in the system.

The investigation that follows pertains to a system containing nuclei with spin $1/2$. Such a situation is encountered in many organic compounds, when inhomogeneous broadening is due to the interaction between the unpaired electron and the protons surrounding it.

In this case[6]

$$F_i(|m_i - m_i'|) = \left[\sin^2\frac{\theta^i_{1/2} - \theta^i_{-1/2}}{2}\right]^{1-|m_i-m_i'|}\left[\cos^2\frac{\theta^i_{1/2} - \theta^i_{-1/2}}{2}\right]^{|m_i-m_i'|}, \qquad (8)$$

where the angles θ^i_M are determined from the following expressions:

$$\operatorname{tg}\theta_M^i = \frac{2M|B_i|}{MA_i - \hbar\omega_n}, \quad 0 \leqslant \theta_M^i \leqslant \pi. \qquad (9)$$

It follows from (6)–(9) that in order for the probabilities of the "forbidden" transitions ($\Delta M = \pm 1$, $\Delta m_i = \pm 1$) to

[1)]Arguments concerning the non-applicability of the packet model to the general case of an unresolved hyperfine structure in the EPR line were advanced by T. I. Sanadze in the course on Magnetic Relaxation (Telavi, October, 1968).

be approximately equal to the probabilities of the "allowed" transitions ($\Delta M = \pm 1$, $\Delta m_i = 0$), it is necessary to satisfy the condition

$$\tfrac{1}{4}A_i^2 + |B_i|^2 \approx \hbar^2\omega_n^2. \tag{10}$$

Under this condition, the spectral diffusion should be most noticeable, since the presence of all possible transitions with nonzero probabilities leads to a change in the differences of the populations of electrons at all possible resonant frequencies.

3. SOLUTION OF KINETIC EQUATIONS

All the subsequent calculations are carried out in the high-temperature approximation accurate to terms of first order in $x \equiv \hbar\omega_e/2kT$. Using (6), we write the kinetic equations for the populations of the spin states $p_{1/2}(\mathbf{m}, t)$ and $p_{-1/2}(\mathbf{m}', t)$:

$$\frac{dp_{1/2}(\mathbf{m},t)}{dt} = -\frac{1+x}{2T_1}p_{1/2}(\mathbf{m},t)\sum_{\mathbf{m}'}\prod_{i=1} F_i(|m_i - m_i'|) \times \frac{1-x}{2T_1}\sum_{\mathbf{m}'} p_{-1/2}(\mathbf{m}',t)\prod_{i=1} F_i(|m_i - m_i'|), \tag{11}$$

$$\frac{dp_{-1/2}(\mathbf{m}',t)}{dt} = -\frac{1-x}{2T_1}p_{-1/2}(\mathbf{m}',t)\sum_{\mathbf{m}}\prod_{i=1}^{N} F_i(|m_i - m_i'|) \times \frac{1+x}{2T_1}\sum_{\mathbf{m}} p_{1/2}(\mathbf{m},t)\prod_{i=1}^{N} F_i(|m_i - m_i'|).$$

With the aid of (8) we can show that

$$\sum_{\mathbf{m}'}\prod_{i=1}^{N} F_i(|m_i - m_i'|) = \sum_{\mathbf{m}}\prod_{i=1}^{N} F_i(|m_i - m_i'|) = 1.$$

The second terms in (11) couple all the 2 exp (N + 1) equations; this corresponds to the coupling of a given level (M, **m**) with all the levels defined by the quantum number −M. The fact that $\Pi F_i(|m_i - m_i'|)$ depends only on the differences $|m_i - m_i'|$ makes it possible to split the system (11) into 2^N independent pairs of equations with the aid of the linear transformation

$$p_M(\mathbf{m}) = \sum_{\mathbf{k}} p_M(\mathbf{k})\exp(i\pi\mathbf{m}\mathbf{k}), \tag{12}$$

where the components of the N-dimensional "vector" $\mathbf{k} = \{k_1, k_2, \ldots, k_N\}$ assume the values $k_i = 0; 1$ ($i = 1, 2, \ldots, N$), and the summation is over all the 2^N possible values of **k**, while

$$p_M(\mathbf{k}) = 2^{-N}\sum_{\mathbf{m}} p_M(\mathbf{m})\exp(-i\pi\mathbf{m}\mathbf{k}). \tag{13}$$

For $p_M(\mathbf{k})$ we obtain the equations

$$\frac{dp_{1/2}(\mathbf{k})}{dt} = -\frac{1+x}{2T_1}p_{1/2}(\mathbf{k}) + \frac{1-x}{2T_1}p_{-1/2}(\mathbf{k})f(\mathbf{k}),$$
$$\frac{dp_{-1/2}(\mathbf{k})}{dt} = -\frac{1-x}{2T_1}p_{-1/2}(\mathbf{k}) + \frac{1+x}{2T_1}p_{1/2}(\mathbf{k})f(\mathbf{k}), \tag{14}$$

where

$$f(\mathbf{k}) = \prod_{i=1}^{N}[F_i(0) + F_i(1)\exp(i\pi k_i)]. \tag{15}$$

The solution of the system (14) is

$$p_{1/2}(\mathbf{k},t) = M_1(\mathbf{k})\exp[-\lambda_1(\mathbf{k})t] + M_2(\mathbf{k})\exp[-\lambda_2(\mathbf{k})t],$$
$$p_{-1/2}(\mathbf{k},t) = N_1(\mathbf{k})\exp[-\lambda_1(\mathbf{k})t] + N_2(\mathbf{k})\exp[-\lambda_2(\mathbf{k})t], \tag{16}$$

where

$$\lambda_{1,2}(\mathbf{k}) = \frac{1 \mp |f(\mathbf{k})|}{2T_1} \tag{17}$$

and

$$N_{1,2}(\mathbf{k}) = [\pm\operatorname{sgn} f(\mathbf{k}) + (1/f(\mathbf{k}) \pm \operatorname{sgn} f(\mathbf{k}))x]M_{1,2}(\mathbf{k}), \tag{18}$$

while the constants $M_{1,2}(\mathbf{k})$ are given by the initial conditions. The symbol $\operatorname{sgn} f = |f|/f$ denotes the sign function. With the aid of (12), (13), and (16)–(18), we can write the general solution of the kinetic equations (11) in the form

$$p_{1/2}(\mathbf{m},t) = 2^{-N-1}\sum_{\mathbf{k}}\sum_{\mathbf{m}''}\Big\{\Big[(1-x)p_{-1/2}(\mathbf{m}'',0)\operatorname{sgn} f(\mathbf{k}) \times\Big(1-\frac{x}{|f(\mathbf{k})|}\Big)p_{1/2}(\mathbf{m}'',0)\Big]\exp\Big(-\frac{1-|f(\mathbf{k})|}{2T_1}t\Big) \times\Big[(x-1)p_{-1/2}(\mathbf{m}'',0)\operatorname{sgn} f(\mathbf{k}) + \Big(1+\frac{x}{|f(\mathbf{k})|}\Big)p_{1/2}(\mathbf{m}'',0)\Big] \times\exp\Big(-\frac{1+|f(\mathbf{k})|}{2T_1}t\Big)\Big\}\exp[i\pi(\mathbf{m}-\mathbf{m}'')\mathbf{k}], \tag{19}$$

$$p_{-1/2}(\mathbf{m}',t) = 2^{-N-1}\sum_{\mathbf{k}}\sum_{\mathbf{m}''}\Big\{\Big[\Big(1+\frac{x}{|f(\mathbf{k})|}\Big)p_{-1/2}(\mathbf{m}'',0) \times(1+x)p_{1/2}(\mathbf{m}'',0)\operatorname{sgn} f(\mathbf{k})\Big]\exp\Big(-\frac{1-|f(\mathbf{k})|}{2T_1}t\Big) \times\Big[\Big(1-\frac{x}{|f(\mathbf{k})|}\Big)p_{-1/2}(\mathbf{m}'',0) - (1+x)p_{1/2}(\mathbf{m}'',0)\operatorname{sgn} f(\mathbf{k})\Big] \times\exp\Big(-\frac{1+|f(\mathbf{k})|}{2T_1}t\Big)\Big\}\exp[i\pi(\mathbf{m}'-\mathbf{m}'')\mathbf{k}].$$

4. OBSERVABLE FORM OF THE EPR LINE

In order to determine the form of the EPR line in terms of the populations (19), let us find the power absorbed by the system in a weak detecting high frequency field $H_x = 2H_1\cos\omega t$. The rate of change of the population difference

$$n(\mathbf{m}',\mathbf{m},t) \equiv p_{-1/2}(\mathbf{m}',t) - p_{1/2}(\mathbf{m},t) \tag{20}$$

under the influence of this field, which induces transitions between the levels ($M = -\tfrac{1}{2}$, **m**′) and ($M = \tfrac{1}{2}$, **m**), is

$$\Big(\frac{dn(\mathbf{m}',\mathbf{m},t)}{dt}\Big)_{rf} = -2W[(\tfrac{1}{2},\mathbf{m})\leftrightarrow(-\tfrac{1}{2},\mathbf{m}')]n(\mathbf{m}',\mathbf{m},t), \tag{21}$$

where $W[(\tfrac{1}{2},\mathbf{m}) \to (-\tfrac{1}{2},\mathbf{m}')]$ is the probability of the transition ($M = \tfrac{1}{2}$, **m**′) ⟷ ($M = \tfrac{1}{2}$, **m**) under the influence of a weak detecting field.

In the first perturbation theory-approximation, using (4), (7), and (8), we obtain

$$W[(\tfrac{1}{2},\mathbf{m})\leftrightarrow(-\tfrac{1}{2},\mathbf{m}')] = \frac{\pi}{2}\omega_1^2 g(\omega - \omega_{\mathbf{m},\mathbf{m}'})\prod_{i=1}^{N}F_i(|m_i - m_i'|). \tag{22}$$

Here $\omega_1 = \gamma_e H_1$, $g(\omega - \omega_{\mathbf{m},\mathbf{m}'})$ is a function of the shape of the packet and determines the broadening of the levels of the spin system, and

$$\omega_{\mathbf{m},\mathbf{m}'} = \hbar^{-1}[E_{1/2,\mathbf{m}} - E_{-1/2,\mathbf{m}'}]. \tag{23}$$

The absorbed power, defined by the expression

$$U_a = -\frac{1}{2}N_e\hbar\omega\sum_{\mathbf{m},\mathbf{m}'}\Big(\frac{dn(\mathbf{m}',\mathbf{m},t)}{dt}\Big)_{rf}, \tag{24}$$

can then be rewritten with the aid of (21) and (22) in the form

$$U_a = \frac{\pi}{2}\hbar\omega\,\omega_1^2 N_e\sum_{\mathbf{m},\mathbf{m}'} g(\omega - \omega_{\mathbf{m},\mathbf{m}'})h(\mathbf{m}',\mathbf{m},t), \tag{25}$$

where N_e is the total number of electrons in the sample, and the function of the shape of the envelope of the packets is

$$h(\mathbf{m}', \mathbf{m}, t) = n(\mathbf{m}', \mathbf{m}, t) \prod_{i=1}^{N} F_i(|m_i - m_i'|). \qquad (26)$$

Under the chosen normalization condition

$$\sum_{\mathbf{m}} [p_{-1/2}(\mathbf{m}, t) + p_{1/2}(\mathbf{m}, t)] = 1$$

it follows from (19) that the equilibrium line shape is determined by the function

$$h(\mathbf{m}', \mathbf{m}, \infty) = 2^{-N} x \prod_{i=1}^{N} F_i(|m_i - m_i'|). \qquad (27)$$

Thus, the obtained solution of the kinetic equations (19) determines completely the shape of the EPR line. However, in order to use these results in each concrete case and to determine the law according to which the system returns to equilibrium, it is necessary to know the populations at the initial instant of time, i.e., at the instant of turning off all the actions that take the system out of equilibrium (of course, H_0 remains). In the general case this information can be obtained only by solving the problem of taking the system out of equilibrium. In one particular but interesting case, it is possible to determine the initial values of the populations quite simply. If a strong high-frequency field with frequency ω_{rf} acts for a short time $\tau \ll T_1$, then changes occur during this time only in the populations $p_{-1/2}(\tilde{\mathbf{m}}')$ and $p_{1/2}(\tilde{\mathbf{m}})$ of the levels between which this pulse produced transitions,

$$\omega_{\tilde{\mathbf{m}}, \tilde{\mathbf{m}}'} = \omega_{rf}, \qquad (28)$$

while the populations of the remaining levels remain in equilibrium, since the transitions (6) cannot occur within a time τ. Then the initial conditions for the populations are as follows:

$$p_{-1/2}(\mathbf{m}', 0) = \begin{cases} 2^{-N-1}(1 + x), & \mathbf{m}' \neq \tilde{\mathbf{m}}' \\ 2^{-N-1}(1 + \alpha x), & \mathbf{m}' \neq \tilde{\mathbf{m}}' \end{cases},$$
$$p_{1/2}(\mathbf{m}, 0) = \begin{cases} 2^{-N-1}(1 - x), & \mathbf{m} \neq \tilde{\mathbf{m}} \\ 2^{-N-1}(1 - \alpha x), & \mathbf{m} = \tilde{\mathbf{m}} \end{cases}, \qquad (29)$$

where $\alpha = n(\tilde{\mathbf{m}}', \tilde{\mathbf{m}}, 0)/n(\tilde{\mathbf{m}}', \tilde{\mathbf{m}}, \infty)$ is the relative change of the population difference under the influence of the high-frequency field pulse. The initial conditions (29) and (19) yield the complete solution of the problem. If the impulse of the high-frequency field equalizes the populations in the saturable part of the line ($\alpha = 0$, strong saturation), then the expression for $n(\mathbf{m}', \mathbf{m}, t)$ is particularly simple:

$$n(\mathbf{m}', \mathbf{m}, t) = n(\mathbf{m}', \mathbf{m}, \infty)\Big\{1 - 2^{-N-1} \times \exp\Big(-\frac{t}{2T_1}\Big) \sum_{\mathbf{k}} [(\exp[i\pi(\mathbf{m}' - \tilde{\mathbf{m}}')\mathbf{k}] + \exp[i\pi(\mathbf{m} - \tilde{\mathbf{m}})\mathbf{k}]) \times \operatorname{ch}\frac{|f(\mathbf{k})|t}{2T_1} - (\exp[i\pi(\mathbf{m}' - \tilde{\mathbf{m}})\mathbf{k}] \times \exp\{i\pi(\mathbf{m} - \mathbf{m}')\mathbf{k}]) \operatorname{sh}\frac{|f(\mathbf{k})|t}{2T_1} \operatorname{sign} f(\mathbf{k})\Big]\Big\}. \qquad (30)$$

Let us analyze qualitatively the temporal dependence of the line shape. At the initial instant (after termination of the action of the high-frequency field pulse) the population $p_{-1/2}(\tilde{\mathbf{m}}')$ is smaller than the equilibrium value and $p_{1/2}(\tilde{\mathbf{m}})$ is larger than the equilibrium value. This means that at all the frequencies corresponding to the transitions from the states ($M = -1/2$, $\mathbf{m}'$) and ($M = 1/2$, $\mathbf{m}'$) (these transitions are designated by solid lines in the figure) the differences correspond to populations lower than the equilibrium values, i.e., "holes" appear in the line. The appearance of additional "holes" was investigated in [2-4] and was called in [2] the "effect" of discrete saturation of the EPR line. The number of relaxation transitions ($M = 1/2$, $\mathbf{m}$) → ($M = -1/2$, $\mathbf{m}'$) per unit time will be larger than the number of transitions ($M = -1/2$, $\tilde{\mathbf{m}}'$) → ($M = 1/2$, $\mathbf{m}$), since the population $p_{-1/2}(\tilde{\mathbf{m}}')$ is smaller than the equilibrium value, i.e., the population of any of the levels with $M = 1/2$ will decrease. In exactly the same way, the population of any level with $M = -1/2$ will increase. This means that the differences of the populations $n(\mathbf{m}', \mathbf{m}, t)$ first increase with time, and the differences of the populations $n(\mathbf{m}', \mathbf{m}, t)$, where $\mathbf{m}' \neq \tilde{\mathbf{m}}'$ and $\mathbf{m} \neq \tilde{\mathbf{m}}$ (levels not affected by the high-frequency pulse) turn out to be larger than the equilibrium values, i.e., bursts of absorption intensity will be observed at the corresponding frequencies $\omega\mathbf{m}$ and $\mathbf{m}'$ (undistorted regions of the EPR line). These bursts reach a maximum after a time $\sim T_1$ (as seen from (19)), and then gradually vanish. The burned-out holes also vanish and the line shape becomes equilibrium.

Expression (30) for $n(\mathbf{m}', \mathbf{m}, t)$ confirms fully this qualitative analysis.

5. CASE OF EQUIVALENT NUCLEAR SPINS

If the nuclear spins determining the hyperfine broadening of the EPR line are equivalent, the results obtained above can be simplified, since the system is described by a smaller number of variables—the populations of the energy levels, the number of which is much smaller than that of the states. For simplicity we shall assume that all N nuclear spins are equivalent. The general case when several groups of equivalent nuclear spins are present can be considered in the same manner. In formula (1) we have $A_i \equiv A$ and $B_i \equiv B$. The energy level is determined by the numbers M and $\sigma = \sum_{i=1}^{N} m_i$:

$$E_{M,\sigma} = M\hbar\omega_e + \sigma\sqrt{(\hbar\omega_n - MA)^2 + |B|^2}. \qquad (31)$$

In this case it is convenient to introduce, for the description of the system, the population $P_M(\sigma, t)$ of the energy level $E_{M,\sigma}$. In order to express the EPR line shape in terms of these populations, we express the populations of the states $p_M(\mathbf{m}, t)$ in terms of $P_M(\sigma, t)$ and use the results obtained above:

$$p_{1/2}(\mathbf{m}, t)|_{\sigma} = \frac{1}{C_N^{N/2-\sigma}} P_{1/2}(\sigma, t),$$
$$p_{-1/2}(\mathbf{m}', t)|_{\sigma'} = \frac{1}{C_N^{N/2-\sigma'}} P_{-1/2}(\sigma', t), \qquad (32)$$

where the index $|_{\sigma}$ denotes the condition $\sum_{i=1}^{N} m_i = \sigma$, and the binomial coefficients $C_N \exp(N/2 - \sigma)$ in (32) indicate the degeneracy multiplicity of the energy level relative to the vectors **m** with a given projection sum $\sum_{i=1}^{N} m_i = \sigma$. Thus, Eqs. (32) and (19) determine the sought populations of the energy levels ($M = \frac{1}{2}, \sigma$) and ($M = -\frac{1}{2}, \sigma'$). In this case (19) can be simplified. For any nucleus, the quantities $F_i(|m_i - m_i'|)$, defined by (8), no longer depend on the number of the nucleus:

$$F_i(0) \equiv F_0 = \sin^2 \frac{\theta_{1/2} - \theta_{-1/2}}{2}, \qquad \operatorname{tg} \theta_M = \frac{2M|B|}{MA - \hbar\omega_n}, \qquad F_i(1) \equiv F_1 = \cos^2 \frac{\theta_{1/2} - \theta_{-1/2}}{2} \tag{33}$$

and consequently (15) can be rewritten in the form

$$f(\mathbf{k}) = (F_0 - F_1)^s \equiv f(s), \qquad F_0 \neq F_1, \tag{34}$$

where $s = \sum_{i=1}^{N} k_i$. Substituting (34) and (19), we obtain with the aid of (32)

$$\begin{aligned} P_{1/2}(\sigma, t) = 2^{-N-1} \sum_{s=0}^{N} \sum_{\sigma''=-N/2}^{N/2} a(s, \sigma, \sigma'') \Big\{ \Big[(1-x) P_{-1/2}(\sigma'', 0) \operatorname{sign} f(s) \\ \times \Big(1 - \frac{x}{|f(s)|}\Big) P_{1/2}(\sigma'', 0) \Big] \exp\Big(-\frac{1-|f(s)|}{2T_1} t\Big) \\ + \Big[(x-1) P_{-1/2}(\sigma'', 0) \operatorname{sign} f(s) + \\ \times \Big(1 + \frac{x}{|f(s)|}\Big) P_{1/2}(\sigma'', 0) \Big] \exp\Big(-\frac{1+|f(s)|}{2T_1} t\Big) \Big\}, \\ P_{-1/2}(\sigma', t) = 2^{-N-1} \sum_{s=0}^{N} \sum_{\sigma''=-N/2}^{N/2} a(s, \sigma', \sigma'') \Big\{ \Big[\Big(1 + \frac{x}{|f(s)|}\Big) P_{-1/2}(\sigma'', 0) \\ \times (1+x) P_{1/2}(\sigma'', 0) \operatorname{sign} f(s) \Big] \exp\Big(-\frac{1-|f(s)|}{2T_1} t\Big) \\ \times \Big[\Big(1 - \frac{x}{|f(s)|}\Big) P_{-1/2}(\sigma'', 0) \\ - (1+x) P_{1/2}(\sigma'', 0) \operatorname{sign} f(s) \Big] \exp\Big(-\frac{1+|f(s)|}{2T_1} t\Big) \Big\}, \end{aligned} \tag{35}$$

where

$$a(s, \sigma, \sigma'') = \frac{C_N^{N/2-\sigma}}{C_N^{N/2-\sigma''}} \sum_{n=0}^{s} (-1)^n C_s^n C_{N-s}^{N/2+\sigma''-n} \sum_{m=0}^{N/2-\sigma} C_{N/2-\sigma}^m C_{N/2+\sigma}^{s-m}.$$

To express the absorption line shape in terms of the population difference (35), it is sufficient to carry out in the expression for the absorbed or (25) summation over the vectors **m** and **m′** with the given sums of the projections

$$\sum_{i=1}^{N} m_i = \sigma \text{ and } \sum_{i=1}^{N} m_i' = \sigma'.$$

It is necessary to take into account here the fact that for equivalent nuclear spins it follows from (33) that

$$\prod_{i=1}^{N} F_i(|m_i - m_i'|) = F_0^{N-(\mathbf{m}-\mathbf{m}')^2} F_1^{(\mathbf{m}-\mathbf{m}')^2}. \tag{36}$$

Then expression (25) is written in the form

$$U_a = \frac{\pi}{2} N_e \hbar \omega \omega_1^2 \sum_{\sigma, \sigma'} g(\omega - \omega_{\sigma, \sigma'}) h(\sigma', \sigma, t), \tag{37}$$

where the packet envelope shape function is determined by the following expression:

$$h(\sigma', \sigma, t) = 2^{-N} \Big[\frac{P_{-1/2}(\sigma', t)}{C_N^{N/2-\sigma'}} - \frac{P_{1/2}(\sigma, t)}{C_N^{N/2-\sigma}} \Big] \sum_{s=0}^{N} b(s, \sigma, \sigma') (F_0 - F_1)^s,$$

and

$$b(s, \sigma, \sigma') = C_N^s \sum_{n=0}^{s} \sum_{m=0}^{s} (-1)^{n+m} C_s^n C_s^m C_{N-s}^{N/2+\sigma-n} C_{N-s}^{N/2+\sigma'-m}, \tag{38}$$

and in the case of equilibrium, as follows from (35)

$$h(\sigma', \sigma, \infty) = 2^{-2N} x \sum_{s=0}^{N} b(s, \sigma, \sigma') (F_0 - F_1)^s. \tag{39}$$

We note that the dependence of all the obtained results on the hyperfine interaction constants enters only via the powers of the difference $F_0 - F_1$. This circumstance allows us to confine ourselves to several of the lower powers of $F_0 - F_1$ in the formulas given above, if the probability of the forbidden transition is close to the probability of the allowed transition, i.e., if condition (10) is satisfied and $F_0 \approx F_1$.

If $|F_0 - F_1| \ll 1$, then the results greatly simplify. In this case we can write in place of (34)

$$f(s) \approx \delta_{s,0}. \tag{40}$$

Substituting (40) in (35), we obtain

$$\begin{aligned} P_{1/2}(\sigma, t) = P_{1/2}(\sigma, \infty) + Q(\sigma) \exp\Big(-\frac{t}{T_1}\Big) + R_{1/2}(\sigma) \exp\Big(-\frac{t}{2T_1}\Big), \\ P_{-1/2}(\sigma', t) = P_{-1/2}(\sigma', \infty) - Q(\sigma') \exp\Big(-\frac{t}{T_1}\Big) + R_{-1/2}(\sigma') \exp\Big(-\frac{t}{2T_1}\Big), \end{aligned} \tag{41}$$

where

$$P_M(\sigma, \infty) = 2^{-N-1}(1 - 2Mx) C_N^{N/2-\sigma},$$

$$Q(\sigma) = 2^{-N-1} \Big[x - \sum_{\sigma''=-N/2}^{N/2} (P_{-1/2}(\sigma'', 0) - P_{1/2}(\sigma'', 0)) \Big] C_N^{N/2-\sigma},$$

$$R_M(\sigma) = 2^{-N} C_N^{N/2-\sigma} \sum_{s=1}^{N} (-1)^s \sum_{m=0}^{N/2-\sigma} C_{N/2-\sigma}^m C_{N/2+\sigma}^{s-m} \sum_{\sigma''=-N/2}^{N/2} \frac{P_M(\sigma'', 0)}{C_N^{N/2-\sigma''}} \times \sum_{n=0}^{s} (-1)^n C_s^n C_{N-s}^{N/2+\sigma''-n}.$$

The packet envelope shape function is then determined from (38) and (41) by means of the following time dependence:

$$h(\sigma', \sigma, t) = 2^{-N} [C_N^{N/2-\sigma} P_{-1/2}(\sigma', t) - C_N^{N/2-\sigma'} P_{1/2}(\sigma, t)]. \tag{42}$$

Thus, the behavior of the EPR line in this simple case of equal probabilities of the forbidden and allowed transitions is described only by two exponentials, $\exp(-t/T_1)$, and $\exp(-t/2T_1)$. From (41) and (42) we get in this case a useful formula for the equilibrium function $h(\sigma', \sigma, \infty)$:

$$h(\sigma', \sigma, \infty) = 2^{-N} x C_N^{N/2-\sigma} C_N^{N/2-\sigma'}. \tag{43}$$

In concluding this part, we note once more that a qualitative description of the process of spectral diffusion in the case of equivalent nuclear spins does not differ in any way from the description of this process indicated in Sec. 4.

On the other hand, a numerical determination of the character of the diffusion requires knowledge of the initial values of the populations $P_M(\sigma, 0)$, which can be readily obtained only upon rapid saturation of the line. Since the procedure for obtaining these populations is described in Sec. 4, we shall not repeat it for the case of equivalent nuclei.

6. DISCUSSION OF RESULTS

As already mentioned in the introduction, the obtained time dependence of the line shape following the action of a "burning" pulse makes it possible to determine the HFI constant for an unresolved hyperfine structure. Let us examine in greater detail the method of determining these constants.

Even the positions of the additional holes can lead to certain definite conclusions concerning the values of the HFI constant.[3,4] Such an analysis, however, is generally speaking ambiguous, especially in the case when the system contains equivalent nuclei, when the frequencies of many transitions coincide. Therefore, to find the HFI constant we need additional information, which can be extracted from observations of the character of the variation of the line shape in time, after pulse saturation of part of the line.

Indeed, as seen from formulas (25), (19), (17), (8), and (9), the time dependence of the rate of absorption of the energy of a control high-frequency field is determined by exponentials having time constants that depend on the HFI constants. Thus, we can obtain additional information that enables us to select uniquely the HFI constants. It should be noted that when the control signal passes through the line the modulation frequency should obviously be larger than $1/T_1$.

In our analysis of the problem we have neglected the effect of spectral diffusion through the line as a result of spin-spin electron interaction. The characteristic time of variation of the populations in the entire line, in the mechanism considered by us, is T_1. The spin-spin interaction of the electrons alters noticeably the populations in the entire line, owing to the cross relaxation mechanism, within a time $T' \gg T_2$,[5] where $1/T_2$ is the broadening of the hyperfine structure component due to the electron spin-spin interaction. Our analysis is therefore valid when

$$T' \gg T_1. \tag{44}$$

At the same time, the condition $T_2 > T_1$ is perfectly admissible. Thus, the non-resolution of the hyperfine structure may be due to dipole-dipole interaction of the electrons, i.e., it depends on the concentration of the electron spins, but the relaxation of the line shape to its equilibrium value is nonetheless ensured by the HFI. The condition that the inequality (44) must be satisfied imposes an upper limit on the electron-spin concentration for which our analysis is valid.

Let us discuss briefly the second type of diffusion, when the nuclear spins relax principally as a result of direct coupling with the lattice. This can occur if the spin of the nucleus exceeds $\frac{1}{2}$, when the quadrupole relaxation turns out to be more rapid than the relaxation due to the HFI.[1] Then, if $|R| \ll A$ and $A \neq 2\hbar\omega_n$ (see condition (10)), each spin flip of the nucleus shifts the resonant frequency of the electron by $\Delta\omega$ (we are considering the case of N equivalent nuclei). If a hole is burned in the EPR line at the frequency ω_0, then, owing to the flips of the nuclei, the population difference in the neighboring packets with frequencies $\omega_0 \pm \Delta\omega$ begins to change, etc. When $\Delta\omega \ll \Delta\omega^*$, we can obtain a differential equation describing such a spreading of the hole. We introduce the relative deviation of the population differences from equilibrium

$$\varepsilon(\omega) = \frac{n(\omega) - n^0(\omega)}{n^0(\omega)}, \tag{45}$$

where $n^0(\omega)$ is the equilibrium population difference, which in the case of equivalent nuclei has a binomial distribution

$$n^0(k\Delta\omega) \sim C_N{}^{N/2-k}.$$

Then $\epsilon(\omega)$ obeys the equation

$$\frac{\partial\varepsilon}{\partial t} = D\frac{\partial^2\varepsilon}{\partial\omega^2} - W\omega\frac{\partial\varepsilon}{\partial\omega} - \frac{\varepsilon}{T_1}, \tag{46}$$

where $D = \frac{1}{2}NW(\Delta\omega)^2$, W is the nuclear spin-flip probability per unit time, and ω is reckoned from the center of the line. Equation (46) is analogous to the spectral-diffusion equation obtained by Portis,[5] if the diffusion is due to dipole-dipole interaction. The second term to the right of (46) leads to a predominant shift of the hole to the edge of the line, and the first term to a gradual spreading of the hole. We shall not investigate the solution (46), since this equation is accurate only for nuclear spins $\frac{1}{2}$. However, the qualitative behavior of the spectral diffusion will be the same also for large nuclear spins.

In conclusion, I am sincerely grateful to the participants of the seminar of the Theoretical Division of the Institute of Chemical Physics for fruitful criticism and discussions.

[1] P. R. Moran, Phys. Rev. **135A**, 247 (1964).

[2] T. I. Sanadze and G. R. Khutsishvili, ZhETF Pis. Red. **8**, 376 (1968) [JETP Lett. **8**, 232 (1968)].

[3] T. I. Sanadze and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. **56**, 454 (1969) [Sov. Phys.-JETP **29**, 248 (1969)].

[4] N. A. Efremov, M. A. Kozhushner, and V. N. Sokolov, ZhETF Pis. Red. **7**, 472 (1968) [JETP Lett. **7**, 365 (1968)].

[5] A. M. Portis, Phys. Rev. **104**, 584 (1956).

[6] G. T. Trammel, H. Zeldes, and R. Livingston, Phys. Rev. **110**, 630 (1958).

[7] A. Abragam, Principles of Nuclear Magnetism, Oxford, 1961.

[8] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

Translated by J. G. Adashko
61