

# Magnetic-resonance line shape in magnetically diluted solids with spatial correlation and inhomogeneous broadening

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A theory of the paramagnetic-resonance line shape in solids with disordered spatially correlated distribution of the spins in the presence of inhomogeneous broadening is developed. The theory is based on the concentration expansion of the memory function (irreducible operator). In the approximation linear in the concentration, the problem is reduced to relatively simple quadratures, which make possible a numerical synthesis of the EPR spectra and their comparison with the experimental spectra. The accuracy of the linear approximation is estimated and the asymptotic form of the decrease of the free induction is found. A phenomenological expression for the memory function is proposed for the case of arbitrary concentration. The general theory is illustrated by several specific examples which show that spatial correlation influences strongly the line shape, and that the influence of the inhomogeneous broadening cannot be represented in the form of a convolution.

## 1. INTRODUCTION

The problem of the paramagnetic-resonance line shape in a solid with disordered spin arrangement is one of the classical problems of the statistical physics of spin systems. Notwithstanding the appreciable efforts made to solve this problem since the discovery of magnetic resonance<sup>1–6</sup> (see also Refs. 7 and 8), there is still no experimentally confirmed theory of the absorption line shape in a magnetically dilute system. The obstacles to a successful solution of the problem is its multiparticle character in the absence of a small parameter in the Hamiltonian. An added difficulty, typical of disordered systems, is the need for configuration averaging (i.e., averaging over all the spatial positions of the particles).

Yet the problem is of significant general-physics interest both for applications and because of the profound analogies with many other branches of physics. Examples are the problem of optical spectra of mixed crystals,<sup>9a</sup> neutron scattering by a dilute paramagnet,<sup>9b</sup> and practically all the other problems in which it is necessary to calculate the temporal correlation functions (TCF) of a disordered system. At the same time, the spectra of a disordered system can be used, for example, to determine the local concentration of particles in polymer coils, since they carry information on the structure of the impurity paramagnetic centers, on their electronic structure, and others.

The first attempt to describe the spectrum of a disordered system was Anderson's classical theory,<sup>1</sup> in which he postulated a model Hamiltonian that differed substantially from the real one, and assumed the medium to be absolutely disordered and homogeneous. Other studies were based either on a comparison of the second and fourth moments,<sup>2</sup> or on unverifiable approximations.<sup>3,5</sup> In Ref. 6, the authors confined themselves to a qualitative discussion of exchange narrowing. The most consistent is Ref. 4, but it is based essentially on the assumption that there are no correlations in the spin positions. Such correlations, however, are frequently observed in experiment; for example, they appear in ion clusters in crystals, in tracks of charged particles, in frozen

solutions of spin-tagged macromolecules, etc. In addition, EPR spectra are almost always subject to inhomogeneous broadening due to the spread of the fields.

We develop here a systematic theory of paramagnetic resonance spectra in magnetically dilute systems, with allowance for the correlations in the spatial distribution of the spins and for the inhomogeneous broadening of the initial spectrum. The theory is a substantial elaboration of the approach indicated in Ref. 10. It is based on a concentration (cluster) expansion of the memory function which is an irreducible operator for the TCF. In an approximation linear in the concentration, the problem is reduced to quadratures. The accuracy of this approximation is estimated. For the cases of arbitrary concentration, a phenomenological expression is proposed for the memory function. The general theory is illustrated by a number of specific examples.

## 2. CLUSTER EXPANSION OF THE MEMORY FUNCTION

It is well known that the line-shape function in magnetic resonance is the Fourier transform of the real part of the time correlation function

$$\Gamma(t) = \text{Sp} \{S_+ S_-(t)\} / \text{Sp}(S_+ S_-), \quad (1)$$

where  $S_{\pm} = S_x \pm iS_y$  are the transverse components of the total-spin operator;

$$S_-(t) = \exp(iH_s t) S_- \exp(-iH_s t),$$

and  $H_s$  is the secular part of the spin Hamiltonian in frequency units.<sup>7,8</sup>

With allowance for the spread of the static local fields, the Hamiltonian takes the form

$$H_s = \sum_{j=1}^N \omega_j S_j^z + \sum_{j=1}^N \sum_{k=j+1}^N H_{jk}, \quad (2)$$

where  $N$  is the number of spins in the system,  $S_j^{\alpha}$  is the  $\alpha$ -

component of the operator of the  $j$ th spin, and  $H_{jk}$  is the Hamiltonian of the interaction of the spins  $j$  and  $k$ .

In the thermodynamic limit,  $\Gamma(t)$  is self-averaging, i.e.,

$$\Gamma(t) = \langle \Gamma(t) \rangle = \langle \langle \Gamma(t) \rangle_c \rangle_\omega, \quad (3)$$

where  $\langle \dots \rangle_c$  denotes averaging over the ensemble of the spatial distributions of the spins, and  $\langle \dots \rangle_\omega$  is averaging over the ensemble of the static local fields.

To formulate the cluster expansion it is convenient to assume that the possible values of the coordinates form a regular lattice. We introduce the occupation number of the sites  $x$  of this lattice

$$n_x = \sum_{k=1}^N \delta(x - x_k). \quad (4)$$

Here  $\delta(x)$  is the Kronecker delta, and  $x_k$  is the coordinate of the impurity. Obviously,  $n_x$  is equal to zero or unity, depending on whether the site  $x$  is empty or occupied. In the occupation-number representation, Eq. (2) takes the form

$$H_x = \sum_x n_x \omega_x S_x^z + \frac{1}{2} \sum_{x \neq q} n_x n_q H_{xq}, \quad S_\pm = \sum_q S_q^\pm n_q. \quad (5)$$

The summation here and below was carried out over the spatial variables and over all the sites of the regular lattice. Any bounded function of the occupation numbers can be expanded in the series

$$\begin{aligned} F(\{n_q\}) = & F^{(0)} + \sum_q n_q (F^{(1)}(q) - F^{(0)}) \\ & + \frac{1}{2!} \sum'_{q_1, q_2} n_{q_1} n_{q_2} (F^{(2)}(q_1, q_2) \\ & - F^{(1)}(q_1) - F^{(1)}(q_2) + F^{(0)}) + \frac{1}{3!} \sum'_{q_1, q_2, q_3} n_{q_1} n_{q_2} n_{q_3} (F^{(3)}(q_1, q_2, q_3) \\ & - F^{(2)}(q_1, q_2) - F^{(2)}(q_1, q_3) - F^{(2)}(q_2, q_3) + F^{(1)}(q_1) + F^{(1)}(q_2) \\ & + F^{(1)}(q_3) - F^{(0)}) + \dots, \quad (6) \end{aligned}$$

$$\begin{aligned} F(\{n_q\}) = & F^{(0)} + \sum_{m=1}^{\infty} \frac{1}{m!} \sum'_{q_1, \dots, q_m} n_{q_1} n_{q_2} \dots n_{q_m} \\ & \times \sum_{p=0}^m C_m^p (-1)^{m-p} F^{(p)}(q_1, \dots, q_p). \quad (7) \end{aligned}$$

Here  $F^{(p)}(q_1, \dots, q_p)$  is  $F(\{n_q\})$  in the case when the numbers  $n_{q_1}, n_{q_2}, \dots, n_{q_p}$  are equal to unity and all the other  $n_q$  are zero. The prime on the summation sign in (6) means exclusion of all coincidences of the coordinates, while the double prime in (7) emphasizes the fact that, in addition, all the summations are restricted to a common volume. Equation (6) follows from (7) upon symmetrization with respect to  $q_i$ . Note that Eq. (7) is more compact, but (6) is more useful for actual calculations.

Equations (6) and (7) can be obtained, for example, by induction, recognizing that for any bounded function

$$\varphi(n_q) = \varphi(0) + n_q (\varphi(1) - \varphi(0)).$$

Another derivation is indicated in Ref. 10.

To apply these relations to our problem, we recognize

that after averaging the system is translationally invariant, and therefore

$$\begin{aligned} \Gamma(t) = & \left\langle \text{Sp} \left\{ S_+ \sum_q n_q S_q^-(t) \right\} / \sum_q n_q \text{Sp} S_q^+ S_q^- \right\rangle \\ = & \langle n_0 \text{Sp} \{ S_+ S_0^-(t) \} / (f \text{Sp} S_0^+ S_0^-) \rangle. \quad (8) \end{aligned}$$

We have introduced here the dimensionless density  $f = \langle n_q \rangle$  and took it into account that the numerator and denominator in (8) are self-averaged. It is convenient to separate the common expression with frequency  $\omega_0$ , i.e., transform from the Hamiltonian (5) to

$$H' = \sum_q n_q \Delta_q S_q^z + \frac{1}{2} \sum_{x \neq q} n_x n_q H_{xq}, \quad \Delta_q = \omega_q - \omega_0. \quad (9)$$

Using now the obvious relation  $n_0 \varphi(n_0) = n_0 \varphi(1)$ , we get

$$\Gamma(t) = \langle \Gamma_0(t) \exp(-i\omega_0 t) \rangle_{\omega_0}, \quad \Gamma_0(t) = \langle \Gamma_0(t) \rangle^0, \quad (10)$$

$$\Gamma_0(t) = \text{Sp} \{ S_+ \exp(iH't) S_0^- \exp(-iH't) \} / \text{Sp} (S_0^+ S_0^-).$$

The symbol  $\langle \dots \rangle_{\omega_0}$  denotes here averaging over the inhomogeneous broadening of the spin at the site "0," while  $\langle \dots \rangle^0$  denotes averaging over all the variables under the condition that the site "0" is definitely occupied, and that value of  $\omega_0$  is fixed.

Under typical experimental conditions, the Larmor precession frequency  $\omega_L$  in an external magnetic field is much larger than the spread of the local-field frequencies and the characteristic frequency of the spin interaction, i.e.,

$$\langle |\omega_j| \rangle \ll \omega_L, \quad \frac{1}{N} \text{Sp} \sum_{j \neq k} H_{jk}^2 \ll \omega_L^2.$$

The known expression for the normalized line-shape function<sup>7,8,11</sup> can now be rewritten in the form

$$g(\omega) = \frac{1}{\pi} \text{Re} \langle \Phi_0(\omega_0 - \omega - i\varepsilon) \rangle_{\omega_0}, \quad \varepsilon \rightarrow +0, \quad (11)$$

$$\Phi_0(z) = \int_0^{\infty} dt e^{-izt} \Gamma_0(t), \quad (12)$$

where  $\omega = \omega_{\text{RF}} - \omega_L$  and  $\omega_{\text{RF}}$  is the frequency of the transverse RF field. It is implied in (11) that the frequency  $\omega_0$  is also reckoned from the Larmor frequency  $\omega_L$ . Using now Eq. (7), we get

$$\tilde{\Gamma}_0(t) = 1 + \sum_{m=1}^{\infty} \frac{1}{m!} \tilde{B}_m(t), \quad (13)$$

$$\tilde{B}_m(t) = \sum'_{q_1, \dots, q_m} n_{q_1} n_{q_2} \dots n_{q_m} \sum_{p=0}^m (-1)^{m-p} C_m^p \Gamma_0^{(p)}(q_1, \dots, q_p, t).$$

It must be assumed here that  $n_0 \equiv 1$  and in the sum over  $q_1, \dots, q_m$  no argument can be equal to another or to zero. Thus,  $\Gamma_0^{(p)}(q_1, \dots, q_p, t)$  is equal to  $\tilde{\Gamma}_0(t)$  for a solitary cluster of  $p+1$  spins located at the sites  $0, q_1, q_2, \dots, q_p$ , i.e.,  $\Gamma_0^{(p)}$  is equal to  $\tilde{\Gamma}_0$  in the case when the numbers  $n_0, n_{q_1}, \dots, n_{q_p}$  are equal to unity and the remaining  $n_q = 0$ .

In a system of finite volume, the series (13) terminates at  $m = N_0 - 1$ , where  $N_0$  is the total number of sites in the lattice, and can be averaged term by term. In this case  $\langle n_{q_1} \dots n_{q_m} \rangle^0$  denotes averaging with  $W_0(q_1, \dots, q_m)$ , the con-

ditional probability of observing spins at the sites  $\mathbf{q}_1, \dots, \mathbf{q}_m$ , if the site "0" is definitely occupied. The averaging over the frequency, on the other hand, is over each  $\Gamma_0^{(p)}$  term by term. Ultimately

$$\Gamma_0(t) = 1 + \sum_{m=1}^{\infty} \frac{1}{m!} B_m(t),$$

$$B_m(t) = \sum_{\mathbf{q}_1, \dots, \mathbf{q}_m} W_0(\mathbf{q}_1, \dots, \mathbf{q}_m) \times \sum_{p=0}^m (-1)^{m-p} C_m^p \langle \Gamma_0^{(p)}(\mathbf{q}_1, \dots, \mathbf{q}_p, t) \rangle_{\omega_0^0}, \quad (14)$$

where  $\langle \dots \rangle_{\omega_0^0}$  denotes averaging over all frequencies  $\omega_{\mathbf{q}}$  except  $\omega_0$ . If the spin arrangement is uncorrelated (uniform) we have

$$W_0(\mathbf{q}_1, \dots, \mathbf{q}_m) = f^m, \quad f = \langle n_{\mathbf{q}} \rangle. \quad (15)$$

Thus, the cluster arrangement (13) yields after averaging the concentration expansion of (14) for  $\Gamma(t)$ .

Equations (14) are accurate in the case when impurity spins in a crystal matrix are considered. To use them for glass or viscous solutions it suffices to go to the limit as the unit cell volume  $\Omega \rightarrow 0$ . In this case

$$\sum_{\mathbf{q}_i} \rightarrow \int (d\mathbf{q}_i / \Omega), \quad W_0(\mathbf{q}_1, \dots, \mathbf{q}_m) \rightarrow \Omega^m c_0(\mathbf{q}_1, \dots, \mathbf{q}_m),$$

where  $c_0(\mathbf{q}_1, \dots, \mathbf{q}_m)$  is the density of the conditional probability of observing points near the points  $\mathbf{q}_1, \dots, \mathbf{q}_m$ , if a spin is definitely located at the point "0". The same replacement of the sums by integrals is expedient also in the limit of low concentrations, i.e., when the change of  $\Gamma(t)$  with time is finite, but  $f \rightarrow 0$ .

The convergence of the series (14) has not yet been investigated. We note, however, that in the related problem of averaging the kinetic equation for random walks in a disordered lattice it has been proved that similar concentration expansions determine entire concentration functions.<sup>12</sup> We shall show that all  $B_m < \infty$ . This is the case if the function under the  $\Sigma^{11}$  sign in (13) decreases rapidly enough after symmetrization with respect to  $\mathbf{q}_1, \dots, \mathbf{q}_m$  when all the particles move away from one another. If, however, the  $\mathbf{q}_1, \dots, \mathbf{q}_p$  move apart enough, then  $\Gamma_0^{(p)}(t)$  is adequately represented by the first terms of its Taylor expansion in  $t$ , i.e., by its moments. In the upshot, the convergence properties of  $B_m$  are similar to the convergence properties of the  $m$ -particle contribution to the moment of order  $2m$ , and since the moments are finite  $B_m$  is also finite.

It is natural to expect the series (14) to determine at least an asymptotic concentration expansion. Note that the real parameter of this expansion is proportional to  $ft$  in the limit of small concentrations. This can be easily verified for dipole-dipole interaction of the spins in the absence of inhomogeneous broadening, by going to the limit of a continuous medium and making the substitution  $q_i \rightarrow q_i t^{1/3}$ . Since the dipole interaction is proportional to  $r^{-3}$ , this substitution eliminates the time from  $\Gamma_0^{(p)}$ , but leads to  $\int d^3 q_i \rightarrow t \int d^3 q_i$

and it turns out that  $B_m \sim (ft)^m$ .

Consequently, no finite segment of the series (14) satisfies the mandatory condition that the correlation functions attenuate as  $t \rightarrow \infty$ . This fact has an analog in the "volume divergence" of the direct cluster expansion of the partition function of a rarefied gas. To obtain a correct virial expansion, various rearrangements of the direct expansions are used, particularly the cumulant expansion. We shall use here, in accord with the general ideas of the many-body theory,<sup>13-16</sup> the cluster expansion of the memory function  $G_0(t)$ , defined by the relation

$$d\Gamma_0/dt = - \int_0^t d\tau G_0(\tau) \Gamma_0(t-\tau). \quad (16)$$

The advantage of this approach is that it guarantees a non-negative form function in the principal approximation. Note that the requirement  $g(\omega) \geq 0$  is not trivial. For example, we do not know how to satisfy it when spatial correlations are introduced in a theory such that of Grant and Standberg.<sup>3</sup> In addition, there are known constructions (e.g., in the Lowe-Norberg theory<sup>7</sup>) in which this property does not hold.

The Fourier transform  $G_0(z)$  of the memory function is determined by the relation

$$G_0(z) = -iz + 1/\Phi_0(z). \quad (17)$$

The gist of the approach proposed is a restructuring of the concentration expansion of  $\Gamma_0(t)$  into a concentration expansion of the memory function on the basis of Eqs. (14), (12), and (17), and retaining its first terms, after which the form function  $g(\omega)$  is determined from (16), (12), and (11).

In calculations of the line shape it is useful to separate the real and imaginary parts of  $G_0(\omega - i\epsilon)$  and introduce

$$\lim_{\epsilon \rightarrow 0} G_0(\omega - i\epsilon) = R(\omega) + iI(\omega), \quad (18)$$

which leads, in view of (16) and (11) to

$$g(\omega) = \langle g_0(\omega_0 - \omega) \rangle_{\omega_0} = \int d\omega_0 \rho(\omega_0) g_0(\omega_0 - \omega), \quad (19)$$

where  $\rho(\omega)$  is the distribution function of the local fields the line shape in an extremely diluted system and

$$g_0(\omega) = \frac{1}{\pi} \frac{R(\omega)}{[\omega + I(\omega)]^2 + R^2(\omega)}. \quad (20)$$

Although the integral in the right-hand side of (19) is in the form of a convolution, the subscript 0 indicates that the function (20) can, generally speaking, depend also on the frequency  $\omega_0$  (see below).

In the approximation linear in the concentration we have

$$G_0(z) = z^2 \Phi_1(z), \quad (21)$$

$$\Phi_1(z) = \int_0^{\infty} dt e^{-izt} B_1(t), \quad (22)$$

$$B_1(t) = \sum_{\mathbf{q} \neq 0} W_0(\mathbf{q}) \langle \Gamma_0^{(4)}(\mathbf{q}, t) - 1 \rangle_{\omega_0}. \quad (23)$$

On going to a continuous spin distribution

$$B_i(t) = \int d^3q \int d\omega_q c_0(\mathbf{q}, \omega_0, \omega_q) [\Gamma_0^{(1)}(\mathbf{q}, \omega_q - \omega_0, t) - 1], \quad (24)$$

where  $c_0(\mathbf{q}, \omega_0, \omega_q)$  is the density of the number of spins near the point  $(\mathbf{q}_0, \omega_q)$  under the condition that the parameters  $\mathbf{q}_0 = 0$  and  $\omega_0$  of the "0" spin are fixed.

Extensive use is made in the analysis of EPR spectra of an assumption which simplifies greatly the calculation, viz., that the distributions of the local fields and the spatial distribution are independent. Then

$$c_0(\mathbf{q}, \omega_0, \omega_q) = c(\mathbf{q})\rho(\omega_q), \quad (25)$$

where  $c(\mathbf{q})$  is a binary function of the spatial distribution of the spins.

Thus, in the approximation linear in the concentration, the calculation of the line shape reduces to solution of a two-spin problem, calculation of  $\Gamma_0^{(1)}(t)$  on the basis of this solution, and calculation of the integrals (24), (22), and (19). Examples will be given below.

### 3. LINE SHAPE IN A SPIN- $\frac{1}{2}$ SYSTEM WITH DIPOLE INTERACTION AND CORRELATED ARRANGEMENT OF THE SPINS

We shall study, in an approximation linear in the concentration, the influence of spin clustering using as an example the spin- $\frac{1}{2}$  system, which is most important for applications, with an interaction Hamiltonian

$$H_{jk} = b_{jk} [S_j^z S_k^z - \frac{1}{4} (S_j^+ S_k^- + S_j^- S_k^+)] = b_{jk} (\frac{3}{2} S_j^z S_k^z - \frac{1}{2} S_j S_k), \quad (26)$$

$$b_{jk} = \gamma^2 \hbar r_{jk}^{-3} (1 - 3 \cos^2 \vartheta_{jk}).$$

Here  $\vartheta_{jk}$  is the angle between the vector  $\mathbf{r}_{jk}$  and the stationary magnetic field. For simplicity we disregard in this section the inhomogeneous broadening. Obviously,  $[S_j S_k, S_j^+ + S_k^+] = 0$ . Recognizing this, we have

$$\Gamma_0^{(1)}(\mathbf{q}, t) = \cos(\frac{3}{4} b_{0\mathbf{q}} t), \quad b_{0\mathbf{q}} = b_{jk} (\mathbf{r}_j = 0, \mathbf{r}_k = \mathbf{q}). \quad (27)$$

From this and from (21)–(23) it follows that

$$G_0(z) = iz \int d^3q c(\mathbf{q}) \frac{9b_{0\mathbf{q}}^2}{9b_{0\mathbf{q}}^2 - 4z^2}. \quad (28)$$

With this expression as an example, we see the cause of the real part of the expansion (18). In the limit as  $\varepsilon \rightarrow 0$ , the integral in the right-hand side of (28) diverges. This means that the limit as  $\varepsilon \rightarrow +0$  should be taken after the integration. (Introduction of a continuous distribution function is equivalent to taking the thermodynamic limit.) Analysis of the integrand in (28) shows that

$$R(\omega) = R(-\omega), \quad I(-\omega) = -I(\omega). \quad (29)$$

It can be verified that relations (29) are valid in all orders of the concentration expansion.

For a qualitative assessment of the influence of the correlation in the spin arrangement, we consider a distribution in the form of a spherical layer:

$$c(\mathbf{q}) = c(q) = \begin{cases} 0, & q < r_i \\ c, & r_i \leq q \leq r_e \\ 0, & q > r_e \end{cases} \quad (30)$$

It follows then from (28) that at  $\omega > 0$

$$R(\omega) = \frac{2\pi^2}{3} \omega_c \{F_1(\text{Re } y_1^i) - F_1(\text{Re } y_1^e) + F_1(\min(1, y_2^i)) - F_1(\min(1, y_2^e))\},$$

$$I(\omega) = \frac{4\pi}{3} \omega_c \{F_2(y_2^e) - F_2(y_1^e) + F_2(y_1^i) - F_2(y_2^i)\}, \quad (31)$$

$$y_{1,2}^{i,e} = \left[ \frac{1}{3} \left( 1 \mp \frac{\omega}{\omega_c} c r_{i,e}^3 \right) \right]^{1/2}.$$

Here

$$\omega_c = \frac{3}{4} c \gamma^2 \hbar, \quad F_1(x) = x - x^3,$$

$$F_2(y) = y^2 + \frac{1}{2} y(y^2 - 1) \ln \left| \frac{1-y}{1+y} \right|, \quad \text{Im } y = 0,$$

$$F_2(y) = -|y|^2 + |y|(|y|^2 + 1) \text{arctg} \frac{1}{|y|}, \quad \text{Re } y = 0.$$

It follows from relations (31) that the line is cut off at the frequency

$$\omega_g = 2\omega_c (c r_i^3)^{-1/2}.$$

As  $r_i \rightarrow 0$  and  $r_e \rightarrow \infty$ , i.e., for an uncorrelated uniform distribution, we have

$$R(\omega) = R_A = (2\pi^2/3\sqrt{3}) \gamma^2 \hbar c, \quad I(\omega) = 0, \quad (32)$$

which leads, when substituted in (19), to Anderson's result.<sup>1</sup>

Figure 1 shows the line-shape functions calculated for layers of various sizes. Analysis shows that the line shapes at  $r_e/l_c > 2$  and  $r_i/l_c < 0.2$ , where  $l_c = c^{-1/2}$ , hardly differs from Lorentzian.

A situation is possible in which the line shape does not differ noticeably in appearance from Lorentzian (e.g., at  $r_i \ll l_c$  and  $r_e \gg l_c$ ), but an estimate, by Anderson's formula, of the local concentration in a bounded cluster, may be too high. This is demonstrated in Fig. 2a, which shows by how much  $c$  is increased if the line half-width (distance from the center to the inflection point, with the central region disregarded) is equated to  $R_A/\sqrt{3}$ .

As a second example of spatial-inhomogeneity that can likewise yield analytic expressions, we consider a spin-tagged polymer molecule in an amorphous matrix of untagged macromolecules or in a frozen solution.<sup>17,18</sup>

The paired distribution function of the links in a poly-

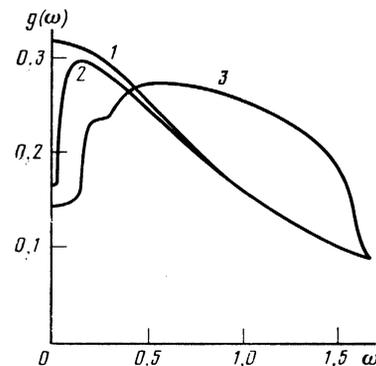


FIG. 1. Absorption spectra for spatial correlations of the type of Eq. (30): 1 -  $r_i = 0$ ,  $r_e = \infty$ ; 2 -  $r_i/l_c = 0.1$ ,  $r_e/l_c = 2$ ; 3 -  $r_i/l_c = 0.5$ ,  $r_e/l_c = 1.1$ .

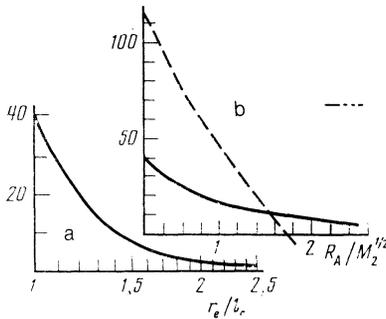


FIG. 2. Relative concentration errors (%) due to: a) neglecting spatial correlations rather than including them in the form (30) with  $r_c/l_c = 0.01$  and with variable  $r_c$ ; b) assuming that the form of the dipole-broadened Gaussian line is determined not by Eq. (38) but by convolution of a homogeneous line with an inhomogeneous one. The solid line corresponds to concentration determined from the width at half maximum, dashed—from the distance to the inflection point close to the center, dash-dot—from the distance to the remote inflection point.

mer coil of infinitely large molecular weight is known to within a numerical factor.<sup>19</sup> Assuming for simplicity that the tags on the chain are arranged regularly and are separated by  $n$  monomers, we can write

$$c(\mathbf{q}) = \lambda n^{-1} l^{-3\alpha} q^{3(\alpha-1)}, \quad (33)$$

where  $\lambda$  is a numerical factor of order unity ( $\lambda = 2/\pi$  for a Gaussian chain<sup>19</sup>),  $l$  is the rms length of the monomer unit,  $\alpha = 1/3\nu$ , and  $\nu$  is the critical exponent of the coil dimensions ( $1/2 \leq \nu < 1$ ).

Of course, Eq. (33) is valid only at distances larger than the radius of the excluded volume. At sufficiently large  $n$ , however, the contribution of distances of the order of this radius will influence only the unobservable line wings. For the same reason, at large  $n$  the region where  $c(q)$  is not small is inessential. Considering this we can assume, after substituting (33) in (28), that (33) is valid for all  $q$ .

As a result we have

$$G_0(\omega) = \lim_{\epsilon \rightarrow 0} G_0(z) = \omega_c^\alpha |\omega|^{1-\alpha} \exp[1/2 i\pi(1-\alpha) \text{sign}(\omega)], \quad (34)$$

where  $\omega_c = \kappa \gamma^2 \hbar / l_c^3$ ,  $\kappa$  is a numerical factor, and  $l_c = n^{\nu} l$  is the rms distance between neighboring tags (as  $n \rightarrow \infty$ ). Substituting (34) in (20) we obtain a rather unique line shape:

$$g(\omega) = \left[ \pi |\omega| \left( \left| \frac{\omega}{\omega_c} \right|^\alpha + 2 \cos \frac{\pi\alpha}{2} + \left| \frac{\omega_c}{\omega} \right|^\alpha \right) \right]^{-1} \sin \frac{\pi\alpha}{2}. \quad (35)$$

The divergence as  $\omega \rightarrow 0$  is due to the assumed infinitely large molecular weight and uniqueness of the tagged macromolecule in the system. It follows from (35) that the characteristic scale of the interaction in spin-tagged macromolecules is the rms distance between neighboring tags, and it precisely on this scale that information can be obtained on the structure of macromolecules can be obtained from observations of the dipole broadening in the corresponding EPR spectra.

Note that by combining the equations obtained for  $R$  and  $I$  in the present section one can obtain form functions  $g(\omega)$  for distributions  $c(q)$  that are linear combinations of Eqs. (30) and (33) with different parameters.

#### 4. SHAPE OF INHOMOGENEOUSLY BROADENED LINE IN A $\frac{1}{2}$ -SPIN SYSTEM WITH DIPOLE INTERACTION

In the presence of magnetic disorder (i.e., at  $\Delta_q = \omega_q - \omega_0 \neq 0$ ) and with the interaction Hamiltonian (26) the solution of the two-spin problem becomes

$$\Gamma_0^{(1)}(q, \Delta_q, t) = \exp\left(-i \frac{\Delta_q t}{2}\right) \left\{ \cos\left(\frac{b_{0q} t}{2}\right) \left[ \cos\left(\frac{D_q t}{2}\right) + i \frac{\Delta_q}{D_q} \sin\left(\frac{D_q t}{2}\right) \right] - \frac{b_{0q}}{2D_q} \sin\left(\frac{b_{0q} t}{2}\right) \sin\left(\frac{D_q t}{2}\right) \right\}, \quad (36)$$

where  $D_q = (\Delta_q^2 + b_{0q}^2/4)^{1/2}$ . If  $|\Delta_q| \gg |b_{0q}|$  then  $\Gamma_0^{(1)}$  ceases to depend on  $\Delta_q$  and takes the very simple form

$$\Gamma_0^{(1)}(q, \Delta_q \rightarrow \infty, t) = \cos\left(\frac{b_{0q} t}{2}\right). \quad (37)$$

This equation differs from the opposite limiting case  $\Delta_q \ll b_{0q}$  only by a numerical factor [cf. (27)].

Substitution of (36) in (19)–(23) yields for a homogeneous spatial distribution  $c(q) = \text{const}$  a line shape in the form

$$g(\omega) = \frac{3}{\pi} \int d\mu \rho(\mu + \omega) \times \frac{R_A(2 + \mu P(\omega))}{\mu^2(3 + \pi R_A \rho(\omega))^2 + R_A^2(2 + \mu P(\omega))^2}, \quad (38)$$

where  $R_A$  is defined in (32) and

$$P(\omega) = \oint \frac{d\mu}{\mu} \rho(\mu + \omega) \quad (39)$$

( $\oint$  stands for an integral in the sense of principal value).

It can be verified that if the local fields have a symmetric distribution ( $\rho(\omega) = \rho(-\omega)$ ) the form function (38) is also symmetric. If the  $\rho(\omega)$  distribution has a finite second moment  $M_2$ , the form function has at  $\omega^2 \gg M_2$  a Lorentzian asymptote that is independent of the inhomogeneous broadening.

In studies of the dipole broadening in EPR spectra, the line shape was usually regarded as a convolution of an initial inhomogeneous line and a Lorentz line (see, e.g., Ref. 20). The relation (38), however, differs noticeably from such a convolution. It turned out, in particular, that for a Gaussian function  $\rho(\omega)$  and at  $R_A/M_2^{1/2} > 2$  the derivative of the form function, calculated from (38) and (39), has at  $\omega > 0$  two peaks rather than the one in the case of convolution. Figure 2b shows the local-concentration error produced if the line shape is calculated as a convolution.

We consider also a situation in which the local fields are generated by hyperfine interaction of the electron spin with a nucleus having a spin  $J$ . We confine ourselves to the case when the dipole broadening  $R_A$  [see (32)] is much smaller than the hyperfine splitting  $A$ , but much larger than the inhomogeneous broadening of another origin. In this case the distribution of the local fields can be written in the form

$$\rho(\omega) = \frac{1}{2J+1} \sum_{m=-J}^J \delta(\omega - Am). \quad (40)$$

Substituting (40) in (38) and (39) we get

$$g(\omega) = \frac{1}{2J+1} \sum_{m=-J}^J g_0(\omega - Am), \quad (41)$$

$$g_0(\omega) = \frac{1}{\pi} \frac{R}{\omega^2 + R^2}, \quad R = \frac{4J+3}{3(2J+1)} R_A.$$

Thus, each line in the spectrum will have a Lorentz shape with a half-width that differs from the Anderson value  $R_A/\sqrt{3}$  by a factor  $(4J+3)/(6J+3)$ . This result can be obtained directly by using (32) and the fact that at  $\omega_q = \omega_0$  we should use in (24) the function  $\Gamma_q^{(1)}$  in the form (27) Eq. in all the remaining cases in the form (37).

### 5. ESTIMATE OF THE ACCURACY OF THE APPROXIMATION LINEAR IN THE CONCENTRATION, AND COMPARISON WITH THE ANDERSON MODEL

A regular method of improving the approximation linear in the concentration and of estimating its reliability can be based on an analysis of the next term, quadratic in the concentration, of the memory function:

$$G_0(z) = z^2 \left\{ \sum_q W_0(\mathbf{q}) \left( \Gamma_0^{(1)}(\mathbf{q}, z) - \frac{1}{iz} \right) + \frac{1}{2} \sum_{q_1 \neq q_2} W_0(\mathbf{q}_1, \mathbf{q}_2) \left[ \Gamma_0^{(2)}(\mathbf{q}_1, \mathbf{q}_2, z) - \Gamma_0^{(1)}(\mathbf{q}_1, z) - \Gamma_0^{(1)}(\mathbf{q}_2, z) + \frac{1}{iz} \right] - iz \left[ \sum_q W_0(\mathbf{q}) \left( \Gamma_0^{(1)}(\mathbf{q}, z) - \frac{1}{iz} \right) \right]^2 \right\}, \quad (42)$$

$$\Gamma_0^{(p)}(z) = \int_0^\infty dt e^{-izt} \Gamma_0^{(p)}(t).$$

It includes the function  $\Gamma_0^{(2)}(\mathbf{q}_1, \mathbf{q}_2, z)$ , which must be calculated by using the solution of the three-spin problem.<sup>21</sup> This procedure, however, is extremely cumbersome. We confine ourselves therefore to another approach and compare the results of the approximation linear in  $f \ll 1$  with the exact one for a number of limiting case. We shall show below the following: 1) Our theory produces the results of the exact solution of the model with the Anderson Hamiltonian (and is by the same token accurate in the limit of large inhomogeneous broadening). 2) The theory is exact at  $\omega \gtrsim R_A$ , where  $R_A$  is of the order of the linewidth and is defined in (32). 3) The theory is valid, at least qualitatively, for  $g(\omega)$  at  $\omega \lesssim R_A$ , as will be shown by a direct estimate of the asymptote  $\Gamma(t \rightarrow \infty)$ . In addition, we propose in the present section, for the calculation of the form function at arbitrary concentration, a phenomenological expression for the memory functions of real functions.

The initial Anderson model<sup>1,7</sup> employed a spatially homogeneous distribution of the spins, with a pair-interaction Hamiltonian chosen in the form

$$H_{jk} = \frac{3}{2} b_{jk} S_j^z S_k^z.$$

For two spins, this Hamiltonian has the same eigenvalues as the exact Hamiltonian (26). In the representation of the occupation numbers on the lattice,

$$H = \frac{3}{4} \sum_{x \neq q} n_x n_q b_{xq} S_x^z S_q^z. \quad (43)$$

Recognizing that

$$S_q^-(t) = S_q^- \exp\left(-\frac{3}{2} i \sum_{x \neq q} n_x b_{xq} S_x^z t\right),$$

we get

$$\begin{aligned} \Gamma(t) &= \left\langle \text{Sp} \exp\left(-\frac{3}{2} i \sum_x n_x b_{xq} S_x^z t\right) \right\rangle / \text{Sp} 1 \\ &= \left\langle \prod_x \cos\left(\frac{3}{4} b_{xq} n_x t\right) \right\rangle = \prod_x \langle \cos\left(\frac{3}{4} b_{xq} n_x t\right) \rangle \\ &= \prod_x \langle 1 + n_x (\cos\left(\frac{3}{4} b_{xq} t\right) - 1) \rangle \\ &= \exp \sum_{x \neq 0} \ln[1 + f(\cos(b_{x0} t) - 1)]. \end{aligned} \quad (44)$$

The final formula (44) was obtained earlier in Ref. 22. Our derivation was borrowed from Ref. 23.

Expansion of the logarithms in (44) in powers of  $f$  yields a cumulant expansion of  $\Gamma(t)$ . If  $f \ll 1$  and  $\max(b_{x0} t) \gg 1$ , the summation over the lattice sites can be replaced by integration. Each term of the cumulant expansion is then proportional to the time:

$$\begin{aligned} \Gamma(t) &= \exp[-R_A t (1 - f/2 + f^2/2 - \dots)], \\ R_A &= (2\pi^2/3\sqrt{3}) \gamma^2 \hbar c, \quad c = f\Omega^{-1}. \end{aligned} \quad (45)$$

Thus,  $f$  is in our case a real small parameter of a cumulant expansion. In the limit of small concentrations, when  $ft$  is finite and  $f \rightarrow 0$ , Eq. (45) coincides with Anderson's result.<sup>1</sup>

Equation (45) confirms the conclusion of Sec. 2 that the expansion of the correlation function  $\Gamma(t)$  in powers of the concentration is in fact an expansion in powers of  $ft$ . We can now elaborate and state that, apart from a numerical factor, the expansion coefficients in (14) are  $B_m \sim (R_A t)^m$ .

Note that the Anderson model describes accurately the case of strong inhomogeneous broadening in a real spin system, for in this case

$$H = \frac{1}{2} \sum_{x \neq q} n_x n_q b_{xq} S_x^z S_q^z + \sum_q n_q \omega_q S_q^z. \quad (46)$$

Now

$$\Gamma(t) = \langle e^{-i\omega_0 t} \rangle_{\omega_0} e^{-\frac{3}{2} R_A t}. \quad (47)$$

We have retained here only the leading terms in  $f$ .

Our method of concentration expansion of the memory function duplicates correctly Eq. (45) in the model problem and Eq. (47) in a real system with strong inhomogeneous broadening at small  $f$ . Equation (45) follows directly from the fact that in this case  $\Gamma_0^{(1)}$  is determined by relation (27), just as for a real interaction, while (47) is obtained from (38) in the limit of large inhomogeneous broadening. We have done this phenomenologically, based on the known success<sup>16</sup> achieved by the method of empirical memory functions in the description of the line shape in nondiluted sys-

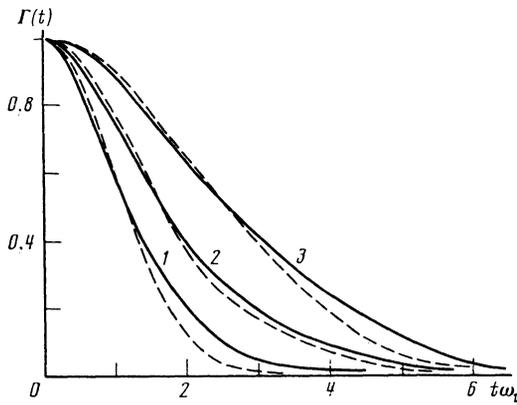


FIG. 3. Correlation function  $\Gamma(t)$  calculated from Eq. (16) with the interpolation kernel (48) (solid lines) and from the exact equation (44) (dashed lines); 1 -  $f=1$ ; 2 - 0.5; 3 - 0.2;  $\omega_l = M_{20}^{1/2}$ , where  $M_{20}$  is the second moment at  $f=1$ .

tems. We propose the following memory function, which is suitable at all concentrations:

$$G_0(t) = f \sum_q (\frac{3}{4} b_{0q})^2 \cos(\frac{3}{4} b_{0q} t) e^{-\frac{1}{2} A^2 t^2}, \quad (48)$$

$$G_0(z) = \int_0^\infty dt e^{-izt} G_0(t).$$

The parameter  $A$  is chosen here so as to ensure a correct fourth moment of  $g(\omega)$  at  $f=1$ . Note that the correctness of the second moment is ensured by (48) automatically. The memory function (48) goes over into (28) both as  $A \rightarrow 0$  and as  $f \rightarrow 0$ . Figure 3 shows the functions  $\Gamma(t)$  calculated with the aid of (48) for a primitive cubic lattice in the orientation [111] at  $M_{40} = 3M_{20}$ ; it corresponds with good accuracy to the Hamiltonian (43). Here  $M_{20}$  and  $M_{40}$  are the second and fourth moments at  $f=1$ . It can be seen that the approximate calculation agrees fairly well with the exact one from Eq. (44). One can therefore expect the memory function (48) to be suitable for the description of the line shape in real systems at arbitrary concentrations.

Calculations using (44) show also that even at  $f=0.1$  the exact correlation function is practically equal to the function calculated with the Anderson formula  $\Gamma(t) = \exp(-R_A t)$ , except, of course, in the initial section, for which the continuous-medium approximation is certainly not valid.

It follows from the foregoing analysis that the proposed theory agrees with the result of the exact solution of the Anderson model at small  $f$ , and if the memory function is phenomenologically corrected it is valid also for all  $f$ . The distinguishing feature of the Anderson model is that  $f$  is for it a truly small parameter, i.e., the corrections to the leading approximation of the memory function are proportional to  $f$ . The situation in real systems is much more complicated. We confine ourselves hereafter to a spatially uniform spin distribution. In this case one should expect the expansion parameter of the memory function, as well as of the function  $\Gamma(t)$  itself, to be not  $f$  but  $R_A t \sim ft$ . Consequently, the theory is quantitatively correct at  $\omega \gtrsim R_A$ . To determine, on the other hand, the accuracy of the leading approximation in the region  $\omega \lesssim R_A$  we shall estimate the asymptote of  $\Gamma(t)$  for large  $t$ .

For long times, the variation of  $\Gamma(t)$  in a disordered system is determined by the damping of the transverse polarization of those spins whose nearest neighbors are located at distances much larger than the average, which is the lattice period multiplied by  $f^{-1/3}$ . This is the situation in the Anderson model. Clearly, the same holds true also for a real system. In a real system, however, the dipole fields fluctuate with time. The aforementioned nearest neighbors have in turn, with high probability, other neighbors at the average distances, so that they are little influenced by the considered "solitary" spins. It can consequently be assumed that the solitary spins are in a random local field that fluctuates at a frequency  $\sim R_A$ . For times  $t \gg R_A^{-1}$ , therefore,

$$\Gamma(t) \sim \left\langle \exp \left( -\kappa \sum_q n_q \frac{b_{0q}^2 t}{R_A} \right) \right\rangle_c, \quad (49)$$

where  $\kappa \sim 1$ . For a spatially homogeneous system this yields

$$\Gamma(t) \sim \exp \sum_q \ln [1 + f(\exp\{-\kappa b_{0q}^2 t / R_A\} - 1)] \quad (50)$$

and at small  $f$

$$\Gamma(t) \sim \exp(-(\kappa_0 R_A t)^{1/2}), \quad (51)$$

where  $\kappa_0$  is a new numerical constant. Note that a similar result, but under conditions of exchange narrowing, was obtained also in Ref. 6.

Generally speaking, other mechanisms, likewise of collective character, are possible and can lead to a slower asymptote of  $\Gamma(t)$  than  $\exp(-R_A t)$ . An experimental verification of (51) would therefore yield information on the type of collective motions that play an important role in the formation of the long-wave asymptote of  $\Gamma(t)$ .

Thus, the principal approximation for the memory function leads mainly to a decreasing function  $\Gamma(t)$ , yields the quantitative value of  $\Gamma(t)$  if  $\Gamma(t) \gtrsim 1/e$ , and, as already noted, ensures satisfaction of the nontrivial condition  $g(\omega) \geq 0$ .

An estimate of the asymptote (51) shows that  $\Gamma(t)$  with large  $t$  decreases rapidly enough to cause

$$g(\omega) = \frac{1}{2\pi} \int dt e^{i\omega t} \Gamma(t)$$

to be determined mainly by the behavior of  $\Gamma(t)$  at  $R_A t \lesssim 1$  and in the region  $\omega \lesssim R_A$ . This means that the form function is correctly determined, at least qualitatively, by the leading term of the memory-function expansion in the region  $\omega < R_A$ . Comparison with the known experimental data on homogeneously broadened lines<sup>20</sup> shows that the theory is apparently exact also quantitatively not only at  $\omega \gtrsim R_A$  but also at  $\omega < R_A$ .

## 6. CONCLUSION

We have developed, on the basis of a cluster expansion of the memory function, a systematic theory for the paramagnetic-resonance line shape in magnetically diluted solids with correlated spin positions and in the presence of inhomogeneous broadening. Our analysis shows that in the lowest order in concentration the theory provides a quantitative description of the line shape at least at  $\omega \gtrsim \omega_c$ , where  $\omega_c$  is the characteristic frequency of the interaction (of the order of the line width, see Secs. 3 and 4). The description of the

line shape in the region  $\omega \ll \omega_c$  may turn out to be correct only qualitatively.

A method of phenomenological interpolation of the memory function was proposed to describe the absorption line shape at arbitrary concentrations.

It follows from the examples in Secs. 3 and 4 that the spatial correlations and the inhomogeneous broadening influence strongly the line shape. From Fig. 2, in particular, it follows that the error in the determination of the local concentration can reach 50% if these factors are not taken into account.

Relations (19)–(24) permit a quantitative analysis of the experimental data. In particular, it becomes possible to compare with experiment the theoretical EPR spectra calculated using model-based paired distribution functions.

We note in conclusion that the method developed for determining the memory function may be useful also for the calculation of other correlation functions in disordered systems.

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