THEORY OF PARAMAGNETIC RESONANCE IN SYSTEMS CONTAINING TWO KINDS OF MAGNETIC MOMENTS

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Submitted to JETP editor March 5, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) 37, 482-489 (August, 1959)

Equations of motion for the partial magnetizations of a system containing two kinds of interacting magnetic moments situated in a weak variable magnetic field are obtained by methods of thermodynamics of irreversible processes. The same equations can be derived from the microscopic theory in the case of sufficiently rapid thermal fluctuations of the local fields. The relaxation times and the shift of the resonance frequency are computed. It is shown that a universal relation, similar to the Kramers-Kronig relation, exists between the quantities determining the transverse relaxation time and the resonance frequency shift.

1. In many problems of the theory of magnetic resonance one has to deal with systems containing two kinds of magnetic moments. Such systems are substances whose molecules contain two kinds of nuclei with different gyromagnetic ratios, viz: isotope mixtures, paramagnetic solutions, metals. In some cases these systems are described by two uncoupled equations for the partial magnetizations. In spite of this, the behavior of the magnetic moments of one kind may depend in an essential manner on the nature of the interaction between the magnetic moments of the other kind, through the relaxation times and the shift of the resonance frequency. An example of such a system is a solution of Mn^{++} in water.[1]

The microscopic theory of relaxation processes in systems which contain the same number of magnetic moments of each kind with spin $\frac{1}{2}$, and which differ only in their gyromagnetic ratios, was developed in Solomon's paper[2] and was applied to the description of nuclear resonance in hydrogen fluoride.[3]

On the other hand, by the method of the thermodynamics of irreversible processes, one of us[4] has obtained equations for the partial magnetizations $\mathbf{M}_1$ and $\mathbf{M}_2$ in weak variable fields of arbitrary orientation with respect to the constant field.

In the present paper we develop a thermodynamic theory more complete than the one given in reference 4, and also a microscopic theory of systems containing two kinds of magnetic moments for weak magnetic fields; we also obtain equations for the partial magnetizations $\mathbf{M}_1$ and $\mathbf{M}_2$.

2. The thermodynamic theory of the systems under consideration may be developed on the basis of the methods of thermodynamics of irreversible processes.[5]

We suppose that the paramagnetic sample is situated in a constant magnetic field $H = H_z$ and in a variable magnetic field $\mathbf{h}(t)$ which violates thermodynamic equilibrium only to a small extent. In this case the partial magnetizations of the subsystems $M_j = M_j(t)$ $(j = 1, 2)$ satisfy the following equations linear in the variable field:[6]

$$\dot{M}_{lj} = \sum_{m,k} L_{lm,jk}(h_m(t) - h_m^k),$$
$$l, m = x, y, z; \qquad j, k = 1, 2, \tag{1}$$

where

$$\mathbf{h}^k = \chi_k^{-1}(\mathbf{M}_k(t) - \mathbf{M}_k^0), \tag{2}$$

while

$$\mathbf{M}_k^0 = \chi_k \mathbf{H} \tag{3}$$

are the equilibrium partial magnetizations of the magnetic subsystems.

On going over to circularly polarized components

$$M_{\pm 1} = \mp (M_x \pm iM_y)/\sqrt{2}, \qquad M_0 = M_z, \tag{4}$$
$$h_{\pm 1} = \mp (h_x \pm ih_y)/\sqrt{2}, \qquad h_0 = h_z, \tag{5}$$

we shall obtain in accordance with (1)

$$\dot{M}_{\alpha j} = \sum_{\beta k} L_{\alpha\beta,jk}(h_\beta(t) - h_\beta^k), \qquad \alpha, \beta = \pm 1, 0. \tag{6}$$

The kinetic coefficients $L_{\alpha\beta,jk}$ satisfy the Onsager relations, which in the case of paramagnetic media $(\chi_j \ll 1)$ have the form

$$\alpha \neq \beta, \quad L_{\alpha\beta,\,jk}(H_0) = -L^*_{\beta\alpha,\,jk}(-H_0) = -L_{-\beta-\alpha,\,jk}(-H_0),$$
$$\alpha = \beta, \quad L_{\alpha\alpha,\,jk}(H_0) = L^*_{\alpha\alpha,\,jk}(-H_0) = L_{-\alpha-\alpha,\,jk}(-H_0). \quad (7)$$

Requirements of axial symmetry with respect to the direction of the constant field H lead to the additional relations

$$L_{\alpha\beta,\,jk}(H_0) = \delta_{\alpha\beta} L_{\alpha\beta,\,jk}(H_0),$$
$$L_{11,\,jk} = L^*_{-1\,-1,\,jk} \neq L_{00,\,jk}, \quad (8)$$

Equations (7) and (8) can be satisfied if we set

$$L_{\alpha\alpha,\,jk}(H_0) = \sqrt{\chi_j \chi_k}\,(1/T^{jk}_\alpha + i\alpha\omega^{jk}), \quad \omega^{jk} = \gamma^{jk} H_0, \quad (9)$$

where γ^{jk} and T^{jk}_α are even functions of H_0 symmetric with respect to an interchange of the indices jk:

$$T^{jk}_\perp = T^{jk}_{\pm 1}(H_0), \quad T^{jk}_\parallel = T^{jk}_0(H_0), \quad \gamma^{jk} = \gamma^{jk}(H_0). \quad (10)$$

In weak fields ($H_0 \to 0$) the system possesses spherical symmetry, and therefore

$$T^{jk}_\perp = T^{jk}_\parallel = T^{jk}. \quad (11)$$

On substituting (9) into (6), and on taking (2) and (3) into account, we obtain a system of linear equations of motion for the partial magnetizations

$$\dot{M}_{\alpha j} + \sum_k \sqrt{\chi_j/\chi_k}\,(1/T^{jk}_\alpha + i\alpha\omega^{jk})(M_{\alpha k} - M^0_{\alpha k})$$
$$= \sum_k \sqrt{\chi_j \chi_k}\,(1/T^{jk}_\alpha + i\alpha\omega^{jk}) h_\alpha(t), \quad (12)$$

which contain undetermined (within the framework of thermodynamics) coefficients T^{jk}_α and γ^{jk}.

For a system containing one kind of magnetic moments ($j = k = 1$) we obtain the equations

$$\dot{M}_\alpha + (1/T_\alpha + i\alpha\omega_0)(M_\alpha - M^0_\alpha)$$
$$= \chi_0 (1/T_\alpha + i\alpha\omega_0) h_\alpha(t), \quad (13)$$

which agree with those which we have obtained earlier in microscopic theory.[7]

In the absence of a radio-frequency field $\mathbf{h}(t) = 0$ and when $\chi_j/\chi_k = (\gamma_j/\gamma_k)^2$ Eqs. (12) reduce to the equations obtained by Solomon.[2] They differ from the equations obtained in reference 4 by the presence of terms containing ω^{12}.

The static susceptibilities appearing in (12) depend on the thermodynamic temperatures of the subsystems which, generally speaking, may differ from the temperature of the remaining degrees of freedom of the magnetic material — the equilibrium lattice temperature. By restricting ourselves in this paper to the case of weak fields $\mathbf{h}(t)$, we neglect variations in the temperatures of the subsystems by setting them equal to the temperature of the sample. The transfer of heat from the spin system to the "lattice" may be taken into account in a manner analogous to that used in reference 6.

3. In order to interpret the coefficients T^{jk}_α and ω^{jk} appearing in Eqs. (12) we consider the case of the free precession of the magnetization $\mathbf{h}(t) = 0$ in the constant field H_0.

On setting

$$M_{\alpha j}(t) = M^0_{\alpha j} + A_{\alpha j}\exp(-\lambda_\alpha t), \quad (14)$$

we obtain for the determination of $A_{\alpha j}$ a system of homogeneous equations, the condition for the solution of which has the form

$$(-\lambda_\alpha + 1/T^{11}_\alpha + i\alpha\omega^{11})(-\lambda_\alpha + 1/T^{22}_\alpha + i\alpha\omega^{22})$$
$$= (1/T^{12}_\alpha + i\alpha\omega^{12})^2. \quad (15)$$

Solving the quadratic equation (15) with respect to λ_α, we obtain the complex eigenvalues $\lambda^\pm_\alpha$. Now the solutions of (12) can be written

$$M_{\alpha 1}(t) = M^0_{\alpha 1} + A^+_\alpha(-\lambda^+_\alpha + 1/T^{22}_\alpha + i\alpha\omega^{22})\exp(-\lambda^+_\alpha t)$$
$$- A^-_\alpha \sqrt{\chi_1/\chi_2}\,(1/T^{12}_\alpha + i\alpha\omega^{12})\exp(-\lambda^-_\alpha t),$$
$$M_{\alpha 2}(t) = M^0_{\alpha 2} - A^+_\alpha \sqrt{\chi_2/\chi_1}\,(1/T^{12}_\alpha + i\alpha\omega^{12})\exp(-\lambda^+_\alpha(t))$$
$$+ A^-_\alpha(-\lambda^-_\alpha + 1/T^{11}_\alpha + i\alpha\omega^{11})\exp(-\lambda^-_\alpha t). \quad (16)$$

In two limiting cases they assume a particularly simple form. If

$$(1/T^{12}_\alpha + i\alpha\omega^{12})^2$$
$$\ll (1/T^{11}_\alpha - 1/T^{22}_\alpha + i\alpha\omega^{11} - i\alpha\omega^{22})^2, \quad (17)$$

then, in accordance with (15),

$$\lambda^+_\alpha = \lambda^2_\alpha = 1/T^{22}_\alpha + i\alpha\omega^{22},$$
$$\lambda^- = \lambda^1_\alpha = 1/T^{11}_\alpha + i\alpha\omega^{11}. \quad (18)$$

In this case

$$M_{\alpha j}(t) = M^0_{\alpha j} + A_{\alpha j}\exp(-\lambda^j_\alpha t), \quad (19)$$

where T^{jj}_α have the meaning of relaxation times, while ω^{jj}_α have the meaning of characteristic frequencies.

If the inequality of (17) is reversed, the eigenvalues are determined in the following manner:

$$\lambda^\pm_\alpha = {}^1/_2\,(1/T^{11}_\alpha + 1/T^{22}_\alpha \pm 2/T^{12}_\alpha)$$
$$+ {}^1/_2\, i\alpha(\omega^{11} + \omega^{22} \pm 2\omega^{12}), \quad (20)$$

and the solutions for $M_{\pm 1 j}(t)$ have the form of damped beats, which are due to the existence of coupling (T^{12}_α, ω^{12}) between the equations for the partial magnetizations.

4. The microscopic theory of relaxation and resonance phenomena in systems containing two kinds of magnetic moments can be developed on the basis of the method of Kubo and Tomita[8] in a manner analogous to the one which we used in the case of one kind of spins.[7]

We shall assume that the g-factors of the particles are isotropic, while the spin-Hamiltonian of the system does not contain products of more than two spin operators $\hat{I}_s^{(j)}$, and therefore contains them in combinations which transform according to the irreducible representations of the rotation group D_0, D_1, and D_2. Then, on taking into account the fact that $\hat{I}_s^{(j)}\hat{I}_s^{(j)} = \text{const}$, we can write

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 + \hat{\mathcal{H}}', \tag{21}$$

where

$$\hat{\mathcal{H}}_1 = -\sum_j \hbar\omega_j \sum_s^{N_j} \hat{I}_{s0}^j \tag{22}$$

is the operator for the interaction of the magnetic moments with the constant external field H_0, $\omega_j = \gamma_j H_0$; $\hat{\mathcal{H}}_2$ represents the part of the total Hamiltonian $\hat{\mathcal{H}}$ which is independent of the spins; $\hat{\mathcal{H}}'$ is the perturbation:

$$\hat{\mathcal{H}}' = \hat{\mathcal{H}}^{11} + \hat{\mathcal{H}}^{12} + \hat{\mathcal{H}}^{22} = \sum_{j\leqslant k}\sum_{\lambda\nu}\hat{\mathcal{H}}_{\lambda\nu}^{jk} = \sum_{j\leqslant k}\sum_{\lambda\nu}\sum_{s<m}^{N_j N_k}\left(F_{sm}^{-(\lambda+\nu),\,jk}\right.$$
$$\left.\times \{\hat{I}_s^{(j)}\hat{I}_m^{(k)}\}_{\lambda\nu} + \delta_{\nu,-\lambda}A_{sm}^{-\lambda,\,jk}\hat{I}_{s\lambda}^{(j)}\hat{I}_{m-\lambda}^{(k)}\right)$$
$$+\sum_{j\leqslant k}\sum_{\lambda\nu}\sum_s^{N_j}\delta_{jk}F_s^{-(\lambda+\nu),\,j}\{\hat{I}_s^{(j)}\hat{I}_s^{(j)}\}_{\lambda\nu}, \tag{23}$$

where

$$\{\hat{I}_s^{(j)}\hat{I}_m^{(k)}\}_{\pm1\,\pm1} = \sqrt{15/2\pi}\,\hat{I}_{s\pm1}^{(j)}\hat{I}_{m\pm1}^{(k)},$$
$$\{\hat{I}_s^{(j)}\hat{I}_m^{(k)}\}_{\pm10} = \sqrt{15/4\pi}\,\hat{I}_{s\pm1}^{(j)}\hat{I}_{m0}^{(k)},$$
$$\{\hat{I}_s^{(j)}\hat{I}_m^{(k)}\}_{0\pm1} = \sqrt{15/4\pi}\,\hat{I}_{s0}^{(j)}\hat{I}_{m\pm1}^{(k)},$$
$$\{\hat{I}_s^{(j)}\hat{I}_m^{(k)}\}_{00} = \sqrt{5/\pi}\,\hat{I}_{s0}^{(j)}\hat{I}_{m0}^{(k)},$$
$$\{\hat{I}_s^{(j)}\hat{I}_m^{(k)}\}_{\pm1\mp1} = \sqrt{5/4\pi}\,\hat{I}_{s\pm1}^{(j)}\hat{I}_{m\mp1}^{(k)}.$$

Under a rotation of coordinates the coefficients $F_{sm}^{-(\lambda+\nu),jk}$, $F_s^{-(\lambda+\nu)j}$ transform according to the representation D_2, while $A_{sm}^{-\lambda,jk}$ transform according to D_0; this determines their angular dependence.

Expression (23) may, in principle, contain combinations of spins which transform according to the representation D_1. However, in this case the coefficients must be functions not only of the coordinates but also of a certain axial vector. The only such vector in the case under consideration is **H**. We shall obtain such an expression, for example, if we take into account the anistropy of the g-factor.[9]

The choice of the Hamiltonian in the form (21) — (23) enables us to take into account the quadrupole moments of nuclei, atoms and ions and their interaction with the local inhomogeneous and, generally speaking, fluctuating field (for nuclei and atoms inside the molecule or for ions inside the complex), and also weak direct and indirect exchange interactions leading to hyperfine splitting. The singling out of coefficients which depend on spherical harmonics leads to simpler calculations in the case of a homogeneous and isotropic medium.

According to reference 7, to compute

$$M_{\alpha j}(t) - M_{\alpha j}^0 = -\sum_\beta\int_0^\infty \frac{dG_{\alpha\beta}(\tau)}{d\tau}h_\beta^*(t-\tau)\,d\tau \tag{24}$$

it is sufficient to determine the form of the relaxation function

$$G_{\alpha\beta}(\tau) = G_{\alpha\beta}^*(-\tau) = \sum_j G_{\alpha\beta j}(\tau), \qquad G_{\alpha\beta}(\infty) = 0, \tag{25}$$

where for the fields ordinarily used ($\hbar\omega_j \ll kT$)

$$G_{\alpha\beta j}(\tau) = \frac{1}{kT}\sum_k \mathrm{Sp}\hat{\rho}_0\{\hat{M}_{\alpha j}(\tau)\hat{M}_{\beta k}\}, \tag{26}$$

and $M_{\alpha j}(\tau)$ is a time-dependent operator in the Heisenberg representation determined by the Hamiltonian $\mathcal{H}$:

$$M_{\alpha j}(\tau) = \exp(i\hat{\mathcal{H}}\tau/\hbar)\hat{M}_{\alpha j}\exp(-i\hat{\mathcal{H}}\tau/\hbar). \tag{27}$$

We seek expressions for $C_{\alpha\beta j}(\tau)$ in the form of expansions in terms of the parameter characterizing the perturbation:

$$G_{\alpha\beta j}(\tau) = G_{\alpha\beta j}^{(0)}(\tau) + G_{\alpha\beta j}^{(1)}(\tau) + G_{\alpha\beta j}^{(2)}(\tau) + \ldots, \tag{28}$$

where

$$G_{\alpha\beta j}^{(0)}(\tau) = \frac{1}{kT}\sum_k \mathrm{Sp}\,\hat{\rho}_0\{\hat{M}_{\alpha j}^0(\tau),\ \hat{M}_{\beta k}\},$$

$$G_{\alpha\beta j}^{(1)}(\tau) = -\frac{i}{kT\hbar}\sum_k\int_0^\tau d\vartheta\,\mathrm{Sp}\,\hat{\rho}_0\{[\hat{M}_{\alpha j}^0(\tau),\ \hat{\mathcal{H}}'(\vartheta)]\,\hat{M}_{\beta k}\}\ \text{etc.},$$

while the dependence of the operators $M_{\alpha j}^0(\tau)$ and $\hat{\mathcal{H}}'(\tau)$ on the time is determined by the Hamiltonian $\hat{\mathcal{H}}_0$ according to the usual formulas analogous to (27).

The character of the subsequent calculations depends on the magnitude of the interactions determined by the operators $\hat{\mathcal{H}}^{11}$, $\hat{\mathcal{H}}^{12}$ and $\hat{\mathcal{H}}^{22}$. If $\hat{\mathcal{H}}^{11} \sim \hat{\mathcal{H}}^{12} \sim \hat{\mathcal{H}}^{22}$ then one should consider to the same extent all terms of the perturbing operator (23). On the other hand, if $\hat{\mathcal{H}}^{11} \gg \hat{\mathcal{H}}^{12} \gg \hat{\mathcal{H}}^{22}$, then in considering the first subsystem we may neglect $\hat{\mathcal{H}}^{12}$ and $\hat{\mathcal{H}}^{22}$, while in considering the second subsystem we may neglect $\hat{\mathcal{H}}^{22}$.

5. In the first case we have for a homogeneous and isotropic medium, if the density matrix may be assumed constant,

$$G_{\alpha\beta j}^{(0)}(\tau) = (-1)^\alpha\chi_j\delta_{\alpha,-\beta}\exp(-i\alpha\omega_j\tau), \tag{29}$$

$$G_{\alpha\beta j}^{(1)}(\tau) = i\alpha\tau G_{\alpha\beta j}^{(0)}(\tau)\frac{1}{\hbar}\sum_m^{N_k}\langle A_{sm}^{jk}\hat{I}_{m0}^{(k)}\rangle = i\alpha\tau G_{\alpha\beta j}^{(0)}(\tau)\,\Delta\omega^{(1)\,jj}. \tag{30}$$

Using the property of the independence of the trace of the time origin, and neglecting the terms with $\lambda,\ \nu \neq -\lambda',\ -\nu'$, we obtain in a manner analogous to the one used in references 7 and 8,

$$G^{(2)}_{\alpha\beta j}(\tau) = -G^{(0)}_{\alpha\beta j}(\tau)\sum_k\sum_{\lambda\nu}\Big\{\int_0^\tau d\vartheta_1\int_0^{\vartheta_1} d\vartheta_2 \times \exp[(i\lambda\omega_j + i\nu\omega_k)(\vartheta_1-\vartheta_2)]\ P^{jk}_{\alpha\lambda\nu}(\vartheta_1-\vartheta_2)$$
$$+\int_0^\tau d\vartheta_1\int_0^{\vartheta_1} d\vartheta_2 \exp[(i\lambda\omega_j + i\nu\omega_k)\vartheta_1 + (i(\alpha-\lambda)\omega_j - i(\alpha+\nu)\omega_k)\vartheta_2]\sqrt{\frac{\chi_k}{\chi_j}}\,Q^{jk}_{\alpha\lambda\nu}(\vartheta_1-\vartheta_2)\Big\}$$
$$-G^{(0)}_{\alpha\beta j}(\tau)(\alpha\Delta\omega^{(1)\,jj})^2\frac{\tau^2}{2}, \tag{31}$$

where the functions

$$P^{jk}_{\alpha\lambda\nu}(\vartheta_1-\vartheta_2) = \frac{\langle\{[\hat M_{\alpha j}\hat{\mathscr H}^{jk}_{-\lambda-\nu}(\vartheta_1-\vartheta_2)][\hat{\mathscr H}^{jk*}_{-\lambda-\nu}(0)\,\hat M^{*}_{\alpha j}]\}\rangle}{\hbar^2\langle|M_{\alpha j}|^2\rangle} - \delta_{\lambda 0}\delta_{\nu 0}\langle\alpha\Delta\omega^{(1)\,jj}\rangle^2, \tag{32}$$

$$\sqrt{\frac{\chi_k}{\chi_j}}\,Q^{jk}_{\alpha\lambda\nu}(\vartheta_1-\vartheta_2) = \frac{\langle\{[\hat M_{\alpha j}\hat{\mathscr H}^{jk}_{-\lambda-\nu}(\vartheta_1-\vartheta_2)][\hat{\mathscr H}^{jk*}_{\alpha-\lambda,\,-(\alpha+\nu)}(0)\,\hat M^{*}_{\alpha k}]\}\rangle}{\hbar^2\langle|M_{\alpha j}|^2\rangle} \tag{33}$$

satisfy the conditions $P^{jk}_{\alpha\lambda\nu}(\infty) = Q^{jk}_{\alpha\lambda\nu}(\infty) = 0$.

The angle brackets denote everywhere averaging over the coordinates and the spins, using a constant density matrix, while figure brackets indicate the symmetrized product of the operators.

The Heisenberg operators $\hat{\mathcal H}^{jk}_{\lambda\nu}(t)$ appearing in (32) and (33) contain a dependence on the time determined by the Hamiltonian $\hat{\mathcal H}_2$.

To ascertain the type of equations of motion for the partial magnetizations $M_{\alpha j}(t)$, we differentiate (24) with respect to the time. Then, after integration by parts we obtain

$$\frac{dM_{\alpha j}(t)}{dt} = -\sum_\beta\frac{dG_{\alpha\beta j}(0)}{d\tau}h^*_\beta(t) - \sum_\beta\int_0^\infty\frac{d^2G_{\alpha\beta j}(\tau)}{d\tau^2}h^*_\beta(t-\tau)\,d\tau. \tag{34}$$

Differentiating (29), (30), and (31) with respect to τ, and adding them together we obtain

$$dG_{\alpha\beta j}(\tau)/d\tau = -i\alpha\omega_j G_{\alpha\beta j}(\tau) - i\alpha G^{(0)}_{\alpha\beta j}(\tau)\,\Delta\omega^{(1)\,jj}_\alpha(1 - i\alpha\Delta\omega^{(1)\,jj}_\alpha\tau)$$
$$- G^{(0)}_{\alpha\beta j}(\tau)\sum_k\sum_{\lambda\nu}\int_0^\tau d\vartheta\exp[(i\lambda\omega_j + i\nu\omega_k)\vartheta]\,P^{jk}_{\alpha\lambda\nu}(\vartheta)$$
$$- G^{(0)}_{\alpha\beta k}(\tau)\sqrt{\chi_j/\chi_k}\sum_{\lambda\nu}\int_0^\tau d\vartheta\exp[i\alpha(\omega_k-\omega_j)\vartheta]\,Q^{jk}_{\alpha\lambda\nu}(\vartheta), \tag{35}$$

where $P^{jk}_{\alpha\lambda\nu}(t)$ and $Q^{jk}_{\alpha\lambda\nu}(t)$, in the case of an isotropic sample, are made up of parts corresponding to different terms in the interaction Hamiltonian (23). If the characteristic times for these functions satisfy the condition of strong narrowing*

$$\tau_p \ll (P^{jk}_{\alpha\lambda\nu}(0))^{-1/2} \qquad \tau_q \ll (Q^{jk}_{\alpha\lambda\nu})^{-1/2}, \tag{36}$$

then the integrals in (35) may be replaced by their asymptotic expressions:[7]

$$P^{jk}_{\alpha\lambda\nu}\tau_{\lambda\nu} = P^{jk}_{\alpha\lambda\nu}(0)(\tau'_{\lambda\nu} + i\tau''_{\lambda\nu}) = \int_0^\infty d\vartheta\exp[(i\lambda\omega_j + i\nu\omega_k)\vartheta]\,P^{jk}_{\alpha\lambda\nu}(\vartheta),$$
$$Q^{jk}_{\alpha\lambda\nu}\varkappa_{\lambda\nu} = Q^{jk}_{\alpha\lambda\nu}(0)(\varkappa'_{\lambda\nu} + i\varkappa''_{\lambda\nu}) = \int_0^\infty d\vartheta\exp[i\alpha(\omega_k-\omega_j)\vartheta]\,Q^{jk}_{\alpha\lambda\nu}(\vartheta). \tag{37}$$

Further, on introducing the notation

$$1/T^{jj}_\alpha + i\alpha\Delta\omega^{(2)\,jj} = \sum_k\sum_{\lambda\nu}P^{jk}_{\alpha\lambda\nu}(0)\,\tau_{\lambda\nu},$$
$$1/T^{jk}_\alpha + i\alpha\Delta\omega^{jk} = \sum_{\lambda\nu}Q^{jk}_{\alpha\lambda\nu}(0)\,\varkappa_{\lambda\nu}, \tag{38}$$

$$\Delta\omega^{jj} = \Delta\omega^{(1)jj} + \Delta\omega^{(2)jj}, \qquad \omega^{jk} = \omega_j\delta_{jk} + \Delta\omega^{jk}, \tag{39}$$

we obtain, up to terms of second-order perturbation theory, the equation satisfied by the relaxation function $G_{\alpha\beta j}$:

$$dG_{\alpha\beta j}(\tau)/d\tau = -\sum_k\sqrt{\chi_j/\chi_k}(1/T_\alpha{}^{jk} + i\alpha\omega^{jk})\,G_{\alpha\beta k}(\tau), \tag{40}$$

where we have approximately replaced

$$G^{(0)}_{\alpha\beta j}(\tau)(1 - i\alpha\Delta\omega^{(1)jj}\tau)\to G_{\alpha\beta j}(\tau).$$

On substituting (40) into (34) we return to Eqs. (12) for the partial magnetizations. If the specific nature of the interaction is given, then the coefficients T^{jk}_α and ω^{jk} appearing in (12) are determined by (38) and (39).

6. In the case when $\hat{\mathcal H}^{22} \ll \hat{\mathcal H}^{12} \ll \hat{\mathcal H}^{11}$ we can write

$$G_{\alpha\beta 1}(\tau) = \frac{1}{kT}\langle\{\hat M_{\alpha 1}(\tau)\ \hat M_{\beta 1}\}\rangle = \frac{\gamma_1^2\hbar^2N_1}{kT}\langle\hat I^{(1)}_{s\alpha}(\tau)\,\hat I^{(1)}_{s\beta}\rangle, \tag{41}$$

$$G_{\alpha\beta,\,2}(\tau) = \frac{1}{kT}\sum_k\langle\{\hat M_{\alpha 2}(\tau),\ \hat M_{\beta k}\}\rangle, \tag{42}$$

where $\hat I^{(1)}_{s\alpha}(\tau)$ and $\hat M_{\alpha 2}(\tau)$ are operators in the Heisenberg representations defined respectively by the Hamiltonians $\hat{\mathcal H}_0 + \hat{\mathcal H}^{11}$ and $\hat{\mathcal H}_0 + \hat{\mathcal H}^{11} + \hat{\mathcal H}^{12}$.

As may be seen from (41), an independent equation is obtained for the first subsystem in this case. If $P^{11}_{\alpha\lambda\nu}(t)$ is a rapidly varying function of time, we obtain, as in the preceding case,

$$dG_{\alpha\beta 1}(\tau)/d\tau = -(1/T^{11}_\alpha + i\alpha\omega^{11})\,G_{\alpha\beta 1}(\tau), \tag{43}$$

*In this case the local fields fluctuate rapidly because of the thermal motion of the magnetic moments.

where T_α^{11} and ω^{11} are calculated for the case of the interaction $\hat{\mathcal{H}}^{11}$ by means of the formulas given earlier. On solving this equation under the condition $G_{\alpha\beta_1}(0) = (-1)^\alpha \chi_1 \delta_{\alpha,-\beta}$ we obtain for the second subsystem

$$dG_{\alpha\beta_2}(\tau)/d\tau = -(1/T_\alpha^{22} + i\alpha\omega^{22})\, G_{\alpha\beta_2}(\tau) - \sqrt{\chi_2/\chi_1}\,(1/T_\alpha^{21} + i\alpha\omega^{21})\, G_{\alpha\beta_1}(\tau), \quad (44)$$

where

$$\frac{1}{T_\alpha^{22}} + i\alpha\Delta\omega^{(2)\,22} = \sum_{\lambda\nu}\int_0^\infty d\vartheta P_{\alpha\lambda\nu}^{21}(\vartheta)\exp\left[\left(i\lambda\omega_2 + i\nu\omega^{11} - \frac{1}{T_\nu^{11}}\right)\vartheta\right],$$

$$\frac{1}{T_\alpha^{21}} + i\alpha\omega^{21} = \sum_{\lambda\nu}\int_0^\infty d\vartheta Q_{\alpha\lambda\nu}^{21}(\vartheta)\exp\left[\left(i\alpha(\omega^{11} - \omega_2) - \frac{1}{T_\alpha^{11}}\right)\vartheta\right]. \quad (45)$$

If $\gamma_1 \gg \gamma_2$, we can neglect the last term in (44), and the equations for the separate subsystems are completely separated, but the coefficients in these equations turn out to be coupled. If T_α^{11} is considerably less than the characteristic time for the function $P_{\alpha\lambda\nu}^{21}(t)$, then we may set in (45) $P_{\alpha\lambda\nu}^{21}(t) = P_{\alpha\lambda\nu}^{21}(0)$. Then, if the condition $T_\nu^{11} \ll (P_{\alpha\lambda\nu}^{21}(0))^{-1/2}$ is satisfied, we shall have

$$\frac{1}{T_\alpha^{22}} + i\alpha\Delta\omega^{(2)\,22} = \sum_{\lambda\nu} P_{\alpha\lambda\nu}^{21}(0)\,\frac{i\lambda\omega_2 + i\nu\omega^{11} + 1/T_\nu^{11}}{(\lambda\omega_2 + \nu\omega^{11})^2 + (T_\nu^{11})^{-2}}. \quad (46)$$

The relaxation time and the shift of the resonance frequency for one substystem turn out to be related to the relaxation time and the resonance frequency of the other subsystem.

7. The real and the imaginary parts of the coefficients $\tau_{\lambda\nu}(\omega_j, \omega_k)$ and $\kappa_{\lambda\nu}(\omega_j, \omega_k)$ which were determined earlier in (37) satisfy the dispersion relations.

We consider the integral $(\omega_j \neq \omega_k)$

$$\tau_{\lambda\nu}(\omega_j, \omega_k) = \tau'_{\lambda\nu}(\omega_j, \omega_k) + i\tau''_{\lambda\nu}(\omega_j, \omega_k) = [1/P_{\alpha\lambda\nu}^{jk}(0)]\int_0^\infty d\vartheta \exp[(i\lambda\omega_j + i\nu\omega_k)\vartheta]\, P_{\alpha\lambda\nu}^{jk}(\vartheta). \quad (47)$$

We let ω_j take on not only real, but also complex values. Then, for $\lambda > 0$ in the upper half-plane, and for $\lambda < 0$ in the lower half-plane, $\tau_{\lambda\nu}$ vanishes when $|\omega_j| \to \infty$. If we represent $\tau_{\lambda\nu}(\omega_j, \omega_k)$ by means of Cauchy's theorem in the form of an integral along a contour consisting of the entire real axis and of a semi-circle of infinite radius (taken, respectively, in the upper half-plane in the case $\lambda > 0$, and in the lower half-plane in the case $\lambda < 0$) then we obtain in the usual way the following dispersion relations

$$\tau'_{\lambda\nu} = \pm\int_{-\infty}^{+\infty}\frac{\tau''_{\lambda\nu}(x, \omega_k)\,dx}{x - \omega_j}, \quad \tau''_{\lambda\nu} = \mp\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\tau'_{\lambda\nu}(x, \omega_k)\,dx}{x - \omega_j}, \quad (48)$$

where $\lambda = \pm 1$. We can, evidently, write down completely analogous relations with respect to the variable ω_k.

Thus, a universal relation, analogous to the Kramers-Kronig relations, exists between $\tau'_{\lambda\nu}$ and $\tau''_{\lambda\nu}$. Expressions (48) are of a very general nature, and do not depend on the specific form of the functions $P_{\alpha\lambda\nu}^{jk}(t)$. Expressions (38) provide a simple connection between the relaxation time and the resonance frequency shift on the one hand, and the quantities $\tau'_{\lambda\nu}$ and $\tau''_{\lambda\nu}$ on the other.

8. When the characteristic time for $P_{\alpha\lambda\nu}^{jk}$ and $Q_{\alpha\lambda\nu}^{jk}$ is great, then we can no longer make use of the asymptotic expressions for the integrals in (35). The concept of relaxation times in this case has no meaning, and we cannot write down simple macroscopic equations for the partial magnetizations. In this case we can calculate directly the partial susceptibilities. By expanding $M_{\alpha j}(t) - M_{\alpha j}^0$ and $h_\beta(t)$ into Fourier integrals with respect to time we shall obtain for the corresponding Fourier components $m_{\alpha j}(\omega)$ and $h_\beta(\omega)$ the following equations

$$m_{\alpha j}(\omega) = \sum_\beta (\chi'_{\alpha\beta j}(\omega) + i\chi''_{\alpha\beta j}(\omega))\, h_{-\beta}(\omega), \quad (49)$$

where

$$\chi'_{\alpha\beta j}(\omega) = \chi_0\delta_{\alpha-\beta} - (-1)^\beta\omega\,\mathrm{Im}\int_0^\infty G_{\alpha\beta j}(\tau)\exp(i\omega\tau)\,d\tau,$$

$$\chi''_{\alpha\beta j}(\omega) = (-1)^\beta\frac{\omega}{2}\int_{-\infty}^\infty G_{\alpha\beta j}(\tau)\exp(i\omega\tau)\,d\tau. \quad (50)$$

The real and imaginary parts of the susceptibility are related to one another by the Kramers-Kronig relations.

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Translated by G. Volkoff
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