

ON THE QUANTUM STATISTICAL THEORY OF RELAXATION IN ISOLATED SPIN SYSTEMS II

by J. A. TJON

Instituut voor theoretische fysica der Rijksuniversiteit, Utrecht, Nederland *)

Synopsis

The investigation of the irreversible behaviour of an isolated spin system, under taken in a previous paper, is continued. The question is studied in how far and in which way the transverse magnetic moments have to be taken into account for a correct description of the long time behaviour of the spin system. All the results obtained previously for the longitudinal magnetic moment are reproduced under the condition that the perturbation is spherically symmetrical in space.

In order to determine the time corrections on the long time behaviour a formal solution is derived for the correlation tensor, valid for all times. It is shown that in the limit $t \rightarrow \infty$ this expression yields a value, which is well in accordance with the predictions of microcanonical theory. In this connection the problem of the equivalence of the isolated and adiabatic susceptibilities is discussed. Furthermore, with the help of the formal solution for the correlation tensor, the line spectrum and line shapes are determined in parallel and perpendicular fields for several special cases.

1. *Introduction.* In a previous paper, to be referred to hereafter as I, we have examined the long time approach of an isolated paramagnetic spin system to statistical equilibrium. It was studied under the assumption that the system could be macroscopically described by means of phase cells, characterized only by the macro energy and the z -component of the total magnetic moment. It was in fact found to be possible to give a simple description of the asymptotic behaviour of the longitudinal magnetic moment in the case of the presence of either a large constant magnetic field along the z -axis or a strong exchange interaction between the spin particles. This long time approach to equilibrium is governed by a master equation.

It is known, however, from experience that the transverse magnetic moments are also macroscopic quantities. Our first aim is to investigate under which conditions and in what way these transverse magnetic moments should be taken into account in order to give a correct description of the asymptotic behaviour of the spin system. From our considerations it will follow that only for systems with strong exchange interaction the transverse moments are also slowly varying observables and accordingly the long time behaviour should in that case be described by means of phase

*) Present address: Instituut voor theoretische fysica der Universiteit, Nijmegen, Nederland.

cells, which are characterized by the total energy and the three components of the total magnetization.

The second purpose of this paper is to determine the time corrections on the asymptotic behaviour of the system. In order to do this an integral equation shall be derived, being valid for all positive times and giving rise to non-markovian effects in the approach of the spin system to statistical equilibrium.

In section 2 the proper quantum-mechanical phase cells and macroscopic operators of the spin system are introduced. Section 3 treats the asymptotic behaviour of the correlation tensor in the case of strong exchange interaction. The method employed here is a natural extension of that in I. The results obtained there for the longitudinal magnetic moments are found again provided that the interaction is spherically symmetrical in space. Moreover, the result for the transverse magnetic moments is the same as that of Kubo and Tomita ²⁾, whose derivation is based on the mathematical assumption of the validity of the semi-invariant method. Section 4 is devoted to a derivation of a formal expression for the autocorrelation function, which is valid for all positive times. In section 5 it is established that the longitudinal magnetic moment approaches in the limit of $t \rightarrow \infty$ a final value, which is well in accordance with the predictions of microcanonical theory, the microcanonical distribution being taken for the total Hamiltonian. In this light the much discussed problem, which has recently been the subject of many authors ³⁾, of the equivalence of the isolated and adiabatic susceptibility is rediscussed. Section 6 deals with the study of the formal expression for the autocorrelation function $\Phi_{33}(t)$ in several limiting cases. Finally in the last section the corrections on the asymptotic behaviour of the transverse magnetic moments are treated.

2. Macroscopic variables. The system to be considered here is the same isolated spin system as in I, consisting of identical paramagnetic ions of spins $\frac{1}{2}$ arranged in a rigid lattice and placed in a constant external magnetic field \mathbf{H} , the direction of which is taken to be the z -axis. Furthermore, the spins are again supposed to be interacting with each other by means of the dipole-dipole and exchange interaction. Our starting point is the relaxation tensor $\Phi_{ij}(t)$ from the linear theory of Kubo and Tomita, which describes the linear response of the i -th component of the total magnetic moment to the j -th component of a vanishing small field \mathbf{h} , being suddenly switched off at $t = 0$. It reduces in the high temperature limit simply to the correlation tensor

$$\Phi_{ij}(t) = \beta(g\mu_0)^2 \langle\langle S_i S_j(t) \rangle\rangle \quad t \geq 0, \quad (2.1)$$

where S_i is the i -th component of the total spin operator. Instead of considering the response of the system to the constant field \mathbf{h} , one may also

as well study the linear behaviour in the presence of a small oscillating field $\mathbf{h}(t) = \mathbf{h} \cos \omega t$ with frequency ω . In this case the macroscopically measured value of the magnetization will be given by

$$\overline{M_i(t)} - \overline{M_i^{(0)}} = \sum_{j=1}^3 h_j \{ \chi'_{ij}(\omega) \cos \omega t + \chi''_{ij}(\omega) \sin \omega t \}, \quad (2.2)$$

where $\chi'_{ij}(\omega)$ and $\chi''_{ij}(\omega)$ are the real and imaginary part of the so-called r.f. susceptibility tensor $\chi_{ij}(\omega) \equiv \chi'_{ij}(\omega) - i\chi''_{ij}(\omega)$. The above mentioned tensor is connected with the relaxation tensor in the following way

$$\chi_{ij}(\omega) = - \int_0^{\infty} \frac{d\Phi_{ij}(\tau)}{d\tau} e^{-i\omega\tau} d\tau. \quad (2.3)$$

It should be noted from (2.3) that $\chi'_{ij}(\omega)$ and $\chi''_{ij}(\omega)$ are obviously related to each other by the Kramers-Kronig relations.

The remaining part of this section will be devoted to the investigation under which suitable conditions the components of the total magnetic moment are slowly varying quantities. As has been shown in I the longitudinal magnetic moment M_3 is a slowly varying observable provided that the unperturbed Hamiltonian \mathcal{H}_0 , defined as

$$\mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_I, \quad (2.4)$$

is large compared to the non-secular term \mathcal{H}_{II} . We shall henceforth confine ourselves to this case. In a good approximation the macro energy of the spin system can then be represented by \mathcal{H}_0 . Since \mathcal{H}_0 and S_3 are commuting operators, they can be diagonalized simultaneously

$$\begin{aligned} \mathcal{H}_0 |E s_3 \alpha\rangle &= E |E s_3 \alpha\rangle \\ S_3 |E s_3 \alpha\rangle &= s_3 |E s_3 \alpha\rangle \end{aligned} \quad (2.5)$$

where E, s_3, α are a complete set of discrete quantum numbers. In case there are no other slowly varying observables than the macro energy and the longitudinal magnetization, the quantummechanical phase cell is characterized by (E, s_3) and consists of the linear subspace of the Hilbert space, spanned by all the eigenfunctions belonging to definite eigenvalues E and s_3 respectively of the operators \mathcal{H}_0 and S_3 . In the following this cell will be called for convenience a macro cell. In terms of it the long time behaviour of S_3 was analysed in I.

We shall now examine to what extent S_1 and S_2 have to be taken into account in order to construct the correct phase cell. For that purpose the secular part of the interaction Hamiltonian \mathcal{H}_I may be conveniently split in the following form, as can readily be seen from the explicit expression for the dipole-dipole and exchange interaction.

$$\mathcal{H}_I = \mathcal{H}_I^{(1)} + \mathcal{H}_I^{(2)} \quad (2.6)$$

with

$$\begin{aligned}\mathcal{H}_I^{(1)} &= \sum_{j \neq k} a_{jk} \mathbf{S}_j \cdot \mathbf{S}_k, \\ \mathcal{H}_I^{(2)} &= \sum_{j \neq k} b_{jk} S_{j3} S_{k3}.\end{aligned}\tag{2.7}$$

In formula (2.7) a_{jk} and b_{jk} are coefficients, which depend only on the relative positions of the ions. Let us now consider S_1 for example. S_2 can be studied in a similar way. The changes of the quantity S_1 occur in several ways.

In the first place S_1 changes in time by transitions between the macro cells with different s_3 . These changes are caused by the non-secular part of the Hamiltonian; consequently they will be slow in case that the unperturbed Hamiltonian \mathcal{H}_0 is large.

Secondly, owing to the secular term there are also transitions between the macro cells with equal s_3 . Since S_1 commutes with the exchange type interaction $\mathcal{H}_I^{(1)}$, the rate of change of S_1 owing to these transitions will be slow provided the Ising term $\mathcal{H}_I^{(2)}$ is weak compared to the exchange. It is to be noted that the Zeeman term does not play any role here, because these processes occur in a "shell" in the Hilbert space with constant s_3 . On the other hand, in the absence of a strong exchange type interaction S_1 approaches very rapidly its equilibrium value. Hence, in this case we don't need to subdivide the macro cells by S_1 and consequently the description given in I will be correct. In order to determine the behaviour of S_1 itself, however, we have to know the evolution of the system as a function of time more precisely than merely in terms of phase cells, characterized by a few number of macro observables.

Thirdly, the Zeeman energy causes also variations of the quantity S_1 , which will be very rapid in case that the magnetic field \mathbf{H} is sufficiently large. These variations in particular, however, are of a reversible character and can readily be taken into account as will be seen in detail in the next section.

From the preceding considerations one may conclude that in the presence of a strong exchange type interaction the macro cells have to be further subdivided by the transverse magnetic moments in order to get the right phase cell. As a matter of fact it will be supposed in addition, that there are no other slowly varying observables. The construction of the phase cells in this case runs as follows.

With any measurement of S_i is involved an experimental inaccuracy ΔS_i . Let δS_i denote the quantum-mechanical uncertainty of S_i . Then these quantities satisfy the inequality

$$\delta S_i \cdot \delta S_j \ll \Delta S_i \cdot \Delta S_j\tag{2.8}$$

in case the experimental inaccuracies ΔS_i are large compared to the distance

between two successive eigenvalues of S_i , that is

$$\Delta S_i \gg 1,$$

which is indeed easily fulfilled in the experiments, since the total number of spin particles in the system is very large. The meaning of the condition (2.8) is that the quantum-mechanical uncertainties are negligible compared to the experimental ones, which implies that these quantities may be treated as classical. From the property

$$[S_i, \mathcal{H}_I^{(1)}] = 0 \quad \text{for all } i$$

it follows that in a representation, in which $\mathcal{H}_I^{(1)}$ is diagonal, there are no non-zero matrix elements of S_i connecting states with different eigenvalues E_e of the operator $\mathcal{H}_I^{(1)}$. Hence we may confine ourselves to the linear subspace of the Hilbert space belonging to a definite E_e . As a result of the condition (2.8) the operators S_i can be truncated in this subspace in a similar way as was done by van Kampen ⁴) into the corresponding coarse grained operators, designated by \tilde{S}_i and which are simultaneously diagonal. Thus

$$\begin{aligned} \tilde{S}_i |E_e\{\bar{s}_k\}\alpha\rangle &= \bar{s}_i |E_e\{\bar{s}_k\}\alpha\rangle \\ \mathcal{H}_I^{(1)} |E_e\{\bar{s}_k\}\alpha\rangle &= E_e |E_e\{\bar{s}_k\}\alpha\rangle \end{aligned} \quad (2.9)$$

where $E_e, \{\bar{s}_k\} = \bar{s}_1, \bar{s}_2, \bar{s}_3$ and α are a complete set of discrete quantum numbers and the eigenstates $|E_e\{\bar{s}_k\}\alpha\rangle$ are orthonormal

$$\langle E_e\{\bar{s}_k\}\alpha | E_{e'}\{\bar{s}'_k\}\alpha' \rangle = \delta_{E_e E_{e'}} \delta_{\alpha\alpha'} \prod_{i=1}^3 \delta_{\bar{s}_i \bar{s}'_i}. \quad (2.10)$$

It should be emphasized that for a description of the macroscopic behaviour of the total magnetic moment one may of course use the truncated operators \tilde{S}_i as well as S_i . The quantum-mechanical phase cell is now characterized by $(E_e, \{\bar{s}_k\})$ and consists of the whole set of eigenfunctions (2.9) belonging to definite eigenvalues E_e and $\{\bar{s}_k\}$ of the operators $\mathcal{H}_I^{(1)}$ and $\{\tilde{S}_k\}$. We note that instead of macro energy, represented in this case in a good approximation by

$$\bar{\mathcal{H}}_0 = \mathcal{H}_z + \mathcal{H}_I^{(1)}, \quad (2.11)$$

we have used the eigenvalue E_e of $\mathcal{H}_I^{(1)}$.

3. *The asymptotic behaviour of the correlation tensor.* This section is devoted to the determination of the correlation tensor for asymptotic long times in the presence of a strong exchange type interaction. The changes of the correlation tensor are the result of the approach of the spin system to statistical equilibrium caused by transitions between the phase cells $(E_e, \{\bar{s}_k\})$, which have been introduced in the previous section. This tensor will be studied again by means of a many particle perturbation treatment.

In order to expand the correlation tensor into a perturbation series, the Hamiltonian of the system may be written in the following form

$$\mathcal{H} = \overline{\mathcal{H}}_0 + V, \quad (3.1)$$

where the unperturbed Hamiltonian $\overline{\mathcal{H}}_0$ is defined by (2.11) and V , being the perturbation, is given by

$$V = \mathcal{H}_I^{(2)} + \mathcal{H}_{II}. \quad (3.2)$$

The physical meaning of the decomposition (3.2) is quite obvious. The transitions between the phase cells ($E_e, \{\bar{s}_{k_j}\}$) are caused by the perturbation V , while $\overline{\mathcal{H}}_0$ describes in a good approximation the macro energy.

The expansion of $\Phi_{ij}(\tau)$ in powers of V is readily found by iteration. It is (cf. Kubo and Tomita l.c.)

$$\begin{aligned} \Phi_{ij}(t) &= \beta(g\mu_0)^2 \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \\ &\ll [S_i^{(1)}(t); V^{(1)}(t_1), V^{(1)}(t_2), \dots, V^{(1)}(t_n)]_n S_j \gg \end{aligned} \quad (3.3)$$

with

$$\begin{aligned} S_i^{(1)}(t) &= e^{i\overline{\mathcal{H}}_0 t/\hbar} S_i e^{-i\overline{\mathcal{H}}_0 t/\hbar}, \\ V^{(1)}(t) &= e^{i\overline{\mathcal{H}}_0 t/\hbar} V e^{-i\overline{\mathcal{H}}_0 t/\hbar}. \end{aligned} \quad (3.4)$$

Using the well-known commutation relations

$$[S_1, S_2] = iS_3, [S_2, S_3] = iS_1, [S_3, S_1] = iS_2$$

we may write for $S_i^{(1)}(t)$

$$\begin{aligned} S_1^{(1)}(t) &= S_1 \cos \omega_L t + S_2 \sin \omega_L t, \\ S_2^{(1)}(t) &= S_2 \cos \omega_L t - S_1 \sin \omega_L t, \\ S_3^{(1)}(t) &= S_3, \end{aligned} \quad (3.5)$$

in which formula $\omega_L = g\mu_0 H/\hbar$ is the Larmor frequency. With the aid of (3.5) it is now possible to separate the rapid variations of S_1 and S_2 due to the Zeeman energy from the slowly varying irreversible changes. For, from this expression it is seen that one may confine oneself to the study of the behaviour of the following tensor

$$\begin{aligned} \varphi_{ij}(t) &= \beta(g\mu_0)^2 \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \\ &\ll [S_i; V^{(1)}(t_1), \dots, V^{(1)}(t_n)]_n S_j \gg. \end{aligned} \quad (3.6)$$

The expressions (3.3) and (3.6) are simply related to each other by

$$\begin{aligned}\Phi_{1j}(t) &= \varphi_{1j}(t) \cos \omega_L t + \varphi_{2j}(t) \sin \omega_L t, \\ \Phi_{2j}(t) &= \varphi_{2j}(t) \cos \omega_L t - \varphi_{1j}(t) \sin \omega_L t, \\ \Phi_{3j}(t) &= \varphi_{3j}(t).\end{aligned}\tag{3.7}$$

For the description of the macroscopic behaviour of $\varphi_{ij}(t)$ one may use S_i as well as the corresponding coarse grained operators \bar{S}_i . However, it should be stressed that in the Schrödinger equation itself and as a consequence also in the exponentials of (3.4) S_3 may not be replaced by \bar{S}_3 . The trace in (3.6) can then be written out in the representation, in which $\mathcal{H}_i^{(1)}$ and \bar{S}_i are simultaneously diagonal. One obtains

$$\varphi_{ij}(t) = \frac{\beta(g\mu_0)^2}{\text{Tr } 1} \sum_{n=0}^{\infty} \sum_{E_i, \{s_k\}} \bar{s}_j T_n^{(i)}(E_e\{\bar{s}_k\}|t)\tag{3.8}$$

with

$$\begin{aligned}T_n^{(i)}(E_e\{\bar{s}_k\}|t) &= \left(\frac{1}{i\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \\ &\sum_{\alpha} \langle E_e\{\bar{s}_k\}\alpha | [\bar{S}_i; V^{(1)}(t_1), \dots, V^{(1)}(t_n)]_n | E_e\{\bar{s}_k\}\alpha \rangle.\end{aligned}\tag{3.9}$$

We shall use the well-known decomposition of the perturbation V into

$$V = \sum_m V_m,\tag{3.10}$$

where V_m has the property

$$[S_3, V_m] = mV_m.\tag{3.11}$$

The explicit expression for V_m is given by

$$\begin{aligned}V_0 &= \mathcal{H}_I^{(2)}, \\ V_1 &= V_{-1}^+ = \frac{1}{2} \sum_{j \neq k} c_{jk} (S_{j+} S_{k3} + S_{j3} S_{k+}), \\ V_2 &= V_{-2}^+ = \sum_{j \neq k} d_{jk} S_{j+} S_{k+}.\end{aligned}\tag{3.12}$$

In formula (3.12) V_m^+ denotes the Hermitian conjugate of V_m and c_{jk} and d_{jk} are functions only of the relative positions of the ions.

The calculations in I of the asymptotic behaviour of the longitudinal magnetic moment in terms of the macro cells can now readily be extended in order to evaluate (3.8). It is easily seen that the term $n = 1$ in (3.8) reduces simply to zero.

Let us examine the second order term of (3.9). Application of (3.10) and

(3.11) gives

$$T_2^{(i)}(E_e\{\bar{s}_k\}|\ell) = -\frac{1}{\hbar^2} \int_0^\ell dt_1 \int_0^{t_1} dt_2 \sum_{m_1, m_2} e^{-i\omega_L(m_1 t_1 + m_2 t_2)} \sum_\alpha \langle E_e\{\bar{s}_k\}\alpha | [\bar{S}_i; V_{m_1}^{(0)}(t_1 - t_2), V_{m_2}]_2 | E_e\{\bar{s}_k\}\alpha \rangle, \quad (3.13)$$

where

$$V_m^{(0)}(\tau) = e^{i\mathcal{H}_1^{(1)}\tau/\hbar} V_m e^{-i\mathcal{H}_1^{(1)}\tau/\hbar}. \quad (3.14)$$

The terms on the right hand side of (3.13) with $m_1 + m_2 = 0$ may be written out explicitly in the representation $|E_e\{\bar{s}_k\}\alpha\rangle$

$$-\frac{2}{\hbar^2} \int_0^\ell d\tau_1' \int_0^{\tau_1'} d\tau_1 \sum_{E_e', \{s_k'\}} (\bar{s}_i - \bar{s}_i') \sum_m \sum_{\alpha, \alpha'} |\langle E_e\{\bar{s}_k\}\alpha | V_m | E_e'\{\bar{s}_k'\}\alpha' \rangle|^2 \cos\left(\frac{(E_e - E_e' - m\hbar\omega_L)\tau_1}{\hbar}\right), \quad (3.15)$$

where the new variables $\tau_1' = t_1$, $\tau_1 = t_1 - t_2$, have been introduced.

Since the total number of spins N is very large, we may restrict ourselves to times, which are much smaller than $\hbar/\delta E_s$, where δE_s indicates the order of the distance between two successive eigenvalues of $\mathcal{H}_1^{(1)}$ and which is proportional to N^{-1} . Moreover, since we will be concerned in this section with times of the order of the relaxation times T_n of the system, the upper limit of the integration variable τ_1 in (3.15) may be taken ∞ , provided that

$$|T_n| \gg \hbar/\delta E_1. \quad (3.16)$$

Here δE_1 denotes an interval over which the variations of

$$\sum_{\alpha, \alpha'} |\langle E_e\{\bar{s}_k\}\alpha | V_m | E_e'\{\bar{s}_k'\}\alpha' \rangle|^2$$

with E_e and E_e' are small. Equation (3.16) implies the existence of two time scales $\hbar/\delta E_1$ and T_n , which are well separated from each other. This is intimately connected with the requirement that there should be a sharp distinction between rapidly and slowly varying quantities. The characteristic time $\hbar/\delta E_1$ indicates how fast the system tends to local equilibrium; consequently after a lapse of this time all other physical quantities than the slowly varying ones may be supposed to be in equilibrium. The condition (3.16) states that $\hbar/\delta E_1$ has to be much shorter than T_n , being the characteristic times in which the slowly varying quantities reach their equilibrium values. This is indeed satisfied under the condition that the exchange interaction is large compared to the dipole-dipole interaction, which is precisely the case we are studying here.

As a result of the asymptotic time integration the expression (3.15) reduces to

$$-2\pi t \sum_{E_e', \{\tilde{s}_k'\}} (\tilde{s}_i - \tilde{s}_i') \sum_m \delta_{E_e - E_e', m\hbar\omega_L} \sum_{\alpha, \alpha'} |\langle E_e \{\tilde{s}_k\} \alpha | V_m | E_e' \{\tilde{s}_k'\} \alpha' \rangle|^2 / \hbar. \quad (3.17)$$

Equation (3.17) allows a simple interpretation. It describes the irreversible changes of the quantity \tilde{S}_i due to transitions between the phase cells and which are characterized by the transition probability per unit time

$$W(E_e \{\tilde{s}_k\} | E_e' \{\tilde{s}_k'\}) = \frac{2\pi}{\hbar \rho(E_e', \{\tilde{s}_k'\})} \sum_m \delta_{E_e - E_e', m\hbar\omega_L} \sum_{\alpha, \alpha'} |\langle E_e \{\tilde{s}_k\} \alpha | V_m | E_e' \{\tilde{s}_k'\} \alpha' \rangle|^2. \quad (3.18)$$

Here $\rho(E_e', \{\tilde{s}_k'\})$ is the total number of eigenstates $|E_e' \{\tilde{s}_k'\} \alpha'\rangle$ in the phase cell $(E_e', \{\tilde{s}_k'\})$. We note that in view of the δ -function in (3.18) the macro energy \mathcal{H}_0 is conserved with these transitions.

Similarly, the terms in (3.13) with $m_1 + m_2 \neq 0$ lead for times much larger than $\hbar/\delta E_1$, to

$$- \sum_{\substack{m_1, m_2 \neq 0 \\ m_1 + m_2 \neq 0}} \int d\tau_1' \exp[-i(m_1 + m_2)\omega_L \tau_1'] \int_0^\infty d\tau_1 e^{im_2\omega_L \tau_1} \sum_{\alpha} \langle E_e \{\tilde{s}_k\} \alpha | [\tilde{S}_i; V_{m_1}^{(0)}(\tau_1), V_{m_2}]_2 | E_e \{\tilde{s}_k\} \alpha \rangle / \hbar^2. \quad (3.19)$$

The contribution (3.19) can be neglected because of the rapidly varying exponentials $\exp[-i(m_1 + m_2)\omega_L \tau_1']$, provided that

$$|T_n| \gg \omega_L^{-1}. \quad (3.20)$$

Hence, under the conditions (3.16) and (3.20) the 2-nd order term of (3.9) reduces simply to (3.17).

Subsequently the general order term of (3.9) can be studied in a similar way as has been done in I. The random phase assumptions of the matrix elements of the perturbation are now however supposed to be valid in the representation $|E_e \{\tilde{s}_k\} \alpha\rangle$. Inserting the result into (3.8) one obtains

$$\varphi_{ij}(t) = \frac{\beta(g\mu_0)^2}{T\gamma} \sum_{\substack{E_e', \{\tilde{s}_k'\} \\ E_e', \{\tilde{s}_k'\}}} \rho(E_e', \{\tilde{s}_k'\}) \tilde{s}_i' \tilde{s}_j \{e^{-\Omega t}\}_{E_e, \{\tilde{s}_k\}; E_e', \{\tilde{s}_k'\}} \text{ for } t \gg \hbar/\delta E_1, \omega_L^{-1} \quad (3.21)$$

where the matrix Ω is of the form

$$\Omega(E_e \{\tilde{s}_k\} | E_e' \{\tilde{s}_k'\}) = \delta_{E_e E_e'} \prod_{i=1}^3 \delta_{\tilde{s}_i, \tilde{s}_i'} \sum_{E_e'', \{\tilde{s}_k''\}} W(E_e'' \{\tilde{s}_k''\} | E_e' \{\tilde{s}_k'\}) - W(E_e \{\tilde{s}_k\} | E_e' \{\tilde{s}_k'\}). \quad (3.22)$$

Obviously, from (3.21) we see that the long-time behaviour of the macroscopic system is described by a markovian process.

The expression (3.21) can now be simplified with the aid of a linearity condition. Since the external field \mathbf{h} is small, one may namely suppose that

the system is not far from statistical equilibrium. Consequently the following expression can be expanded to linear order in the deviation of the macroscopic quantities $\{\bar{s}_k\}$ from their equilibrium values

$$\sum_{E_e, \{\bar{s}_k\}} \bar{s}_j \Omega(E_e\{\bar{s}_k\}|E'_e\{\bar{s}'_k\}) = \sum_{l=1}^3 \Gamma_{lj}(\bar{s}'_l - c_l), \quad (3.23)$$

where c_l is given by the microcanonical average $\langle \bar{S}_l \rangle_{\bar{\mathcal{H}}_0}$ with respect to the unperturbed Hamiltonian $\bar{\mathcal{H}}_0$.

Hereafter we shall frequently use the relation

$$\langle\langle A \rangle_{\bar{\mathcal{H}}_0} \langle B \rangle_{\bar{\mathcal{H}}_0} \rangle = \frac{\langle\langle A \bar{\mathcal{H}}_0 \rangle \langle B \bar{\mathcal{H}}_0 \rangle \rangle}{\langle\langle \bar{\mathcal{H}}_0^2 \rangle \rangle}, \quad (3.24)$$

where the physical quantities A , B and $\bar{\mathcal{H}}_0$ fulfil

$$\langle\langle A \rangle \rangle = \langle\langle B \rangle \rangle = \langle\langle \bar{\mathcal{H}}_0 \rangle \rangle = 0.$$

The relation (3.24) is proved with the help of statistical mechanics of equilibrium processes in the same way as has been done in the appendix of I for

$$\langle\langle S_3 \rangle_E^2 \rangle = \frac{\langle\langle S_3 \bar{\mathcal{H}}_0 \rangle \rangle^2}{\langle\langle \bar{\mathcal{H}}_0^2 \rangle \rangle}, \quad (3.25)$$

where $\langle S_3 \rangle_E$ designates the microcanonical average with respect to $\bar{\mathcal{H}}_0$.

Equation (3.21) reduces with the aid of the linearity condition (3.23) and the relation (3.24) to

$$\varphi_{ij}(t) = \beta(g\mu_0)^2 [\langle\langle S_i \rangle_{\bar{\mathcal{H}}_0}^2 \rangle \delta_{ij} + (\langle\langle S_i^2 \rangle \rangle - \langle\langle S_i \rangle_{\bar{\mathcal{H}}_0}^2 \rangle) (e^{-\Gamma t})_{ij}]. \quad (3.26)$$

Moreover, the matrix elements Γ_{ij} can be found after some manipulations from (3.23) by multiplying with $\bar{s}'_{i\rho}(E'_e, \{\bar{s}'_k\})$ and summing over E'_e and $\{\bar{s}'_k\}$. The result is

$$\Gamma_{ij} = \frac{1}{\hbar^2(\langle\langle S_i^2 \rangle \rangle - \langle\langle S_i \rangle_{\bar{\mathcal{H}}_0}^2 \rangle)} \int_0^\infty d\tau \sum_m \langle\langle [S_i; V_m^{(1)}(\tau), V_{-m}]_2 S_j \rangle \rangle. \quad (3.27)$$

Here we have again neglected the dependence of Γ_{ij} on E'_e . It can now be shown from (3.27) that the following matrix elements of Γ_{ij} are zero.

$$\Gamma_{13} = \Gamma_{31} = \Gamma_{23} = \Gamma_{32} = 0. \quad (3.28)$$

This means that the behaviour of the longitudinal magnetic moment is independent of the transverse moments under the conditions (3.16) and (3.20)

Although the matrix Γ_{ij} is not symmetrical, it can be diagonalized. With

this equation (3.26) reduces to

$$\begin{aligned}\varphi_{11}(t) &= \varphi_{22}(t) = \frac{1}{2}\beta(g\mu_0)^2 \langle\langle S_1^2 \rangle\rangle [e^{-\gamma_1 t} + e^{-\gamma_2 t}], \\ \varphi_{12}(t) &= -\varphi_{21}(t) = \frac{i}{2}\beta(g\mu_0)^2 \langle\langle S_1^2 \rangle\rangle [e^{-\gamma_1 t} - e^{-\gamma_2 t}], \\ \varphi_{33}(t) &= \beta(g\mu_0)^2 [\langle\langle S_3 \rangle_{\mathcal{H}_0}^2 \rangle\rangle + (\langle\langle S_3^2 \rangle\rangle - \langle\langle S_3 \rangle_{\mathcal{H}_0}^2 \rangle\rangle) e^{-\gamma_3 t}].\end{aligned}\quad (3.29)$$

The remaining matrix elements of the tensor $\varphi_{ij}(t)$ are zero. The relaxation constants γ_i are given by

$$\begin{aligned}\gamma_1 &= \int_0^\infty d\tau \langle\langle [S_+; V^{(1)}(\tau), V]_2 S_- \rangle\rangle / \hbar^2 \langle\langle S_+ S_- \rangle\rangle, \\ \gamma_2 &= \int_0^\infty d\tau \langle\langle [S_-; V^{(1)}(\tau), V]_2 S_+ \rangle\rangle / \hbar^2 \langle\langle S_+ S_- \rangle\rangle, \\ \gamma_3 &= \int_0^\infty d\tau \langle\langle [S_3; V^{(1)}(\tau), V]_2 S_3 \rangle\rangle / \hbar^2 (\langle\langle S_3^2 \rangle\rangle - \langle\langle S_3 \rangle_{\mathcal{H}_0}^2 \rangle\rangle).\end{aligned}\quad (3.30)$$

Here we have used the notation $S_\pm \equiv S_1 \pm iS_2$ and applied the relation (3.24). Moreover, in (3.29) and (3.30) the coarse grained operators $\{\mathcal{S}_k\}$ have been replaced by their corresponding operators $\{S_k\}$. Since the Ising term in \mathcal{H}_0 is much smaller than the exchange term, we see from (3.29) that the outcome for the autocorrelation function $\Phi_{33}(t)$ is well in accordance with that found in I, which was to be expected on account of the independence of the behaviour of the longitudinal and transverse magnetic moments, expressed by (3.28).

Combining (3.29) with (2.3) and (3.7) we find immediately for the susceptibility tensor

$$\begin{aligned}\chi_{11}(\omega) &= \chi_{22}(\omega) = \chi_0 - \frac{i\omega\chi_0}{2} \left[\frac{1}{i(\omega - \omega_L) + \gamma_2} + \frac{1}{i(\omega + \omega_L) + \gamma_1} \right], \\ \chi_{12}(\omega) &= -\chi_{21}(\omega) = -\frac{\omega\chi_0}{2} \left[\frac{1}{i(\omega - \omega_L) + \gamma_2} - \frac{1}{i(\omega + \omega_L) + \gamma_1} \right], \\ \chi_{33}(\omega) &= \beta(g\mu_0)^2 (\langle\langle S_3^2 \rangle\rangle - \langle\langle S_3 \rangle_{\mathcal{H}_0}^2 \rangle\rangle) \frac{\gamma_3}{i\omega + \gamma_3}.\end{aligned}\quad (3.31)$$

The result for $\chi_{11}(\omega)$ is not new. It describes the well-known exchange narrowing phenomenon and was among others found by Kubo and Tomita. From (3.31) we see that the absorption lines in perpendicular fields, which are represented by the imaginary part of $\chi_{11}(\omega)$ are Lorentz curves. They are broadened by $\text{Re } \gamma_i$ and shifted by $\text{Im } \gamma_i$ due to the perturbation V . As a result, the condition (3.20) for the validity of the expression (3.31) implies that the widths and shifts of the absorption lines should be much

smaller than the Larmor frequency, that is the field \mathbf{H} must be strong. If, on the other hand, the field is so weak that ω_L is no longer much larger than $|\gamma_i|$, one may not neglect the contribution (3.19). In particular, at $\mathbf{H} = 0$ one finds that (3.19) becomes proportional to t and must therefore be added to Γ_{ij} . The matrix Γ_{ij} is then given by

$$\Gamma_{ij} = \Gamma_{ji} = \int_0^{\infty} d\tau \ll [S_i; V^{(1)}(\tau), V]_2 S_j \gg / \hbar^2 \ll S_i^2 \gg. \quad (3.32)$$

As a result we now obtain

$$\varphi_{ij}(t) = \sum_{n=1}^3 c_n^{(i,j)} e^{-\gamma_n' t}, \quad (3.33)$$

where γ_n' designate the eigenvalues of the matrix (3.32), which are in general different from each other. The constants $c_n^{(i,j)}$ can in principle be determined from the diagonalization of (3.32).

Thus the behaviour of the three components of the magnetic moment will in general not be independent. From (3.32), however, we obtain for the special case that the perturbation V is spherically symmetrical in space, only one relaxation time and accordingly $\varphi_{ij}(t)$ reduces simply to

$$\varphi_{ij}(t) = \beta(g\mu_0)^2 \ll S_i^2 \gg \delta_{ij} e^{-\gamma t} \quad (3.34)$$

with

$$\gamma \equiv \Gamma_{ii} = \int_0^{\infty} d\tau \ll [S_i; V^{(1)}(\tau), V]_2 S_i \gg / \hbar^2 \ll S_i^2 \gg. \quad (3.35)$$

In addition, it follows that in this case equation (3.29) will also be valid for all fields \mathbf{H} . Henceforth we shall confine ourselves to this case and consequently the longitudinal and transverse magnetic moments may be treated separately.

In conclusion it should be noted that the so-called 10/3 effect in perpendicular fields, which is the increase of the line width $\text{Re } \gamma_i$ (with $i = 1, 2$) with decreasing field \mathbf{H} and the Kronig-Bouwkamp effect in parallel fields, which is the increase of the relaxation constant γ_3 with decreasing field \mathbf{H} , are essentially the same effects. It can easily be seen namely from the preceding treatment that they are the result of the irreversible changes of the macroscopic quantities of the system, which are caused by transitions between the phase cells with different longitudinal magnetic moments.

4. *The integral equation.* Up to now we have studied the long time behaviour of the total magnetic moment. We now want to derive a formal expression for the correlation tensor, which should be valid for all positive times. In this and the next two sections we will be concerned only with the behaviour in parallel fields, that is, with the dependence of the autocorrelation function $\Phi_{33}(t)$ on t . Since the longitudinal and transverse magnetic

moments may be treated separately, we can, in order to determine the behaviour of the longitudinal magnetic moment, go back to the following expression, which is obtained with the aid of the assumption of randomly varying phases of the matrix elements of the non-secular perturbation \mathcal{H}_{II}

$$\Phi_{33}(t) = \beta(g\mu_0)^2 \sum_{E, s_3, \alpha} s_3 \langle E s_3 \alpha | S_3(t) | E s_3 \alpha \rangle, \quad (4.1)$$

where

$$\begin{aligned} \langle E s_3 \alpha | S_3(t) | E s_3 \alpha \rangle &= \sum_{n=0}^{\infty} \left(\frac{-1}{\hbar^2} \right)^n \int_0^t d\tau_1' \int_0^{\tau_1'} d\tau_1 \dots \int_0^{\tau_{n-1}' - \tau_{n-1}} d\tau_n' \int_0^{\tau_n'} d\tau_n \\ \langle E s_3 \alpha | [S_3; \mathcal{H}'_{II}(\tau_n), \mathcal{H}_{II}]_d \mathcal{H}'_{II}(\tau_{n-1}), \mathcal{H}_{II}]_d \dots]_{2n, d} | E s_3 \alpha \rangle & \quad (4.2) \end{aligned}$$

with

$$\mathcal{H}'_{II}(\tau) = e^{i\mathcal{H}_0\tau/\hbar} \mathcal{H}_{II} e^{-i\mathcal{H}_0\tau/\hbar}. \quad (4.3)$$

In equation (4.2) the subscript d means the diagonal part of the operator between the brackets in the representation $|E s_3 \alpha\rangle$.

In order to write (4.2) more conveniently we shall use the following mathematical device. The usual quantum-mechanical operators, which are diagonal in the representation $|E s_3 \alpha\rangle$, may be regarded as constituting themselves a linear space. The scalar product of two elements A and B of this "operator space" is defined by

$$(A, B) \equiv \text{Tr } A^+ B / \text{Tr } 1,$$

where A^+ means the Hermitian conjugate of A . We introduce a linear operator $f(\tau)$, which acts in this operator space and is defined by

$$\begin{aligned} \langle E s_3 \alpha | f(\tau) A | E' s_3' \alpha' \rangle &= \delta_{E'E} \delta_{s_3 s_3'} \delta_{\alpha \alpha'} \\ & \langle E s_3 \alpha | [A; \mathcal{H}'_{II}(\tau), \mathcal{H}_{II}]_2 | E s_3 \alpha \rangle / \hbar^2. \end{aligned} \quad (4.4)$$

Obviously, according to (4.4) $f(\tau)A$ is again an element of this space.

With the aid of this definition the expression (4.2) can be written as

$$\begin{aligned} \{S_3(t)\}_d &= \sum_{n=0}^{\infty} (-1)^n \int_0^t d\tau_1' \int_0^{\tau_1'} d\tau_1 \dots \int_0^{\tau_{n-1}' - \tau_{n-1}} d\tau_n' \int_0^{\tau_n'} d\tau_n \\ & f(\tau_1) f(\tau_2) \dots f(\tau_n) S_3. \end{aligned} \quad (4.5)$$

In differentiating formula (4.5) with respect to t , we obtain the linear integral equation

$$\frac{\partial}{\partial t} \{S_3(t)\}_d = - \int_0^t d\tau f(\tau) \{S_3(t - \tau)\}_d \quad (4.6)$$

with the initial condition $\{S_3(0)\}_d = S_3$. The integral equation can now readily be solved in a formal way by Laplace transformation. Inserting

the result into (4.1) we obtain

$$\hat{\Phi}_{33}(\rho) = \beta(g\mu_0)^2 \left(S_3, \frac{1}{\hat{f}(\rho) + \rho} S_3 \right) \quad \text{Re } \rho \geq 0, \tag{4.7}$$

where the quantities $\hat{\Phi}_{33}(\rho)$ and $\hat{f}(\rho)$ are the Laplace transforms of $\Phi_{33}(t)$ and $f(t)$ respectively

$$\begin{aligned} \hat{\Phi}_{33}(\rho) &= \int_0^\infty dt e^{-\rho t} \Phi_{33}(t), \\ \hat{f}(\rho) &= \int_0^\infty dt e^{-\rho t} f(t). \end{aligned} \quad \text{Re } \rho \geq 0 \tag{4.8}$$

The solution (4.7) can of course also be found directly in applying Laplace transformation to (4.5).

In particular, the result obtained previously in I for asymptotic large times can readily be found back from (4.7) by replacing in it the operator $\hat{f}(\rho)$ by $\hat{f}(0)$, which is equivalent to the asymptotic time integration previously used. Indeed, as a result of this approximation equation (4.7) reduces to

$$\hat{\Phi}_{33}(\rho) = \beta(g\mu_0)^2 \left[\frac{\langle S_3 \rangle_E, \langle S_3 \rangle_E}{\rho} + \frac{(S_3, S_3) - \langle S_3 \rangle_E, \langle S_3 \rangle_E}{\rho + 1/\tau_s} \right], \tag{4.9}$$

where in addition we have made use of the second random phase assumption with respect to the microscopic quantum numbers α and the linearity condition, given in I. In (4.9) τ_s is the spin-spin relaxation time, given by I(3.25).

5. *The equivalence between adiabatic and isolated susceptibility.* We shall now investigate more accurately the autocorrelation function $\Phi_{33}(t)$ in the limit of $t \rightarrow \infty$. Previously this has already been studied, but only after the application of the asymptotic time integration. It should be remarked that obviously in this approximation $\Phi_{33}(t)$ tends to a final value, which is in accordance with the microcanonical theory, the microcanonical distribution being taken for the unperturbed Hamiltonian \mathcal{H}_0 .

In view of (4.8) the limiting value of $\Phi_{33}(t)$ can also be written as

$$\lim_{t \rightarrow \infty} \Phi_{33}(t) = \lim_{\rho \rightarrow +0} \rho \hat{\Phi}_{33}(\rho). \tag{5.1}$$

In order to determine this expression we shall make use of the following expansion of the resolvent operator $(\hat{f}(\rho) + \rho)^{-1}$

$$\begin{aligned} \frac{1}{\hat{f}(\rho) + \rho} &= \frac{1}{\hat{f}(0) + \rho} + \frac{1}{\hat{f}(0) + \rho} (\hat{f}(0) - \hat{f}(\rho)) \frac{1}{\hat{f}(0) + \rho} + \frac{1}{\hat{f}(0) + \rho} (\hat{f}(0) - \hat{f}(\rho)) \\ &\quad \frac{1}{\hat{f}(0) + \rho} (\hat{f}(0) - \hat{f}(\rho)) \frac{1}{\hat{f}(0) + \rho} + \dots \end{aligned} \tag{5.2}$$

Furthermore, we have the property

$$\lim_{p \rightarrow +0} \frac{\dot{p}}{\dot{f}(0) + p} A = \langle A \rangle_E, \quad (5.3)$$

which is equivalent with the statement that A must approach its micro-canonical average with respect to the unperturbed Hamiltonian \mathcal{H}_0 . This follows from the irreducibility of the matrix Ω , defined in I, in the subspace of the Hilbert space spanned by all the eigenfunctions $|E_{S_3\alpha}\rangle$ with definite eigenvalue of \mathcal{H}_0 . With the help of (5.2) and (5.3) we obtain

$$\lim_{p \rightarrow +0} p \hat{\Phi}_{33}(p) = \beta(g\mu_0)^2 \left(S_3, \left\{ \langle S_3 \rangle_E - \left\langle \frac{df(0)}{dp} \langle S_3 \rangle_E \right\rangle_E + \left\langle \frac{df(0)}{dp} \left\langle \frac{df(0)}{dp} \langle S_3 \rangle_E \right\rangle_E \right\rangle_E + \dots \right\} \right). \quad (5.4)$$

This expression can be simplified considerably by the repeated use of the relation (3.24) into

$$\lim_{p \rightarrow +0} p \hat{\Phi}_{33}(p) = \beta(g\mu_0)^2 \frac{(S_3, \mathcal{H}_0)^2}{(\mathcal{H}_0, \mathcal{H}_0) + (\mathcal{H}_0, \frac{df(0)}{dp} \mathcal{H}_0)}. \quad (5.5)$$

The quantities on the right hand side of equation (5.5) can now be evaluated explicitly. Thus we find

$$\lim_{p \rightarrow +0} p \hat{\Phi}_{33}(p) = \frac{H^2}{H^2 + \frac{1}{2}H_i^2} \chi_0, \quad (5.6)$$

where the internal field H_i is defined in the following way

$$\frac{1}{2}H_i^2 = \frac{1}{2}H_{i, \text{sec}}^2 + \frac{1}{2}H_{i, n. \text{sec}}^2, \quad (5.7)$$

with

$$\begin{aligned} \frac{1}{2}H_{i, \text{sec}}^2 &= \text{Tr } \mathcal{H}_I^2 / (g\mu_0)^2 \text{Tr } S_3^2, \\ \frac{1}{2}H_{i, n. \text{sec}}^2 &= \text{Tr } \mathcal{H}_{II}^2 / (g\mu_0)^2 \text{Tr } S_3^2. \end{aligned} \quad (5.8)$$

This result enables us to rediscuss the question of the equivalence between the adiabatic susceptibility calculated in a thermodynamical way and the so-called isolated susceptibility. The latter is defined as the rate of change of the longitudinal magnetization in an isolated spin system owing to a sufficiently slow variation of the magnetic field along the z -axis. The rate of change should be calculated in a dynamical way. As a result, we may take the real part of $\chi_{33}(\omega)$ at $\omega = 0$ as an appropriate definition of the isolated susceptibility, denoted by χ_{is} . This reduces with the

aid of (2.3) and (5.6) readily to

$$\chi_{is} \equiv \chi_{33}(0) = \frac{\frac{1}{2}H_i^2}{H^2 + \frac{1}{2}H_i^2} \chi_0. \quad (5.9)$$

The expression (5.9) is indeed the same result as that obtained from the definition of the adiabatic susceptibility.

On the other hand most authors have used previously for the definition of the isolated susceptibility

$$\chi_{is}^B = g\mu_0 \sum_n \frac{\partial(S_3)_{nn}}{\partial H} e^{-\beta E_n} / \sum_n e^{-\beta E_n}, \quad (5.10)$$

in which n and E_n are the eigenstates and eigenvalues of the total Hamiltonian. This expression is found by means of the adiabatic theorem of Ehrenfest. One supposes that the magnetic field is varied so slowly that no transitions are induced and consequently the system being in a definite eigenstate shall remain in it. Ehrenfest's theorem is valid under the condition that the time characterizing the rate of change of the magnetic field is much larger than the time $\tau_0 = \hbar/\delta E$, where δE is the order of the distance between two neighbouring energy levels. Since, however, δE is proportional to N^{-1} , this condition cannot be in practice fulfilled in general for large spin systems. In fact, we see from our treatment of the autocorrelation function that we even have restricted ourselves to times much smaller than τ_0 . This corresponds physically to allowing transitions between the eigenstates in an energy shell E with an experimental inaccuracy $\Delta \tilde{E}$, which are caused by the non-secular perturbation. Accordingly this leads us to take eventually as a possible definition for the isolated susceptibility

$$\chi_{is}^* = g\mu_0 \sum_{\tilde{E}} \frac{\partial}{\partial H} \{ \rho_{\tilde{E}} \langle \tilde{S}_3 \rangle_{\tilde{E}} \} e^{-\beta \tilde{E}} / \sum_{\tilde{E}} \rho_{\tilde{E}} e^{-\beta \tilde{E}} \quad (5.11)$$

instead of (5.10). In equation (5.11) \tilde{E} are the eigenvalues of the coarse grained operator $\tilde{\mathcal{H}}$ of the total Hamiltonian \mathcal{H} , which commutes with \tilde{S}_3 . Furthermore $\rho_{\tilde{E}}$ is the number of eigenstates between \tilde{E} and $\tilde{E} + \Delta \tilde{E}$ and $\langle \tilde{S}_3 \rangle_{\tilde{E}}$ designates the microcanonical average of \tilde{S}_3 with respect to the total Hamiltonian, which implies that we have averaged the macro observable \tilde{S}_3 over all the eigenstates in the energy shell between \tilde{E} and $\tilde{E} + \Delta \tilde{E}$. As a matter of fact recently Yamamoto³⁾ has used a similar definition, although his arguments in introducing the idea of an approximate Hamiltonian with negligible perturbations are not clear.

The proof of the equivalence between (5.11) and (5.9) can readily be carried out. As can readily be shown, expression (5.11) reduces in the limit of high temperatures to

$$\chi_{is}^* = \beta(g\mu_0)^2 [\langle \langle S_3^2 \rangle \rangle - \sum_{\tilde{E}} \rho_{\tilde{E}} \langle \tilde{S}_3 \rangle_{\tilde{E}}^2 / \sum_{\tilde{E}} \rho_{\tilde{E}}]. \quad (5.12)$$

With the aid of the relation

$$\langle\langle S_3 \rangle_{\mathcal{E}}^2 \rangle\rangle = \frac{\langle\langle S_3 \mathcal{H} \rangle\rangle^2}{\langle\langle \mathcal{H}^2 \rangle\rangle}, \quad (5.13)$$

which can be proved in a similar way as has been done in I for (3.22) i.e., one indeed finds for (5.12)

$$\chi_{is}^* = \frac{\frac{1}{2}H_i^2}{H^2 + \frac{1}{2}H_i^2} \chi_0. \quad (5.14)$$

According to (5.11) we may conclude that the final value reached by the autocorrelation function $\Phi_{33}(t)$ is well in accordance with the expectation that the system should tend to the microcanonical equilibrium with respect to the total Hamiltonian.

It should be emphasized that in deriving (3.25) and (5.13) we have supposed that the (coarse grained) microcanonical averages are differentiable functions respectively of the unperturbed and the total energy. Owing to the coarse graining, however, these assumptions are much weaker than the requirement of Caspers³⁾ and Rosenfeld³⁾ that the diagonal elements of S_3 in the representation of the total Hamiltonian constitute differentiable functions of the total energy.

6. Calculation of the line spectrum in parallel fields in several special cases.

The discussion in this section is also based on the expansion (5.2) of the resolvent operator $(\hat{f}(\phi) + \phi)^{-1}$ which has already been used in the previous section. The quantity $(A, \hat{f}(\phi)B)$ may also be written in the following form with the aid of (3.10) and (3.11)

$$(A, \hat{f}(\phi)B) = \sum_{\substack{m_1, m_2 \\ m_1 + m_2 = 0}} \int_0^{\infty} d\tau e^{-(\rho + im_1\omega_L)\tau} (A, f_{m_1 m_2}(\tau)B) \quad (6.1)$$

with

$$(A, f_{m_1 m_2}(\tau)B) = \langle\langle A^+[B; e^{i\mathcal{H}\tau/\hbar} V_{m_1} e^{-i\mathcal{H}\tau/\hbar}, V_{m_2}]_2 \rangle\rangle / \hbar^2. \quad (6.2)$$

According to (6.1) the spectrum of $(A, \hat{f}(\phi)B)$ exhibits peaks at $\pm i\omega_L$ and $\pm 2i\omega_L$. Moreover, from (6.1) we see that the following condition is fulfilled, since we have confined ourselves to systems where there are present either a large magnetic field \mathbf{H} or a strong exchange interaction

$$|(A, \{\hat{f}(\phi) - \hat{f}(0)\}B)| \ll |(A, \{\hat{f}(0) + \phi\}B)|. \quad (6.3)$$

As a consequence we may keep in a good approximation only the first two terms in the expansion (5.2) with which the corrections on the asymptotic behaviour of the autocorrelation function can be studied. With the

aid of the linearity condition this reduces to

$$\hat{\Phi}_{33}(\rho) = \beta(g\mu_0)^2 \left[\frac{(\langle S_3 \rangle_E, \langle S_3 \rangle_E)}{\rho} + \frac{(S_3, S_3) - (\langle S_3 \rangle_E, \langle S_3 \rangle_E)}{\rho + 1/\tau_s} + \left(\left\{ \frac{\langle S_3 \rangle_E}{\rho^*} + \frac{S_3 - \langle S_3 \rangle_E}{\rho^* + 1/\tau_s} \right\}, \{f(0) - f(\rho)\} \left\{ \frac{\langle S_3 \rangle_E}{\rho} + \frac{S_3 - \langle S_3 \rangle_E}{\rho + 1/\tau_s} \right\} \right) \right]. \quad (6.4)$$

This expression can now be simplified considerably in two cases.

In the first place when the magnetic field \mathbf{H} is zero we have in view of the relation (3.25)

$$\frac{\hat{\Phi}_{33}(\rho)}{\chi_0} = \frac{1}{\rho + 1/\tau_s} \left[1 + \frac{\hat{F}(0) - \hat{F}(\rho)}{\rho + 1/\tau_s} \right], \quad (6.5)$$

where $\hat{F}(\rho)$ is defined by

$$\hat{F}(\rho) = (S_3, f(\rho)S_3)/(S_3, S_3). \quad (6.6)$$

We note that here in the case of zero field \mathbf{H} one has $\hat{F}(0) = 1/\tau_s$. It need of course not be said that the result (6.5) is only valid in the presence of rather strong exchange interaction. The two terms between the brackets in (6.5) may now be thought of being the first two terms of a geometric series and consequently owing to the condition (6.3) equation (6.5) can well be approximated by

$$\frac{\hat{\Phi}_{33}(\rho)}{\chi_0} = \frac{1}{\rho + \hat{F}(\rho)}. \quad (6.7)$$

With the help of (2.3) and (6.7) we obtain immediately for the real and imaginary part of the r.f. susceptibility

$$\frac{\chi''_{33}(\omega)}{\omega\chi_0} = \frac{\text{Re}\hat{F}(i\omega)}{\{\text{Re}\hat{F}(i\omega)\}^2 + \{\omega + \text{Im}\hat{F}(i\omega)\}^2}, \quad (6.8)$$

$$\frac{\chi'_{33}(\omega)}{\chi_0} = 1 - \frac{\omega\{\omega + \text{Im}\hat{F}(i\omega)\}}{\{\text{Re}\hat{F}(i\omega)\}^2 + \{\omega + \text{Im}\hat{F}(i\omega)\}^2}.$$

The computation of $(S_3, f(\tau)S_3)$ is in general impossible. One may however for simplicity assume that this function has a Gaussian shape, in which approximation it is fully determined by the first two even moments of it. So we find

$$(S_3, f(\tau)S_3)/(S_3, S_3) = \langle \nu^2 \rangle \exp\left(-\frac{\langle \nu^4 \rangle}{2\langle \nu^2 \rangle} \tau^2\right). \quad (6.9)$$

Here $\langle \nu^2 \rangle$ and $\langle \nu^4 \rangle$ denote the 2-nd and 4-th moments respectively and

are defined by

$$\begin{aligned}\langle \nu^2 \rangle &= -\text{Tr} [S_3, \mathcal{H}_{\text{II}}][S_3, \mathcal{H}_{\text{II}}]/\hbar^2 \text{Tr} S_3^2, \\ \langle \nu^4 \rangle &= \text{Tr} [S_3; \mathcal{H}_{\text{II}}, \mathcal{H}_0]_2 [S_3; \mathcal{H}_{\text{II}}, \mathcal{H}_0]_2 / \hbar^4 \text{Tr} S_3^2,\end{aligned}\quad (6.10)$$

where only the latter expression depends on the exchange interaction. It need not be said that in general one has to be very careful in making this Gaussian assumption. A direct check for this should be the calculation of the 6-*th* moment.

In order to analyse their experiments at $\mathbf{H} = 0$, Locher and Gorter⁵⁾ have recently introduced phenomenologically a mixed curve for $\chi''_{33}(\omega)$, consisting of a product of a Lorentzian and Gaussian function, that is

$$\frac{\chi''_{33}(\omega)}{\omega\chi_0} = \frac{\rho' \exp(-\alpha^2 \rho^2 \omega^2)}{1 + \rho^2 \omega^2} \quad (6.11)$$

with

$$\begin{aligned}\rho' &= \rho / (\exp \alpha^2) \text{Erfc } \alpha \\ \text{Erfc } \alpha &= \frac{2}{\pi^{\frac{1}{2}}} \int_{\alpha}^{\infty} (\exp - \xi^2) d\xi.\end{aligned}$$

In (6.11) α and ρ are parameters, which can be determined with the aid of the 2-nd and 4-th moments of the expression (6.11). These moments are given by

$$\begin{aligned}\langle \nu^2 \rangle &= (B - 1)/\rho^2, \\ \langle \nu^4 \rangle / \langle \nu^2 \rangle^2 &= \{1 + B(\frac{1}{2}\alpha^{-2} - 1)\} / (B - 1)^2,\end{aligned}\quad (6.12)$$

in which

$$B = \{\alpha\tau^{\frac{1}{2}} (\exp \alpha^2) \text{Erfc } \alpha\}^{-1}.$$

For moderately strong exchange the mixed curve (6.11) can be found from (6.8), if we replace $\hat{F}(i\omega)$ by $\hat{F}(0)$ in the denominators of (6.8), which is allowed because the width of the Lorentzian curve is much smaller than that of the Gaussian one owing to the presence of the strong exchange interaction. With this we obtain in view of (6.9)

$$\begin{aligned}\frac{\chi''_{33}(\omega)}{\omega\chi_0} &= \frac{\tau_s \exp(-\omega^2 \langle \nu^2 \rangle / 2 \langle \nu^4 \rangle)}{1 + \tau_s^2 \omega^2}, \\ \frac{\chi'_{33}(\omega)}{\chi_0} &= \frac{1 - 2\omega\tau_s C\left(\omega \left\{ \frac{\langle \nu^2 \rangle}{2 \langle \nu^4 \rangle} \right\}^{\frac{1}{2}}\right) / \tau^{\frac{1}{2}}}{1 + \tau_s^2 \omega^2},\end{aligned}\quad (6.13)$$

in which $C(x) = (\exp - x^2) \int_0^x (\exp \xi^2) d\xi$. It should be noted that the real

and imaginary part of the r.f. susceptibility from (6.8) are connected with each other by the Kramers-Kronig relations, whereas this is not the case with (6.13). Furthermore the parameters α and ρ , determined by means of (6.13), are identical to those given by the expression (6.12) in the limit of small α , which corresponds to the case of strong exchange.

The second case where formula (6.4) can be simplified is when the interval, in which $\hat{F}(p)$ is considerable, can well be distinguished from the region, which is described by the long time behaviour of $\Phi_{33}(t)$. From the experimental point of view this corresponds to the situation in which the resonance bands can well be separated from the low frequency band. It will be realized under the conditions

$$1/\tau_s \ll \omega_L; (\Delta\omega)_m \ll \omega_L \quad (6.14)$$

that is, for sufficiently high fields H . In (6.14) $(\Delta\omega)_m$ denotes the half width of $\hat{F}_m(p)$, where the latter is defined by

$$\hat{F}_m(p) = \int_0^{\infty} d\tau e^{-(p+im\omega_L)\tau} (S_3, f_{m,-m}(\tau)S_3)/(S_3, S_3). \quad (6.15)$$

Under the condition (6.14) equation (6.4) reduces simply to

$$\frac{\hat{\Phi}_{33}(p)}{\chi_0} = \frac{H^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \left(1 - \frac{\frac{1}{2}H_{i, n. \text{sec}}^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \right) \frac{1}{p} + \frac{\frac{1}{2}H_{i, \text{sec}}^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \frac{1}{p+1/\tau_s} + \frac{1}{\omega_L^2} \sum_{m \neq 0} \frac{1}{m^2} \hat{F}_m(p), \quad (6.16)$$

where we have made use of the relation (3.25). With the aid of (2.3) and (6.16) one finds readily for the r.f. susceptibility

$$\frac{\chi_{33}(\omega)}{\chi_0} = 1 - \frac{H^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \left(1 - \frac{\frac{1}{2}H_{i, n. \text{sec}}^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \right) - \frac{\frac{1}{2}H_{i, \text{sec}}^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \frac{i\omega}{i\omega + 1/\tau_s} - \frac{i\omega}{\omega_L^2} \sum_{m \neq 0} \frac{1}{m^2} \hat{F}_m(i\omega). \quad (6.17)$$

We see from (6.17) that the first two terms on the right hand side of it, which are the only contributions to the final value of $\chi_{33}(\omega)$ for $\omega \rightarrow 0$, is well in agreement with the general result (5.9). Furthermore, the third term in (6.17) represents the low frequency band, while the last term describes the absorption in parallel fields at the Larmor frequency and at twice that frequency. The calculation of the function $(S_3, f_{m,-m}(\tau)S_3)$ is in general impossible. Similar to the case of $(S_3, f(\tau)S_3)$ we may also suppose here for simplicity a Gaussian shape for them. As a result, one needs only to compute the first two moments of these functions, which as a matter

of fact have already been done independently by Caspers⁶⁾ and Hung Cheng⁷⁾ for several simple lattices.

7. *Analysis of the behaviour in perpendicular fields.* The method employed in the preceding sections can easily be extended in order to describe the behaviour of the transverse magnetic moments. In this case the Hamiltonian is split according to (3.1) into an unperturbed part \mathcal{H}_0 and a perturbation V defined respectively by (2.11) and (3.2). We may now introduce in a similar way as in section 4 formally a linear operator $g(\tau)$ defined by

$$\langle E_e\{\bar{s}_k\}\alpha | g(\tau)A | E_e'\{\bar{s}'_k\}\alpha' \rangle = \delta_{E_e E_e'} \delta_{\alpha\alpha'} \prod_{i=1}^3 \delta_{\bar{s}_i, \bar{s}'_i} \sum_m \langle E_e\{\bar{s}_k\}\alpha | [A; V_m^{(1)}(\tau), V_{-m}]_2 | E_e\{\bar{s}_k\}\alpha \rangle / \hbar^2. \quad (7.1)$$

Here A is an arbitrary operator, which is diagonal in the representation $|E_e\{\bar{s}_k\}\alpha\rangle$. As a result, we obtain for the formal solution of $\varphi_{ij}(t)$ (with $i, j = 1, 2$) in terms of Laplace transforms

$$\hat{\varphi}_{ij}(p) = \beta(g\mu_0)^2 \left(S_i, \frac{1}{\hat{g}(p) + p} S_j \right) \quad \text{Re } p \geq 0. \quad (7.2)$$

In formula (7.2) $\hat{\varphi}_{ij}(p)$ and $\hat{g}(p)$ are the Laplace transforms of $\varphi_{ij}(t)$ and $g(t)$ respectively. The expression (7.2) reduces readily to the old result of section 3, if we replace $\hat{g}(p)$ by $\hat{g}(0)$ together with the application of the linearity condition (3.23). It is furthermore also possible to determine the limiting value of $\varphi_{ij}(t)$ for $t \rightarrow \infty$, for which we find that it vanishes. This is obviously in agreement with the establishment of microcanonical equilibrium with respect to the total Hamiltonian.

In order to evaluate the corrections on the asymptotic behaviour, equation (7.2) can be approximated by the first two terms of an expansion similar to (5.2) of the resolvent operator $(\hat{g}(p) + p)^{-1}$ owing to the presence of the strong exchange interaction. With the aid of this approximation we find for the r.f. susceptibility tensor $\chi_{ij}(\omega)$ ($i, j = 1, 2$)

$$\begin{aligned} \frac{\chi_{11}(\omega)}{\chi_0} = \frac{\chi_{22}(\omega)}{\chi_0} &= 1 - \frac{i\omega/2}{i(\omega - \omega_L) + \gamma_2} \left[1 + \frac{\hat{G}^-(0) - \hat{G}^-(i(\omega - \omega_L))}{i(\omega - \omega_L) + \gamma_2} \right] - \\ &- \frac{i\omega/2}{i(\omega + \omega_L) + \gamma_1} \left[1 + \frac{\hat{G}^+(0) - \hat{G}^+(i(\omega + \omega_L))}{i(\omega + \omega_L) + \gamma_1} \right], \quad (7.3) \\ \frac{\chi_{12}(\omega)}{\chi_0} = -\frac{\chi_{21}(\omega)}{\chi_0} &= -\frac{\omega/2}{i(\omega - \omega_L) + \gamma_2} \left[1 + \frac{\hat{G}^-(0) - \hat{G}^-(i(\omega - \omega_L))}{i(\omega - \omega_L) + \gamma_2} \right] + \\ &+ \frac{\omega/2}{i(\omega + \omega_L) + \gamma_1} \left[1 + \frac{\hat{G}^+(0) - \hat{G}^+(i(\omega + \omega_L))}{i(\omega + \omega_L) + \gamma_1} \right], \end{aligned}$$

in which formula $\hat{G}^\pm(p)$ are given by $\int_0^\infty d\tau e^{-p\tau} (S_\mp, g(\tau)S_\pm)/(S_+, S_-)$, which in view of (3.10) and (3.11) can also be written as

$$\hat{G}_m^\pm(p) = \sum_m \int_0^\infty d\tau e^{-(p+im\omega_L)\tau} G_m^\pm(\tau) \quad (7.4)$$

with

$$G_m^\pm(\tau) = \text{Tr} [S_\pm; V_m^{(0)}(\tau), V_{-m}]_2 S_\mp / \hbar^2 \text{Tr} S_+ S_-.$$

We note from (7.4) by comparing it with (3.30) that $\gamma_1 = \hat{G}^+(0)$ and $\gamma_2 = \hat{G}^-(0)$. On account of the smallness of the second term between the brackets on the right hand side of (7.3) we may again as in the previous section write instead of (7.3)

$$\begin{aligned} \frac{\chi_{11}(\omega)}{\chi_0} &= 1 - \frac{i\omega/2}{i(\omega-\omega_L) + \hat{G}^-(i(\omega-\omega_L))} - \frac{i\omega/2}{i(\omega+\omega_L) + \hat{G}^+(i(\omega+\omega_L))} \quad (7.5) \\ \frac{\chi_{12}(\omega)}{\chi_0} &= -\frac{\omega/2}{i(\omega-\omega_L) + \hat{G}^-(i(\omega-\omega_L))} + \frac{\omega/2}{i(\omega+\omega_L) + \hat{G}^+(i(\omega+\omega_L))}. \end{aligned}$$

In particular, we see from (7.5) that the real and imaginary part of $\chi_{11}(\omega)$ are given by

$$\begin{aligned} \frac{\chi''_{11}(\omega)}{\omega\chi_0} &= \frac{1}{2} \left[\frac{\text{Re } \hat{G}^-(i(\omega-\omega_L))}{\{\omega-\omega_L + \text{Im } \hat{G}^-(i(\omega-\omega_L))\}^2 + \{\text{Re } \hat{G}^-(i(\omega-\omega_L))\}^2} + \right. \\ &\quad \left. + \frac{\text{Re } \hat{G}^+(i(\omega+\omega_L))}{\{\omega+\omega_L + \text{Im } \hat{G}^+(i(\omega+\omega_L))\}^2 + \{\text{Re } \hat{G}^+(i(\omega+\omega_L))\}^2} \right] \quad (7.6) \\ \frac{\chi'_{11}(\omega)}{\chi_0} &= 1 - \frac{\omega}{2} \left[\frac{\omega-\omega_L + \text{Im } \hat{G}^-(i(\omega-\omega_L))}{\{\omega-\omega_L + \text{Im } \hat{G}^-(i(\omega-\omega_L))\}^2 + \{\text{Re } \hat{G}^-(i(\omega-\omega_L))\}^2} + \right. \\ &\quad \left. + \frac{\omega+\omega_L + \text{Im } \hat{G}^+(i(\omega+\omega_L))}{\{\omega+\omega_L + \text{Im } \hat{G}^+(i(\omega+\omega_L))\}^2 + \{\text{Re } \hat{G}^+(i(\omega+\omega_L))\}^2} \right]. \end{aligned}$$

According to equation (7.4) the spectrum of $\hat{G}^\pm(p)$ possesses peaks at the points $im\omega_L$ with $m = 0, \pm 1, \pm 2$. Hence the function $\chi''_{11}(\omega)$ from (7.6) exhibits main lines at $\pm\omega_L$ and furthermore weak satellite lines at the frequencies 0 and $\pm 2\omega_L$.

In order to calculate $G_m^\pm(\tau)$ we may again suppose for simplicity a Gaussian shape for the functions so that one needs only to evaluate explicitly the first two even moments of them. Furthermore, it is again allowed owing to the presence of the strong exchange interaction to replace in the denominators in (7.6) $\hat{G}^\pm(i(\omega \pm \omega_L))$ by $\hat{G}^\pm(0)$. In doing so, equation (7.6) re-

duces to

$$\begin{aligned} \frac{\chi''_{11}(\omega)}{\omega\chi_0} &= \frac{1}{2} \sum_{m=-1}^2 c_m \left[\frac{\exp\{-\alpha_m^2(\omega + (m-1)\omega_L)^2\}}{\{\omega - \omega_L - \text{Im } \gamma_1\}^2 + \{\text{Re } \gamma_1\}^2} + \right. \\ &\quad \left. + \frac{\exp\{-\alpha_m^2(\omega - (m-1)\omega_L)^2\}}{\{\omega + \omega_L + \text{Im } \gamma_1\}^2 + \{\text{Re } \gamma_1\}^2} \right], \\ \frac{\chi'_{11}(\omega)}{\chi_0} &= 1 - \frac{\omega}{2} \left[\frac{\omega - \omega_L}{\{\omega - \omega_L - \text{Im } \gamma_1\}^2 + \{\text{Re } \gamma_1\}^2} + \right. \\ &\quad \left. + \frac{\omega + \omega_L}{\{\omega + \omega_L + \text{Im } \gamma_1\}^2 + \{\text{Re } \gamma_1\}^2} \right] - \\ &- \frac{\omega}{\pi^{\frac{1}{2}}} \sum_{m=-1}^2 c_m \left[\frac{C(\alpha_m\{\omega + (m-1)\omega_L\})}{\{\omega - \omega_L - \text{Im } \gamma_1\}^2 + \{\text{Re } \gamma_1\}^2} + \right. \\ &\quad \left. + \frac{C(\alpha_m\{\omega - (m-1)\omega_L\})}{\{\omega + \omega_L + \text{Im } \gamma_1\}^2 + \{\text{Re } \gamma_1\}^2} \right] \end{aligned} \quad (7.7)$$

in which formula

$$c_m = \left[\frac{\pi \langle v^2 \rangle_m^3}{2 \langle v^4 \rangle_m} \right]^{\frac{1}{2}}, \quad \alpha_m = \left[\frac{\langle v^2 \rangle_m}{2 \langle v^4 \rangle_m} \right]^{\frac{1}{2}}$$

with

$$\langle v^2 \rangle_m = \text{Tr} [S_-, V_m] [S_+, V_{-m}] / \hbar^2 \text{Tr } S_+ S_-$$

$$\langle v^4 \rangle_m = \text{Tr} [S_-; V_m, \mathcal{H}_I^{(1)}]_2 [S_+; V_{-m}, \mathcal{H}_I^{(1)}]_2 / \hbar^4 \text{Tr } S_+ S_-$$

From (7.7) we see that for sufficiently high fields, that is for $\omega_L \gg \alpha_m^{-1}$, the main absorption line at ω_L of $\chi''(\omega)$ is described by a combination of a Lorentzian and Gaussian curve. This function has been extensively used by Lacroix⁸⁾ for the description of the absorption lines obtained from the experiments. In conclusion it should be noted that the line shape (7.7) differs from the one introduced by Locher and Gorter in formula (6) i.c. in that it has extra terms, which are the contributions of the satellite lines.

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