CONTRIBUTION TO THE FORMAL THEORY OF NONLINEAR RESPONSE

A. A. SAMOKHIN

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

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A method is presented for the formal solution of the equation for the density matrix of an isolated macroscopic system whose temporal correlation functions are not known. A paramagnetic spin system in a given alternating field is considered as a system of this type. An exact formal equation for the mean magnetic moment of the system is derived by summation of the complete series of the non-stationary perturbation theory for a nonequilibrium density matrix. Adiabatic response and the saturation effect in all orders of the varying field amplitude are taken into account explicitly in the equation. It is shown that at low frequencies and amplitudes of the alternating field the nonlinear response of the nonequilibrium spin system can be expressed in terms of characteristics of the linear response. In particular, a formula that contains the spin-spin relaxation time τ and the second derivative of τ with respect to the stationary field is obtained in this approximation for the saturation rate. The formula can be verified experimentally.

1. In determining the response of an isolated macroscopic system, frequent use is made of nonstationary perturbation theory (NPT) with respect to the external alternating field. The first NPT approximation yields the well known formula for the linear response [1], which relates the generalized susceptibility of the system with the corresponding correlations functions (CF).

Inasmuch as the calculation of correlation functions for real systems is as a rule a very complicated problem, it is of interest to know what results can be obtained for the nonlinear response from the NPT in general form, without calculating the CF.

In an earlier paper [2] we have shown, using an isolated paramagnetic spin system of a solid as an example, by separating the terms containing only the lower CF from each order of NPT we can obtain an expression for the adiabatic response of a system, without assuming a quasi-equilibrium form of the density matrix. In this way it is possible to take into account, even in the lowest order in the alternating-field amplitude, the saturation effect which becomes appreciable after a prolonged action of the alternating field.

In the present paper we separate all the CF of lower order from each order of the NPT for the density matrix of a paramagnetic spin system in a rigid lattice. This makes it possible, after summation, to obtain the exact formal equation for the mean value of the magnetic moment of the system, with account taken explicitly of the adiabatic response and of the saturation effect in all orders in the alternating-field amplitude.

2. The equation for the density matrix of the system under consideration has the form

$$i\hbar\,\partial\rho/\partial t = [\hat{\mathcal{H}}_0 - \hat{M}h(t), \rho]. \qquad (1)$$

As before [2], we use the high-temperature approximation for the density matrix and confine ourselves to the case when the perturbation operator $\hat{M}h(t)$ does not contain a diagonal part in the representation that diagonalizes the unperturbed Hamiltonian $\hat{\mathcal{H}}_0$. As a result of the latter limitation, the magnetic moment of the system contains only odd powers of the amplitude $h(t) = h_0 \sin\omega t$ of the alternating field applied along the z axis. The Hamiltonian $\hat{\mathcal{H}}_0$ includes the Zeeman energy of the spins in a constant magnetic field and the energy of the magnetic dipole-dipole interaction of the spins with each other, while $\hat{M}$ stands for the z-component of the magnetic moment.

Going over in (1) to the interaction representation, and writing the solution of the equation obtained thereby in the form of an iteration NPT series with initial condition $\rho(0) = [\hat{I} - \alpha_0\hat{\mathcal{H}}_0]/\mathrm{Sp}\,\hat{I}$, we obtain for the mean value of the magnetic moment

$$M(t) = \mathrm{Sp}\,\hat{M}\rho(t) = \sum_{n=1,3\ldots}^{\infty} M^{(n)},$$

$$M^{(n)} = \alpha_0 \int_0^t dt_1 h(t_1) \ldots \int_0^{t_{n-1}} dt_n h(t_n) \,\mathrm{Sp}\, \hat{M}(t) \hat{F}^{(n-1)} / \mathrm{Sp}\, \hat{I},$$

$$\hat{F}^{(n-1)} = (i\hbar)^{1-n} [\hat{M}(t_1) \ldots [\hat{M}(t_{n-1}), \hat{M}'(t_n)] \ldots], \tag{2}$$

$$d\hat{M}(t)/dt = [\hat{M}(t), \hat{\mathscr{H}}_0]/i\hbar \equiv \hat{M}'(t).$$

In the case of a time-dependent perturbation, there appear in the NPT series (2), terms that increase with t and characterize the saturation effect. The occurrence of such terms is connected with the fact that in n-th order, $(n > 1)$ there are contained CF of lower order. Therefore the problem consists of separating from each order of NPT all the terms that contain CF of lower order, and to sum them in some manner.

3. This problem can be solved as follows. Representing $\mathrm{Sp}\, \hat{M}\hat{F}^{(n-1)}$ successively in the form of a sum of traces of the products of diagonal and off-diagonal operators, we find

$$\mathrm{Sp}\, \hat{M}(t) \hat{F}^{(n-1)} = (i\hbar)^{-1} \mathrm{Sp}\, [\hat{M}(t), \hat{M}(t_1)]_0 \hat{F}_0^{(n-2)} + \ldots$$
$$\ldots + (i\hbar)^{1-n} \mathrm{Sp}\, [\ldots [\hat{M}(t), \hat{M}(t_1)]_I \hat{M}(t_2)] \ldots] \hat{M}'(t_n). \tag{3}$$

All the terms on the right side of (3) but the last one, which contains the CF of maximal order, can be transformed with the aid of the next relation for those parts $\hat{A}_0$ and $\hat{B}_0$ of the macroscopic operators $\hat{A}$ and $\hat{B}$ which are diagonal simultaneously with $\mathscr{H}_0$ [3-10]:

$$\mathrm{Sp}\, \hat{A}_0 \hat{B}_0 = \mathrm{Sp}\, \hat{A} \hat{\mathscr{H}}_0 \,\mathrm{Sp}\, \hat{B} \hat{\mathscr{H}}_0 / \mathrm{Sp}\, \hat{\mathscr{H}}_0^2. \tag{4}$$

This transformation leads to the recurrence formula

$$\mathrm{Sp}\, \hat{M}(t) \hat{F}^{(n-1)} = \mathrm{Sp}\, \hat{M}^2 G_n'$$
$$- H^{-2} \sum_{k=1}^{(n-1)/2} G'_{2k-1} \mathrm{Sp}\, \hat{M}'(t_{2k}) \hat{F}^{(n-2k-1)}, \tag{5}$$
$$G_n'(t, t_1, \ldots, t_n)$$
$$= \mathrm{Sp}\, [\ldots [\hat{M}(t), \hat{M}(t_1)]_I \hat{M}(t_2)] \ldots] \hat{M}'(t_n) / \mathrm{Sp}\, \hat{M}^2 (i\hbar)^{(n-1)}.$$

Using (5), we express $M^{(n)}$ from (2) in terms of CF of different orders and in terms of the time derivatives of $M^{(k)}$ with $k < n$:

$$M^{(n)} = M_0^{(n)}$$
$$- H^{-2} \sum_{k=1}^{(n-1)/2} \int_0^t dt_1 h(t_1) \ldots \int_0^{t_{2k-1}} dt_{2k} h(t_{2k}) G'_{2k-1} M'^{(n-2k)},$$

$$M_0^{n)}(t) = \chi_0 \int_0^t dt_1 h(t_1) \ldots \int_0^{t_{n-1}} dt_n h(t_n) G_n'(t, \ldots, t_n),$$

$$\chi_0 = \alpha_0 \,\mathrm{Sp}\, \hat{M}^2 / \mathrm{Sp}\, \hat{I}; \quad H^2 = \mathrm{Sp}\, \hat{\mathscr{H}}_0^2 / \mathrm{Sp}\, \hat{M}^2. \tag{6}$$

In the derivation of (6) we took into account the fact that the derivative with respect to the upper limit in $M'^{(n)} = dM^{(n)}/dt$ vanishes, since

$$\mathrm{Sp}\, \hat{M}(t) \hat{F}^{(n-1)}(t_1, t_2, \ldots, t_n) = 0 \text{ при } t_1 = t.$$

For the mean value of the magnetic moment we get from (6)

$$M = M_0 - H^{-2} \sum_{m=0}^{\infty} \sum_{k=1}^{m+1}$$
$$\times \int_0^t dt_1 h(t_1) \ldots \int_0^{t_{2k-1}} dt_{2k} h(t_{2k}) G'_{2k-1} M'^{(2m-2k+3)}, \tag{7}$$

$$M_0(t) = \sum_{n=1,3\ldots}^{\infty} M_0^{(n)}(t). \tag{8}$$

By direct comparison for any finite m we can verify that (7) is equivalent to

$$M(t) = M_0(t) - H^{-2} \sum_{k=1}^{\infty} \int_0^t dt_1 h(t_1) \ldots \int_0^{t_{2k-1}} dt_{2k} h(t_{2k})$$
$$\times G'_{2k-1}(t, \ldots, t_{2k-1}) M'(t_{2k}). \tag{9}$$

Equation (9) is an exact equation for the mean value of the magnetic moment of a macroscopic spin system situated in a spatially homogeneous constant or alternating magnetic field. In the derivation of this equation we assumed that the solution of (1) can be represented in the form of an infinite NPT series, and we essentially made use of relation (4).

The fact that the perturbation operator does not have a diagonal part is not a fundamental limitation of this approach, and can be eliminated by suitable generalization. The same holds apparently also for the use of the high-temperature approximation. However, these problems require, generally speaking, further investigations which will not be dealt with at present.

4. Equation (9) takes into account in closed form the adiabatic response and the effective saturation in any order in the alternating-field amplitude. The expression for the magnetic moment without allowance for the saturation and the higher orders of the adiabatic response would be formula (8). By retaining only the first term of each sum in (8) and (9), we can get from (9) an exact expression for the adiabatic response and take into account the effect of saturation in the lower (second) order in the amplitude of the alternating field.

We now consider an approximate solution of (9) with $h_0^2 < H^2$, retaining in (9) the CF of only the first two orders and limiting ourselves to low frequencies of the alternating field, $\omega\tau < 1$, where τ denotes the spin-spin relaxation time. As will be shown below, the case of small frequencies is of special interest.

Using the following relation for the energy, which follows from (1):

$$E = E_0 + \int_0^t dt_1 h(t_1) M'(t_1),$$
$$E_0 = \mathrm{Sp}\,\hat{\mathscr{H}}_0 \rho(0) = -\chi_0 H^2, \quad E = \mathrm{Sp}\,\hat{\mathscr{H}}_0 \rho(t), \tag{10}$$

we can reduce (9) to the form

$$H^2 M(t) = -\sum_{n=1,3\ldots}^{\infty} \int_0^t dt_1 h(t_1) \ldots \int_0^{t_{n-1}} dt_n h(t_n) G_n'(t, \ldots, t_n) E(t_n). \tag{11}$$

Retaining only the first two terms from the sum in the right part of (11), we get when $t > \tau$, after integrating by parts,

$$H^2 M = -hE + (hE)'(\tau + h^2 \tilde{G}_3),$$
$$\tau = \tilde{G}_1 = \int_{-\infty}^0 dt G_1(0, t), \quad \tilde{G}_3 = \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 G_3(0, t_1, t_2, t_3). \tag{12}$$

The quantities $(hE)'$ and $h^2(hE)'$ were taken here outside the integration sign, and the integration limits were extended to $-\infty$.

Such a transformation is based on the assumption that G_n differs noticeably from zero only if the difference $t_i - t_k$ of any of its two arguments does not exceed a value on the order of τ. This assumption signifies, in particular, when a constant perturbation is turned on at the instant $t = 0$, that the time of establishment of equilibrium in the given system depends little on the magnitude of this perturbation, at least so long as the change in the energy of the system does not exceed in order of magnitude its initial energy.

It is convenient further to go over from (12) to an equation for E:

$$H^2 E' = -h(hE)' + h(hE)''(\tau + h^2 \tilde{G}_3) + 2h^2 h'(hE)' \tilde{G}_3. \tag{13}$$

The solution of this equation will be sought in the form $E = E_s U$, where $H^2 E_s' = -h(E_s h)'$, and U is a slowly varying function of the time. The latter signifies that we neglect the second derivative of U with respect to the time, going over in this manner from (13) to a first-order equation for U:

$$H^2 U' = U\{\tau h h'' - \tau[2h^3 h'' + 3(hh')^2]/2H^2 + \tilde{G}_3[h^3 h'' + 2(hh')^2]\}. \tag{14}$$

In the right side of (14) we have retained terms in h to not higher than the fourth power, for otherwise we would exceed the accuracy of the initial approximation, in which the non-equilibrium nature is taken into account with the aid of CF of only the first two orders.

Equation (14) is solved in elementary fashion, and for E we obtain in the approximation in question

$$E = E_0\{1 - h(h - \tau h')/2H^2\} e^{-\Gamma_0 t},$$
$$\Gamma_0 = \frac{\tau(\omega h_0)^2}{2H^2}\left[1 - \frac{3h_0^2}{4H^2}\right] + \tilde{G}_3 \frac{\omega^2 h_0^4}{8H^2}. \tag{15}$$

For brevity we have omitted from the curly brackets in (15) the terms with h to the fourth power.

If we take the entire expression (15) accurate to h^2 and use relation (12), then we obtain the following formula for the mean value of the magnetic moment:

$$M^{(1)} + M^{(3)} = \chi_0(h - \tau h')[1 - \tau t(\omega h_0)^2/2H^2] - \chi_0 h^2(h - 4\tau h')/2H^2 - \chi_0 h^2 h' \tilde{G}_3, \tag{16}$$

which corresponds to the first two terms of the NPT series (2).

However, formula (16) can be used only for sufficiently small t, whereas formula (15) is valid in the entire time interval. Taking saturation into account, we get in lieu of (16)

$$M = \chi_0\{h - \tau h' - h^2(h - 4\tau h')/2H^2 - \tilde{G}_3 h^2 h'\} e^{-\Gamma_0 t}. \tag{17}$$

The factor $\exp(-\Gamma_0 t)$ leads to vanishing of the mean values of E and M in the case of prolonged action of the alternating field, corresponding to heating of the spin system to an infinitely high temperature. It is easy to verify that Γ_0 coincides with the relative rate of energy absorption by the system during one period of the alternating field; this rate is calculated with the aid (16) using the formula

$$\Gamma_0 = -\frac{\omega}{2\pi E_0} \int_0^{2\pi/\omega} dt\, h(t)\{M'^{(1)}(t) + M'^{(3)}(t)\}. \tag{18}$$

5. In the general case, the higher CF cannot be expressed in terms of the CF of lower order. However, at lower frequencies of the alternating field it is possible to express the nonlinear response of the nonequilibrium spin-system in terms of the characteristics of the linear response.

Let us consider for this purpose the following expression:

$$\left[\frac{\partial^2 G_1(t)}{\partial H_z^2}\right]_0 = 2\int_0^t dt_1 \int_0^{t_1} dt_2 \{G_3(-t, -t_1, -t_2, 0) - G_1'(t_1 - t) G_1'(t_2) H^{-2}\}, \tag{19}$$

which is obtained by differentiation with respect to the z-component of the constant magnetic field, with subsequent use of relation (14) with $H_z = 0$. Introducing the CF for $H_z \neq 0$, which is normalized to unity at $t = 0$ and vanishes when $t > \tau$,

$$g_1(t) = \{G_1(t)(H^2 + H_z^2) - H_z^2\}/H^2, \quad (20)$$

we get from (19) and (20)

$$\left[\frac{\partial^2 g_1(t)}{\partial H_z^2}\right]_0 = -2\int_0^t dt_1 \Big\{ g_1'(t_1 - t) g_1(t_2) H^{-2} - \int_0^{t_1} dt_2 G_3(-t, -t_1, -t_2, 0) \Big\} \quad (21)$$

from which we get after integrating with respect to t from $-\infty$ to zero:

$$(\partial^2\tau/\partial H_z^2)_0 = 2\tilde{G}_3 - 2\tau/H^2, \quad (22)$$

$$\tau = \int_{-\infty}^0 dt g_1(t) \equiv \tilde{g}_1. \quad (23)$$

We have retained the previous symbol for τ, since the quantities $\tilde{G}_1$ and $\tilde{g}_1$ coincide when $H_z = 0$. To avoid misunderstandings, we must assume that τ is given by formula (23) for all values of H_z. When $H_z \neq 0$, the formula for $M^{(1)}$ takes the form

$$M^{(1)} = \chi_s(h - \tau h'), \quad \chi_s = \chi_0 H^2/(H^2 + H_z^2), \quad (24)$$

where χ_s is the adiabatic susceptibility and τ is given by (23).

With the aid of (22) we can express M from (17) in terms of the characteristics of the linear response, in our case in terms of $(\partial^2\tau/\partial H_z^2)_0$ and τ. For the third harmonic of the magnetic moment we get

$$M_{(3)} = \chi_0 \frac{h_0^3}{8H^2}\Big\{\sin 3\omega t - \omega\Big[2\tau - H^2\Big(\frac{\partial^2\tau}{\partial H_z^2}\Big)_0\Big]\cos 3\omega t\Big\} e^{-\Gamma_0 t}, \quad (25)$$

$$\Gamma_0 = \frac{\tau(\omega h_0)^2}{2H^2}\Big[1 - \frac{h_0^2}{2H^2}\Big] + \frac{\omega^2 h_0^4}{16H^2}\Big(\frac{\partial^2\tau}{\partial H_z^2}\Big)_0. \quad (26)$$

These expressions are valid accurate to higher powers of the small parameters $\omega\tau$ and h_0^2/H^2. Formulas (25) and (26) can be verified experimentally for the nuclear paramagnetic spin system of a solid. The quantity Γ_0 was measured earlier only in an approximation linear in h_0^2 [11], owing to the lack of theoretical data for the more complicated case. Formula (26) yields a quadratic correction to the linear dependence of Γ_0 on h_0^2, the observation of which is experimentally feasible. Such a verification is of fundamental interest, for in the derivation of these formulas we used rather general assumptions concerning the behavior of the CF.

As already noted, the even harmonics of the magnetic moment vanish in our case, since $H_z = 0$. The expressions for the second harmonic of the moment in terms of the characteristics of the linear response can be obtained from formula (59) of [12] (see also [13]). However, the procedure used in these papers does not make it possible to obtain our expression for τ_0 unless a special investigation is made.

6. The procedure presented in the present paper for finding the nonlinear response is formal, inasmuch as it is not its purpose to calculate the CF. The problem consists of expressing the nonlinear response in terms of the characteristics of the external perturbation and the corresponding CF. Equation (9) can be regarded as the principal solution of this problem for the system in question.

It should be noted that the use of only formal devices for compactly writing down the NPT series [14,15] cannot solve our problem. Equation (9) was obtained by separating from each order of the NPT all the CF of lower order and by subsequent summation. In factorizing the traces of the products of the diagonal operators, it is essential to use relation (14), this being an important feature of the present work.

At the same time, the idea of separating from the perturbation-theory series different kinds of principal or "secular" terms is far from new. This method was used, for example, to obtain generalized kinetic equations [16,7]. We emphasize in this connection that in equation (9) account is taken formally of all terms of the NPT series (2). In addition, the "secular" terms (that is, those increasing with time) appear in the series (2) only for a time-dependent perturbation, and do not appear for a constant perturbation turned on at $t = 0$.

We have obtained with the aid of (9) a formal expression for the nonlinear response at $\omega\tau < 1$ and $h_0^2 < H^2$; this expression is valid in the entire time interval and for small values of t it coincides with the expression obtained from the first two terms of the NPT series (2). We have shown at the same time that the non-equilibrium behavior of the system in such an approximation is characterized by the parameters of the linear response, namely the spin-spin relaxation time τ and the second derivative of τ with respect to the constant magnetic field.

We can similarly obtain from (9) a formal expression for the nonlinear response of the non-equilibrium spin system without limitation on the amplitude of the alternating field. This expression will be valid for an arbitrarily long action of the alternating field.

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38