

ON THE QUANTUM STATISTICAL THEORY OF RELAXATION IN ISOLATED SPIN SYSTEMS

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Synopsis

The long time approach to statistical equilibrium of a spin system, isolated from the lattice vibrations, is studied, starting from the relaxation function of Kubo and Tomita. Only the behaviour of the longitudinal magnetization is considered. The formalism used is based on the fact that in general a coarse grained description of the behaviour of macroscopic variables is sufficient. For this purpose quantum-mechanical phase cells are introduced, which are characterized by the macro energy and the longitudinal magnetization.

It is derived that in terms of these phase cells the asymptotic behaviour of the system is described by a first order differential equation, the so-called master equation. From this derivation the important condition follows that this master equation is only valid in the presence of either a large magnetic field or a strong exchange interaction between the spins. In investigating the relaxation function with the aid of the master equation use is also made of a linearity condition, which implies that the system is not far from statistical equilibrium. The result for the spin-spin relaxation time, computed in this way, disagrees with that of Caspers, but is the same as found by Hartmann and Anderson. Finally the theories of these authors on spin-spin relaxation are discussed.

1. *Introduction.* The behaviour of the spin-spin relaxation of a paramagnetic system in strong fields and isolated from the lattice vibrations has been the subject of a controverse between the theory of Kronig and Bouwkamp¹⁾, who predicted that the relaxation time should increase as a function of the constant external field and that of Broer²⁾³⁾ who found a decrease. Recently several authors⁴⁾⁵⁾⁶⁾ have evaluated the relaxation time with more dynamical methods and confirmed, although qualitatively, the outcome of the theory of Kronig and Bouwkamp.

The main aim of this paper is to evaluate the spin-spin relaxation time with the help of methods, which are used extensively in the statistical mechanical theory of irreversible processes. In order to compute this characteristic time one may investigate the related problem of how an isolated spin system approaches internal equilibrium. The value, calculated by us in this way for the relaxation time, corresponds to that of Hartmann and Anderson⁵⁾, but differs from the result of Caspers⁶⁾. Furthermore from

our treatment it follows, that the outcome is not only valid for large fields, but also for weak and zero fields, provided the exchange interaction between the paramagnetic ions is strong enough.

Like Caspers we shall use the formalism of Kubo and Tomita⁷⁾, the results of which are briefly given in section 2. In this linear theory an expression is derived for the change of the total magnetic moment of the spin system, after a small magnetic field is suddenly switched off at $t = 0$. In this paper we shall only be interested in the behaviour of the longitudinal magnetization, while the small field is applied along the z -axis. The linear response to this field is given by the so-called relaxation function which becomes proportional to an autocorrelation function for high temperatures.

Since the spin system consists of a very large number of particles, it is to be anticipated that the methods of statistical mechanics can be applied. The macroscopic behaviour of such a many particle system need only be described by a limited number of macroscopic quantities. Examples of these are the total energy and the longitudinal magnetization. The assumption, we shall make here, is that these are the only ones required to describe the behaviour of the magnetization along the z -axis.

In section 3 the quantum-mechanical phase cell is introduced, the general definition of which has been given by Van Kampen⁸⁾. Subsequently the asymptotic behaviour of the autocorrelation function is studied in terms of these phase cells with the aid of the master equation and the assumption that the system is not far from statistical equilibrium. Section 4 deals with the derivation of the master equation for long times in the formalism of Kubo and Tomita with certain assumptions with respect to the randomness of the matrix elements of the non-secular perturbation. In conclusion a short discussion is given in the last section of the theories mentioned above.

2. The relaxation function. We consider here a perfect crystal at whose lattice sites identical paramagnetic ions with spin $s = \frac{1}{2}$ are situated. The particles are supposed to be fixed in space, a not unreasonable assumption in many crystals even at room temperature. This corresponds to the situation that the spin system is isolated from the lattice, that is, the spin-lattice effects are neglected and accordingly the spin-lattice relaxation time is infinite. For simplicity we further confine ourselves to systems of ions having isotropic g -tensors.

A constant magnetic field \mathbf{H} is now applied along the z -axis. In addition to this field \mathbf{H} we suppose there is a small external field \mathbf{h} , which is suddenly switched off at $t = 0$. The linear response of the system to this change is given by the so-called relaxation tensor. Thus, if we assume that from $t = -\infty$ to $t = 0$ the total applied field is equal to $\mathbf{H} + \mathbf{h}$ and for $t > 0$ to \mathbf{H} , then the magnetic moment, if we restrict ourselves to the linear term

in \mathbf{h} , is given by

$$\overline{\mathbf{M}}(t) - \overline{\mathbf{M}}^{(0)} = \Phi(t) \cdot \mathbf{h} \quad (2.1)$$

where $\overline{\mathbf{M}}(t)$ designates the average total magnetic moment at the time t , $\overline{\mathbf{M}}^{(0)}$ the static magnetization in the presence of only the external field \mathbf{H} and $\Phi(t)$ the relaxation tensor.

Kubo and Tomita have derived a general formula for the relaxation tensor in terms of microscopic operators. This is given by the expression

$$\Phi_{ij}(t) = \int_0^\beta d\lambda \operatorname{Tr} \{ \rho_0 M_i M_j(t + i\hbar\lambda) \} - \beta \overline{M_i^{(0)}} \cdot \overline{M_j^{(0)}} \quad \text{for } t \geq 0 \quad (2.2)$$

$$(\chi_0)_{ij} \quad \text{for } t < 0.$$

Here $(\chi_0)_{ij}$ denotes the static susceptibility tensor and $\beta = 1/kT$, k being the Boltzmann's constant and T the temperature of the lattice, with which the spin system is supposed to be in statistical equilibrium for $t < 0$. M_i is the i -th component of the total magnetic moment operator and $M_j(z)$ the Heisenberg operator of M_j for any value of z , given by

$$M_j(z) = e^{iz\mathcal{H}/\hbar} M_j e^{-iz\mathcal{H}/\hbar}, \quad (2.3)$$

where \mathcal{H} is the total Hamiltonian of the system in the absence of the small field \mathbf{h} . Furthermore ρ_0 in equation (2.2) designates the equilibrium density matrix

$$\rho_0 = e^{-\beta\mathcal{H}} / \operatorname{Tr} e^{-\beta\mathcal{H}}. \quad (2.4)$$

The Hamiltonian \mathcal{H} of the spin system is supposed to consist of a Zeeman term, dipole-dipole and exchange interaction, which are denoted by \mathcal{H}_z , \mathcal{H}_{d-d} and \mathcal{H}_{ex} respectively

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{d-d} + \mathcal{H}_{ex}. \quad (2.5)$$

The Zeeman energy is given by

$$\mathcal{H}_z = -HM_3, \quad (2.6)$$

where M_3 is proportional to the total spin operator in the z -direction

$$M_3 = g\mu_0 \sum_j S_{j3}. \quad (2.7)$$

In formula (2.7) S_{j3} is the z -component of the spin operator of the j -th spin, g the gyromagnetic ratio and μ_0 the Bohr magneton.

The last two terms on the right hand side of (2.5) can be divided into a part \mathcal{H}_I , the so-called secular term, which in the representation diagonalizing M_3 consists of all the matrix elements connecting the eigenstates with equal magnetization M_3 , and the non-secular part \mathcal{H}_{II}

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_I + \mathcal{H}_{II} \equiv \mathcal{H}_0 + \mathcal{H}_{II}. \quad (2.8)$$

From the definition it follows directly that a sufficient condition for operator to be secular is that it commutes with M_3 . Consequently we note that the exchange interaction contributes only to the secular part.

The relaxation tensor (2.2) is of a rather complicated form. In most experimental situations, however, the temperatures are so high that we may expand (2.2) up to the first order in β . With the aid of this approximation one obtains the simple result

$$\Phi_{ij}(t) = \beta \text{Tr } M_i M_j(t) / \text{Tr } 1 \quad \text{for } t \geq 0. \quad (2.1)$$

Moreover in this same high temperature limit the only non-zero elements of the static susceptibility $(\chi_0)_{ii} \equiv \chi_0$ are given by

$$\chi_0 = \frac{C}{T} N, \quad (2.2)$$

$$C = \frac{1}{3}s(s+1) (g\mu_0)^2/k,$$

in which formula N is the number of spins in the system, C the Curie constant and $s = \frac{1}{2}$.

In this paper we shall confine ourselves only to the study of the behavior of $\Phi_{33}(t)$ for large systems and under certain conditions on the Hamiltonian which will be specified in the next section.

3. *Evaluation of the asymptotic behaviour of the autocorrelation function with the aid of the master equation.* In order to describe the irreversible approach of the spin system to statistical equilibrium after the turning on of the constant external field \mathbf{h} at $t = 0$, it is not necessary to know precisely in which microscopic state it is. Sufficient for that purpose is to specify the macroscopic state of the system, being characterized by a complete set of slowly varying quantities, the so-called gross or macro observables. This corresponds to the well-known coarse grained description of the behavior of a many particle system. Possible gross observables of the spin system are the macro energy and the magnetization.

The rate of change of a physical quantity is quantum-mechanically given by its commutator with \mathcal{H} , which yields for M_3

$$\frac{\partial M_3}{\partial t} = - \frac{i}{\hbar} [M_3, \mathcal{H}_{\text{II}}], \quad (3.1)$$

where \mathcal{H}_{II} is the non-secular term, defined in the previous section. We shall only be interested in those cases, that there is a clear-cut distinction possible between slowly and rapidly varying quantities. If this is not so, it will not be possible to derive a markovian process for the long time approach to equilibrium. An obvious example of this is the case when the field is zero and there is no exchange interaction. From (3.1) it follows that M_3

slowly varying quantity provided that either the field \mathbf{H} or the exchange interaction is large compared to the non-secular term. Hence we shall confine ourselves to these cases. In a good approximation the macro energy can then be described by the unperturbed Hamiltonian \mathcal{H}_0 .

Since \mathcal{H}_0 commutes with the z -component of the total magnetic moment operator S_3 , a common orthonormal set of eigenfunctions can be found for these operators

$$\begin{aligned}\mathcal{H}_0 |Es\alpha\rangle &= E |Es\alpha\rangle \\ S_3 |Es\alpha\rangle &= s |Es\alpha\rangle\end{aligned}\quad (3.2)$$

with

$$\langle Es\alpha | E's'\alpha' \rangle = \delta_{EE'} \delta_{ss'} \delta_{\alpha\alpha'}. \quad (3.3)$$

Here E, s, α designates a complete set of discrete quantum numbers and the δ -functions represent the Kronecker symbols.

When there are no other slowly varying observables, as will be assumed here, the quantum-mechanical phase cell, denoted by (E, s) , consists of the linear subspace of the Hilbert space, spanned by the set of all eigenfunctions $|Es\alpha\rangle$ with definite eigenvalues E and s .

Since the trace is independent of any representation one uses, the autocorrelation function can be written out explicitly in terms of the set of eigenfunctions (3.2). One obtains readily

$$\langle\langle M_3 M_3(t) \rangle\rangle = \frac{(g\mu_0)^2}{\text{Tr } 1} \sum_{\substack{E, s \\ E', s'}} \rho_{E'}(s') ss' P_t(Es | E's') \quad (3.4)$$

with

$$P_t(Es | E's') = \frac{1}{\rho_{E'}(s')} \sum_{\alpha, \alpha'} |\langle Es\alpha | e^{-it\mathcal{H}/\hbar} | E's'\alpha' \rangle|^2 \quad (3.5)$$

and where $\rho_{E'}(s')$ is the number of the microscopic states $|E's'\alpha'\rangle$ in the phase cell (E', s') . We have used in (3.4) the notation

$$\langle\langle A \rangle\rangle = \text{Tr } A / \text{Tr } 1$$

for the normalized trace of an operator A . With the help of (3.3) we find directly for the initial condition of (3.5)

$$P_{t=0}(Es | E's') = \delta_{EE'} \delta_{ss'}. \quad (3.6)$$

Hence, one sees from the definition (3.5) that $P_t(Es | E's')$ is the probability of finding the system at the time t in the phase cell (E, s) provided that it was initially at $t = 0$ in the phase cell (E', s') .

The processes, occurring here, can now be described in the following way. The system, as a result of the sudden change of the external field from $\mathbf{H} + \mathbf{h}$ to \mathbf{H} , will be in a non-equilibrium state for $t > 0$. The non-secular perturbation, however, causes quantum transitions between the phase cells

and as a consequence this leads to the irreversible change of M_3 . In fact, the asymptotic approach of the system to statistical equilibrium is a Markov process, that is, the probability distribution $P_t(Es|E's')$ satisfies a linear differential equation, the so-called master equation

$$\frac{\partial}{\partial t} P_t(Es|E's') = \sum_{E''s''} W(Es|E''s'') P_t(E''s''|E's') - \left\{ \sum_{E''s''} W(E''s''|Es) \right\} P_t(Es|E's') \quad (3.7)$$

with the initial condition (3.6). In equation (3.7) $W(Es|E''s'')$ is the transition probability per unit time from the phase cell (E'', s'') to (E, s) . From the Dirac time dependent perturbation theory it is easily found that this is given to lowest order in the perturbation by

$$W(Es|E''s'') = \frac{2\pi\delta_{EE''}}{\rho_{E''}(s'')} \sum_{\alpha, \alpha''} |\langle Es\alpha | \mathcal{H}_{II} | E''s''\alpha'' \rangle|^2. \quad (3.8)$$

In the next section the validity of this master equation shall be proved for asymptotic times.

As can readily be seen from (3.8) the following important symmetry relation is valid

$$W(Es|E''s'') \rho_{E''}(s'') = W(E''s''|Es) \rho_E(s). \quad (3.9)$$

Moreover, we note that the unperturbed energy \mathcal{H}_0 is conserved with these transitions and hence the system, being initially in a certain energy shell, will always stay in it. Thus, we have

$$P_t(Es|E's') = \delta_{EE'} P_t(Es|Es'). \quad (3.10)$$

The quantity in (3.8) can now be considered as the matrix elements of an operator W . Then the master equation (3.7) together with the initial conditions (3.6) can readily be solved formally. The result is

$$P_t(Es|E's') = \{e^{-\Omega t}\}_{Es, E's'} \quad (3.11)$$

with

$$\Omega(Es|E's') = \delta_{EE'} [\delta_{ss'} \sum_{s''} W(Es''|Es') - W(Es|Es')]. \quad (3.12)$$

Inserting this into the autocorrelation function (3.4) we obtain

$$\langle\langle M_3 M_3(t) \rangle\rangle = \frac{(g\mu_0)^2}{\text{Tr } 1} \sum_{E, s, s'} \rho_E(s') s \cdot s' \{e^{-\Omega t}\}_{Es, Es'}. \quad (3.13)$$

Owing to the property

$$\sum_s \Omega(Es|Es') = 0 \quad (3.14)$$

and the assumption that $W(Es|Es')$ is an irreducible matrix, it can easily

be shown that

$$\lim_{t \rightarrow \infty} \langle M_3 M_3(t) \rangle = \frac{(g\mu_0)^2}{\text{Tr } 1} \sum_E \rho_E \langle S_3 \rangle_E^2 \quad (3.15)$$

in which formula $\langle S_3 \rangle_E$ is the microcanonical average of S_3 with respect to the unperturbed Hamiltonian \mathcal{H}_0

$$\langle S_3 \rangle_E \equiv \sum_s \rho_E(s) s / \rho_E \quad (3.16)$$

and where ρ_E is the number of microscopic states in the energy shell E

$$\rho_E = \sum_s \rho_E(s). \quad (3.17)$$

Since the change of the external magnetic field at $t = 0$ is taken to be small, we may suppose that the system is not very far from its equilibrium state. As a consequence the expression

$$\sum_s s \Omega(Es|Es')$$

may be expanded up to the linear term in the deviation of s' from its equilibrium value

$$\sum_s s \Omega(Es|Es') = \Gamma(s' - \langle S_3 \rangle_E). \quad (3.18)$$

In general the quantity Γ is still a function of the energy shell E . The auto-correlation function (3.13) reduces with the aid of (3.14) and the approximation (3.18) simply to

$$\langle M_3 M_3(t) \rangle = \frac{(g\mu_0)^2}{\text{Tr } 1} \left[\sum_E \rho_E \langle S_3 \rangle_E^2 + \sum_E \left\{ \sum_s \rho_E(s) s^2 - \rho_E \langle S_3 \rangle_E^2 \right\} e^{-\Gamma t} \right]. \quad (3.19)$$

It is now anticipated that Γ depends very little on E and consequently this dependency shall be neglected here. Accordingly instead of (3.19) we obtain

$$\langle M_3 M_3(t) \rangle = (g\mu_0)^2 \left[\langle \langle S_3^2 \rangle_E \rangle + \{ \langle S_3^2 \rangle - \langle \langle S_3 \rangle_E^2 \rangle \} e^{-\Gamma t} \right]. \quad (3.20)$$

Moreover the spin-spin relaxation time τ_s , defined as $\tau_s \equiv \Gamma^{-1}$, can readily be evaluated from equation (3.18). By multiplying this with $s' \cdot \rho_E(s')$ and summing over E and s' , one obtains

$$\tau_s^{-1} = \Gamma = \frac{1}{\langle \langle S_3^2 \rangle \rangle - \langle \langle S_3 \rangle_E^2 \rangle} \frac{\sum_{E, s, s'} \rho_E(s') s \cdot s' \Omega(Es|Es')}{\text{Tr } 1}. \quad (3.21)$$

It is shown in the appendix with the help of equilibrium theory that the quantity $\langle \langle S_3 \rangle_E^2 \rangle$ in a good approximation is given by

$$\langle \langle S_3 \rangle_E^2 \rangle = \frac{\langle \langle S_3 \mathcal{H}_0 \rangle \rangle^2}{\langle \langle \mathcal{H}_0^2 \rangle \rangle}. \quad (3.22)$$

Furthermore the second factor on the right hand side of (3.21) can also be written in the following form

$$\frac{\sum_{E, s, s'} \rho_E(s') s \cdot s' \Omega(Es|Es')}{\text{Tr } 1} = \frac{1}{\hbar^2} \int_0^\infty d\tau \langle \langle [S_3, \mathcal{H}'_{\text{II}}(\tau)], \mathcal{H}_{\text{II}} S_3 \rangle \rangle \quad (3.23)$$

with

$$\mathcal{H}'_{\text{II}}(\tau) = e^{i\mathcal{H}_{\text{II}}\tau/\hbar} \mathcal{H}_{\text{II}} e^{-i\mathcal{H}_{\text{II}}\tau/\hbar}. \quad (3.24)$$

In deriving formula (3.23) we have made use of the Fourier representation of the δ -function and of the fact that the integrand in it is an even function of t . Combining the formulae (3.22) and (3.23) with (3.21) yields finally after some algebra for the relaxation time

$$\tau_s = \frac{\frac{1}{2}H_{i, \text{sec}}^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \cdot \frac{\hbar^2 \langle \langle S_3^2 \rangle \rangle}{\int_0^\infty d\tau \langle \langle [S_3, \mathcal{H}'_{\text{II}}(\tau)], \mathcal{H}_{\text{II}} S_3 \rangle \rangle}, \quad (3.25)$$

where the quantity $H_{i, \text{sec}}^2$ is defined as

$$\frac{1}{2}H_{i, \text{sec}}^2 = \frac{\text{Tr } \mathcal{H}_1^2}{\text{Tr } M_3^2}. \quad (3.26)$$

Comparing the expression (3.25) with

$$\tau_c = \hbar^2 \langle \langle S_3^2 \rangle \rangle / \int_0^\infty d\tau \langle \langle [S_3, \mathcal{H}'_{\text{II}}(\tau)], \mathcal{H}_{\text{II}} S_3 \rangle \rangle, \quad (3.27)$$

which is derived by Caspers in lowest order of the non-secular perturbation for the spin-spin relaxation time, one finds

$$\tau_s = \frac{\frac{1}{2}H_{i, \text{sec}}^2}{H^2 + \frac{1}{2}H_{i, \text{sec}}^2} \tau_c. \quad (3.28)$$

4. *Derivation of the master equation.* This section shall be devoted to the derivation of the equation (3.13) in the formalism of Kubo and Tomita. Moreover, from this treatment it will be seen under what conditions and for which times the master equation can be justified.

In order to evaluate the autocorrelation function, this can be expanded in the non-secular perturbation in the following way, as have been shown among others by Kubo and Tomita.

$$\begin{aligned} \langle \langle M_3 M_3(t) \rangle \rangle &= \sum_{n=0}^{\infty} \frac{1}{(i\hbar)^n} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \\ &\quad \langle \langle [M_3; \mathcal{H}'_{\text{II}}(t_1), \mathcal{H}'_{\text{II}}(t_2), \dots, \mathcal{H}'_{\text{II}}(t_n)]_n M_3 \rangle \rangle, \end{aligned} \quad (4.1)$$

where the notation for the n -th commutator

$$[M_3; \mathcal{H}'_{II}(t_1), \mathcal{H}'_{II}(t_2), \dots, \mathcal{H}'_{II}(t_n)]_n = \\ = [[\dots [[M_3, \mathcal{H}'_{II}(t_1)], \mathcal{H}'_{II}(t_2)], \dots], \mathcal{H}'_{II}(t_n)] \quad (4.2)$$

has been used for convenience. In terms of the unperturbed eigenfunctions (3.2) formula (4.1) can readily be written as

$$\langle\langle M_3 M_3(t) \rangle\rangle = \frac{(g\mu_0)^2}{\text{Tr}1} \sum_{n=0}^{\infty} \sum_{E, s} s T_t^{(n)}(Es) \quad (4.3)$$

with

$$T_t^{(n)}(Es) = \frac{1}{(i\hbar)^n} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \\ \sum_{\alpha} \langle Es\alpha | [S_3; \mathcal{H}'_{II}(t_1), \mathcal{H}'_{II}(t_2), \dots, \mathcal{H}'_{II}(t_n)]_n | Es\alpha \rangle. \quad (4.4)$$

Before considering the general term in (4.3) we shall first investigate the lowest order terms. It can simply be seen that the term $n = 1$ vanishes. Since the integrand of the second order term depends on the time difference $t_1 - t_2$, one obtains by introducing in it the new variables $\tau'_1 = t_1$, $\tau_1 = t_1 - t_2$ and explicitly writing it out in the representation $|Es\alpha\rangle$

$$T_t^{(2)}(Es) = -\frac{2}{\hbar^2} \int_0^t d\tau'_1 \int_0^{\tau'_1} d\tau_1 \\ \sum_{E', s'} (s - s') \sum_{\alpha, \alpha'} |\langle Es\alpha | \mathcal{H}_{II} | E's'\alpha' \rangle|^2 \cos \frac{(E - E')\tau_1}{\hbar}. \quad (4.5)$$

In contrast to the Zeeman energy, which possesses a discrete eigenvalue spectrum, although with tremendous degeneration, the energy levels of the unperturbed Hamiltonian \mathcal{H}_0 are lying, due to the secular interaction, very densely together constituting a quasi-continuous spectrum. The order of the distance between two neighbouring levels of \mathcal{H}_0 , designated by δE_0 , is proportional to N^{-1} , so that for sufficiently large systems we can restrict ourselves to times, with

$$t \ll \hbar/\delta E_0. \quad (4.6)$$

Under this condition the summation over the energy in (4.5) can be replaced by an integration. Mathematically this is achieved by studying the expression (4.5) in the limit of $N \rightarrow \infty$, while the distance between the spins is kept constant. Consequently the recurrence time of the spin system is thus taken to be infinitely large.

Moreover, if δE_1 denotes an energy interval, over which the variations of the function $\sum_{\alpha, \alpha'} |\langle Es\alpha | \mathcal{H}_{II} | E's'\alpha' \rangle|^2$ with E and E' are small, then for

times, satisfying

$$t \gg \hbar/\delta E_1 \quad (4.7)$$

we may replace the integration bound τ_1 in (4.5) by ∞ , so that we obtain

$$T_t^{(2)}(Es) = -\frac{2t}{\hbar^2} \sum_{s'} \int_0^\infty d\tau \int dE' \cos \frac{(E-E')\tau}{\hbar} (s-s') \sum_{\alpha, \alpha'} |\langle Es\alpha | \mathcal{H}_{\text{II}} | E's'\alpha' \rangle|^2. \quad (4.8)$$

This asymptotic time approximation is justified under the condition

$$\frac{\hbar}{\delta E_1} \ll \left[\frac{2}{\hbar^2} \sum_{s'} \int_0^\infty d\tau \int dE' \cos \frac{(E-E')\tau}{\hbar} (s-s') \sum_{\alpha, \alpha'} |\langle Es\alpha | \mathcal{H}_{\text{II}} | E's'\alpha' \rangle|^2 \right]^{-1} \quad (4.9)$$

that is, the relaxation time of the system has to be much larger than the characteristic time $\hbar/\delta E_1$. After multiplication of the integrand in (4.9) with s and taking the trace over it, one can obtain an estimation of $\hbar/\delta E_1$ by evaluating the correlation time of this quantity. The condition (4.9) is indeed fulfilled if the unperturbed Hamiltonian \mathcal{H}_0 is large compared to the non-secular term. Hence, the asymptotic approximation is valid provided either the external field \mathbf{H} or the exchange interaction is strong.

With the aid of the well-known formula

$$\int_0^\infty dt \cos xt = \pi \delta(x) \quad (4.10)$$

the expression (4.8) can be rewritten in the following form after some algebraic manipulations

$$T_t^{(2)}(Es) = -t \sum_{s'} \rho_E(s') s' \Omega(Es|Es'), \quad (4.11)$$

where $\Omega(Es|Es')$ is defined by equation (3.12).

Our aim is now to investigate the behaviour of the autocorrelation function (4.3) for times, satisfying the conditions (4.6) and (4.7), that is

$$\hbar/\delta E_1 \ll t \ll \hbar/\delta E_0. \quad (4.12)$$

Instead of considering the diagonal matrix element $T_t^{(2)}(Es)$, we could have studied in general the expression

$$\begin{aligned} T_t^{(2)}(Es\alpha|E's'\alpha') &= \\ &= -\frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \langle Es\alpha | [S_3; \mathcal{H}'_{\text{II}}(t_1) \mathcal{H}'_{\text{II}}(t_2)]_2 | E's'\alpha' \rangle. \end{aligned} \quad (4.13)$$

Writing this out in the representation $|E s \alpha\rangle$ yields

$$\begin{aligned} T_t^{(2)}(E s \alpha | E' s' \alpha') &= \\ &= -\frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_{E'', s'', \alpha''} \langle E s \alpha | \mathcal{H}_{II} | E'' s'' \alpha'' \rangle \cdot \langle E'' s'' \alpha'' | \mathcal{H}_{II} | E' s' \alpha' \rangle. \\ &[(s-s') e^{i\{(E-E'')t_1 - (E'-E'')t_2\}/\hbar} + (s'-s'') e^{-i\{(E-E'')t_1 - (E'-E'')t_2\}/\hbar}]. \end{aligned} \quad (4.14)$$

Equation (4.14) is a sum over a very large number of terms, which will tend to cancel each other, if $\langle E s \alpha | \neq \langle E' s' \alpha' |$, since the matrix elements $\langle E s \alpha | \mathcal{H}_{II} | E'' s'' \alpha'' \rangle$ are complex numbers with wildly varying phases. Because of this random phase assumption the non-diagonal elements may be discarded in a good approximation, that is

$$T_t^{(2)}(E s \alpha | E' s' \alpha') = T_t^{(2)}(E s \alpha | E s \alpha) \delta_{EE'} \delta_{ss'} \delta_{\alpha\alpha'}. \quad (4.15)$$

A similar assumption has been used by Van Hove⁹) to derive the master equation in terms of the unperturbed eigenstates in the limit of weak coupling. It is the so-called δ -singularity property of the perturbation.

By means of the equation (4.15) we may now write for the $2n$ -th order term of (4.4)

$$\begin{aligned} T_t^{(2n)}(E s) &= \left(\frac{-1}{\hbar^2}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{2n-1}} dt_{2n} \\ &\sum_{\alpha} \langle E s \alpha | [S_3; \mathcal{H}'_{II}(t_1), \mathcal{H}'_{II}(t_2)]_d \mathcal{H}'_{II}(t_3), \mathcal{H}'_{II}(t_4)]_d \dots]_{2n, d} | E s \alpha \rangle \end{aligned} \quad (4.16)$$

where the subscript d indicates that we only keep the diagonal elements in the representation $|E s \alpha\rangle$ of the operator between the brackets. Since (4.16) is only a function of the time differences $t_1 - t_2, t_3 - t_4, \dots$ and $t_{2n-1} - t_{2n}$, the new variables

$$\tau_1 = t_1 - t_2, \tau_2 = t_3 - t_4, \dots, \tau_n = t_{2n-1} - t_{2n}, \tau'_1 = t_1, \tau'_2 = t_3, \dots, \tau'_n = t_{2n-1}$$

can be introduced, so that equation (4.16) reduces to

$$\begin{aligned} T_t^{(2n)}(E s) &= \left(\frac{-1}{\hbar^2}\right)^n \int_0^t d\tau'_1 \int_0^{\tau'_1} d\tau_1 \dots \int_0^{\tau'_{n-1}-\tau_{n-1}} d\tau'_n \int_0^{\tau'_n} d\tau_n \\ &\sum_{\alpha} \langle E s \alpha | [S_3; \mathcal{H}'_{II}(\tau_1) \mathcal{H}_{II}]_d \mathcal{H}'_{II}(\tau_2) \mathcal{H}_{II}]_d \dots]_{2n, d} | E s \alpha \rangle. \end{aligned} \quad (4.17)$$

As we are interested in times satisfying the condition (4.12), one obtains by using the asymptotic time integration in equation (4.17)

$$\begin{aligned} T_t^{(2n)}(E s) &= \frac{1}{n!} \left(\frac{-t}{\hbar^2}\right)^n \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \dots \int_0^\infty d\tau_n \\ &\sum_{\alpha} \langle E s \alpha | [S_3; \mathcal{H}'_{II}(\tau_1) \mathcal{H}_{II}]_d \mathcal{H}'_{II}(\tau_2) \mathcal{H}_{II}]_d \dots]_{2n, d} | E s \alpha \rangle \end{aligned} \quad (4.18)$$

or explicitly writing it out in the representation $|Es\alpha\rangle$ and application of formula (4.10)

$$T_t^{(2n)}(Es) = \frac{1}{n!} \left(\frac{-t}{\hbar^2} \right)^n \sum_{\alpha, \{s^{(i)}, \alpha^{(i)}\}} \tilde{\Omega}(Es\alpha | Es^{(1)}\alpha^{(1)}) \tilde{\Omega}(Es^{(1)}\alpha^{(1)} | Es^{(2)}\alpha^{(2)}) \dots \tilde{\Omega}(Es^{(n-1)}\alpha^{(n-1)} | Es^{(n)}\alpha^{(n)}) s^{(n)} \quad (4.19)$$

with

$$\tilde{\Omega}(Es\alpha | Es'\alpha') = 2\pi [\delta_{ss'} \sum_{s'', \alpha''} |\langle Es\alpha | \mathcal{H}_{II} | Es''\alpha'' \rangle|^2 - |\langle Es\alpha | \mathcal{H}_{II} | Es'\alpha' \rangle|^2]. \quad (4.20)$$

In equation (4.19) the summation is taken over the whole set of quantum numbers $\{s^{(i)}, \alpha^{(i)}\}$, $i = 1 \dots n$.

A second random phase assumption has yet to be made in the expression (4.19), namely the quantity $\tilde{\Omega}(Es\alpha | Es'\alpha')$ between two definite phase cells (E, s) and (E', s') shall also be a wildly varying function of the microscopic quantum numbers α and α' , so that we can replace the factors in (4.19) by their averages. In doing so we get

$$T_t^{(2n)}(Es) = \frac{1}{n!} \left(\frac{-t}{\hbar^2} \right)^n \sum_{\{s^{(i)}\}} \Omega(Es | Es^{(1)}) \Omega(Es^{(1)} | Es^{(2)}) \dots \Omega(Es^{(n-1)} | Es^{(n)}) \rho_E(s^{(n)}) s^{(n)} \quad (4.21)$$

in which formula $\Omega(Es | Es')$ is given by (3.12). Inserting this into equation (4.3) yields for the autocorrelation function for asymptotic times

$$\langle\langle M_3 M_3(t) \rangle\rangle = \frac{(g\mu_0)^2}{\text{Tr}1} \sum_{n=0}^{\infty} \sum_{E, s, \{s^{(i)}\}} \frac{1}{n!} \left(\frac{-t}{\hbar^2} \right)^n \Omega(Es | Es^{(1)}) \Omega(Es^{(1)} | Es^{(2)}) \dots \Omega(Es^{(n-1)} | Es^{(n)}) \rho_E(s^{(n)}) s^{(n)} \cdot s \quad (4.22)$$

which is precisely formula (3.13) in matrix notation.

From the experimental point of view this long time behaviour corresponds to the so-called relaxation or low frequency band. Resonance phenomena, which are also found in parallel fields, are strongly connected with terms that have been here neglected due to the asymptotic time integrations. These terms are clear manifestations of the non-markovian character of the approach of the spin system to statistical equilibrium. They will be further investigated in a subsequent paper.

5. *Discussion.* Several authors among whom Caspers⁶⁾ and Hartmann and Anderson⁵⁾, have recently evaluated the spin-spin relaxation time, thereby finding different results. The relaxation time, computed by Hartmann and Anderson is identical to our result. In their more phenomenological derivation they suppose that the Zeeman energy and the

secular interaction constitutes two different statistical systems, each describable by a temperature, that is the density matrix is assumed to be in the high temperature approximation of the form

$$\rho(t) = 1 - \mathcal{H}_z/kT_z - \mathcal{H}_I/kT_I. \quad (5.1)$$

However, it is not at all obvious under what conditions this assumption is justified. Moreover, their derivation is not valid in the case of zero external field. From our point of view (5.1) can well be understood in the following way. The long time behaviour of the density matrix, being only a function of the macro observables E and S_3 , can be expanded in the high temperature limit up to the linear order in these variables, provided the system is not far from statistical equilibrium. Instead of E and S_3 one may also use of course the quantities \mathcal{H}_I and S_3 to characterize the phase cells. With this one obtains directly

$$\rho(t) = 1 - \alpha(t) S_3 - \beta(t) \mathcal{H}_I \quad (5.2)$$

which for the case of $\mathbf{H} \neq 0$ is equivalent to the assumption (5.1) and where the changes of the coefficients $\alpha(t)$ and $\beta(t)$, being functions of the time t , are caused by transitions between the different phase cells due to a perturbation viz. the non secular term.

The theory of Caspers, whose final result disagrees with ours, is also based on the formalism of Kubo and Tomita. His starting point is equation (4.1), representing the expression of the autocorrelation function in a perturbation series of the non-secular interaction. In order to study the asymptotic behaviour of this function, however, he does not consider it like us in the representation diagonalizing the unperturbed Hamiltonian \mathcal{H}_0 , but writes it out explicitly in the representation of the total Hamiltonian \mathcal{H} . Hence

$$\langle\langle M_3 M_3(t) \rangle\rangle = \frac{(g\mu_0)^2}{\text{Tr } 1} \left[\sum_{\alpha} (S_3)_{\alpha\alpha}^2 + \Omega(t) \right] \quad (5.3)$$

with

$$\Omega(t) = \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar} \right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \sum_{\alpha \neq \gamma} ([S_3; \mathcal{H}'_{II}(t_1), \mathcal{H}'_{II}(t_2), \dots, \mathcal{H}'_{II}(t_n)]_n)_{\alpha\gamma} (S_3)_{\gamma\alpha} \quad (5.4)$$

and where α, γ are the eigenstates of the total Hamiltonian. Subsequently the n -th commutator is divided into a part proportional to S_3 and the remaining part T_n , which are called respectively the principal diagonal and non-diagonal part

$$\begin{aligned} [S_3; \mathcal{H}'_{II}(t_1), \mathcal{H}'_{II}(t_2), \dots, \mathcal{H}'_{II}(t_n)]_n = \\ = g_n(t_1 - t_2; t_2 - t_3; \dots; t_{n-1} - t_n) S_3 + T_n(t_1, t_2, \dots, t_n) \end{aligned} \quad (5.5)$$

where $g_n(t_1-t_2; \dots; t_{n-1}-t_n)$ is a c -number. The assumption, which is now made is that the non-diagonal parts T_n , inserted in (5.4) can be neglected in the case of the presence of a large magnetic field with respect to the long time behaviour of the autocorrelation function. Here lies the difference with our derivation.

In our opinion there are no physical reasons to ascribe the contributions of these terms T_n for the greater part to the resonance processes, as is done by Caspers. Moreover one could, since the splitting (5.5) is independent of any representation, substitute this into the expression (4.1). From the definition of T_n it follows that

$$\text{Tr } S_3 T_n = 0. \quad (5.6)$$

Consequently one would find by the same derivation for the asymptotic behaviour of the autocorrelation function

$$\langle\langle M_3 M_3(t) \rangle\rangle = \chi_0 e^{-t/\tau_c} / \beta. \quad (5.7)$$

The expression (5.7), however, does not represent the correct behaviour of isolated spin systems, because as can be seen thermodynamically the autocorrelation function has to reach a non-zero value equal to $(\chi_0 - \chi_s)/\beta$, where χ_s is the adiabatic susceptibility. We shall return to this point in a future paper.

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APPENDIX

It will be shown in this appendix that the following equality holds to a good approximation

$$\frac{\langle\langle S_3 \mathcal{H}_0 \rangle\rangle^2}{\langle\langle \mathcal{H}_0^2 \rangle\rangle} = \langle\langle S_3^2 \rangle_E \rangle = \int \rho_E \langle S_3 \rangle_E^2 dE / \int \rho_E dE, \quad (\text{A. 1})$$

where we have made use of the relation

$$\text{Tr } 1 = \int \rho_E dE$$

in writing out the normalized trace.

Let us consider the average value $\langle\langle A \rangle\rangle$ of a physical quantity A . Obviously it can also be written as

$$\langle\langle A \rangle\rangle = \int \rho_E \langle A \rangle_E dE / \int \rho_E dE. \quad (\text{A. 2})$$

The micro-canonical average $\langle A \rangle_E$, being a smooth function of the energy, can now be expanded in powers of the difference $(E - \bar{E})$. As a consequence

we obtain up to the second order in $(E - \bar{E})$ for the expression

$$\begin{aligned} \langle\langle A \rangle\rangle &= \int \rho_E \left[\langle A \rangle_E + (E - \bar{E}) \frac{\partial \langle A \rangle_E}{\partial \bar{E}} + \frac{1}{2} (E - \bar{E})^2 \frac{\partial^2 \langle A \rangle_E}{\partial \bar{E}^2} \right] dE / \int \rho_E dE = \\ &= \langle A \rangle_E + \frac{1}{2} (\langle \mathcal{H}_0^2 \rangle - \bar{E}^2) \frac{\partial^2 \langle A \rangle_E}{\partial \bar{E}^2}. \end{aligned} \quad (\text{A. 3})$$

Here \bar{E} is the average energy

$$\bar{E} = \int \rho_E E dE / \int \rho_E dE \equiv \langle \mathcal{H}_0 \rangle. \quad (\text{A. 4})$$

The expansion of $\langle A \rangle_E$ is allowed, because the density distribution of the energy levels is a sharply peaked function around \bar{E} with a width proportional to $N^{\frac{1}{2}}$, whereas in general $\langle A \rangle_E$ is varying little over this region. Since according to (A. 4) \bar{E} vanishes, equation (A. 3) reduces simply to

$$\langle\langle A \rangle\rangle = \langle A \rangle_E + \frac{1}{2} \langle \mathcal{H}_0^2 \rangle \frac{\partial^2 \langle A \rangle_E}{\partial \bar{E}^2}. \quad (\text{A. 5})$$

We may now apply this general formula to

$$\langle\langle S_3 \mathcal{H}_0 \rangle\rangle = \langle S_3 \mathcal{H}_0 \rangle_E + \frac{1}{2} \langle \mathcal{H}_0^2 \rangle \frac{\partial^2 \langle S_3 \mathcal{H}_0 \rangle_E}{\partial \bar{E}^2}. \quad (\text{A. 6})$$

Moreover, this equation can be simplified with the aid of

$$\langle S_3 \mathcal{H}_0 \rangle_E = \langle S_3 \rangle_E \bar{E} = 0$$

to the form

$$\langle\langle S_3 \mathcal{H}_0 \rangle\rangle = \frac{1}{2} \langle \mathcal{H}_0^2 \rangle \frac{\partial^2 \langle S_3 \mathcal{H}_0 \rangle_E}{\partial \bar{E}^2}. \quad (\text{A. 7})$$

In a similar way it can be derived that

$$\langle\langle S_3^2 \rangle\rangle = \langle S_3^2 \rangle_E + \frac{1}{2} \langle \mathcal{H}_0^2 \rangle \left[\langle S_3 \rangle_E \frac{\partial^2 \langle S_3 \rangle_E}{\partial \bar{E}^2} + 2 \left(\frac{\partial \langle S_3 \rangle_E}{\partial \bar{E}} \right)^2 \right]. \quad (\text{A. 8})$$

Furthermore, application of (A. 5) gives for

$$\langle\langle S_3 \rangle\rangle = \langle S_3 \rangle_E + \frac{1}{2} \langle \mathcal{H}_0^2 \rangle \frac{\partial^2 \langle S_3 \rangle_E}{\partial \bar{E}^2}. \quad (\text{A. 9})$$

Owing to the fact, that equation (A. 9) is zero, one finds instead of (A. 8)

$$\langle\langle S_3^2 \rangle\rangle = \langle \mathcal{H}_0^2 \rangle \left(\frac{\partial \langle S_3 \rangle_E}{\partial \bar{E}} \right)^2. \quad (\text{A. 10})$$

Combining the formulae (A. 7) and (A. 10) leads readily to the desired result (A. 1).

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