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High-temperature dynamics of one-dimensional magnetic systems

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A self-consistent theory is presented which describes the long-wavelength dynamics of one-dimensional Heisenberg systems in the presence of a static magnetic field at high temperatures. The dipole-dipole interaction between the electronic spins (and/or single-ion anisotropy) plays the role of a symmetry-breaking field. Incorporation of interchain coupling is possible within this framework and lowest-order corrections due to this perturbation have been given explicitly. The mode-coupling theory is valid for all orientations of the magnetic field and treats both secular and nonsecular terms of the dipolar interaction. The results can be used to describe magnetic-resonance phenomena (EPR and NMR) in (quasi-)one-dimensional paramagnets. These resonance experiments include the normal EPR transition, the EPR satellites, and the NMR relaxation times including diffusion cutoff effects. The mode-coupling equations generated by the theory have to be solved numerically. Numerical calculations are presented which are relevant to experimental results. A completely new feature of the theory is a "reverse 10/3 effect": at some orientations of the magnetic field the introduction of the nonsecular part of the dipolar interaction produces a *decrease* in the normal EPR linewidth. This pure one-dimensional effect seems in agreement with experiment. The satellite lines present in the spectral functions of the two-spin correlation functions are a consequence of the very pronounced resonance structure of the self-energies associated with these spectral functions. This resonance structure is very sensitive to interchain Heisenberg exchange. Numerical results demonstrate that a small interchain exchange interaction broadens the resonances of the self-energies substantially. A comparison is made between existing theories and this work.

I. INTRODUCTION

The dynamic properties of magnetic systems at high temperatures can be studied with magnetic-resonance techniques.[1] It turns out that the correlation functions being sampled depend strongly on the dimensionality of the magnetic interactions.[2] The theory of magnetic resonance in three-dimensional magnets is simpler than the theory for one- and two-dimensional systems. In three-dimensional paramagnets one can explain the magnetic-resonance phenomena with simple time-dependent perturbation theory. The part of the Hamiltonian which is responsible for the broadening of the resonance lines (hyperfine or dipole-dipole interaction) can be taken into account in a perturbative way. In general, this is not possible in one-dimensional systems. The relative weight of the $\vec{k} \approx 0$ modes is much larger in one-dimensional systems than in three-dimensional paramagnets. The inapplicability of simple time-dependent perturbation theory can be understood readily if one assumes that the long-wavelength modes are diffusive. We expect this hydrodynamic behavior because the magnetization is a conserved quantity. As a consequence of the conservation of the magnetization the $k \approx 0$ modes are very slow, and this, together with their relatively large weight, indicates that these modes will dominate the exchange-narrowing process. The simple time-dependent perturbation theories are not applicable anymore because their validity is based on a difference in time scales, for instance the time scales of the exchange interaction ($\hbar J^{-1}$, J being the Heisenberg exchange constant) and the time scale set by the dipolar interaction. The most dramatic consequence is that the Fourier transforms of correlation functions showing one-dimensional diffusion (i.e., $\propto t^{-1/2}$) have zero-frequency poles. One can conclude from this fact that one-dimensional diffusion is "slow." Usually, the sampled correlation functions decay faster because there are terms present in the Hamiltonian which break the spherical symmetry of the Heisenberg Hamiltonian. These low-symmetry terms, like dipole-dipole interactions between the electronic spins, give rise to a finite lifetime of the $k=0$ mode. An inefficient decay of the long-wavelength modes occurs if the broadening mechanism consists of nonsecular terms. In that case the convergence of zero-frequency Fourier transforms becomes dependent on the resonance frequency. Experimentally, this frequency dependence can be measured by doing magnetic-field-swept resonance experiments at different frequencies of the electromagnetic radiation, or by performing frequency-swept experiments at different magnetic fields. The measurements can sometimes be done directly in the time domain. The determination of the dependence on the Larmor frequency of the experimental results constitutes a powerful tool for investigating

one-dimensional systems.[3-5] The relative importance of secular and nonsecular terms can be influenced easily because both are highly anisotropic in one-dimensional magnetic systems. It is a fascinating consequence of the one dimensionality that the experimentalist can turn on the secular terms of the dipole-dipole interaction, the nonsecular terms, or both, just by changing the orientation of the magnetic field. This effect has no three-dimensional analog.

Several theories have been put forward to explain the magnetic-resonance experiments in one-dimensional magnets. Dietz *et al.*,[6] who studied for the first time the EPR spectrum of a one-dimensional magnetic system, used the theory of Kubo and Tomita.[7] Reiter and Boucher[2] pointed out that the success of the theory of Kubo and Tomita is highly accidental. They used mode-coupling arguments to calculate the EPR spectrum with the magnetic field along the chain ($\theta = 0°$). Recently, Lagendijk and Schoemaker[8] observed a half-field transition in the EPR spectrum of the one-dimensional paramagnet tetramethylammonium-manganese-chloride (TMMC). They used mode-coupling arguments, too. It is interesting to note that the Kubo and Tomita theory fails completely in describing this half-field EPR resonance. This satellite line is a direct consequence of the presence of the nonsecular terms in the dipole-dipole interaction and could not be explained with the theory of Reiter and Boucher[2] because they did not keep the nonsecular terms. These nonsecular terms complicate the situation considerably and therefore Lagendijk and Schoemaker[8] used a simplified mode-coupling theory. The results, however, were satisfactory, because the half-field resonance could be accounted for in a consistent way.

In this paper we want to show that the mode-mode coupling treatment is capable of treating all high-temperature magnetic resonance phenomena which are observed so far in one-dimensional systems in a consequent way. This comprises NMR T_1 data including cutoff effects and all EPR experiments. Some additional EPR experiments have been performed in order to compare the results with our theory. The method we use is an extension of the one used to explain the half-field EPR transition.[8] Our results will be close to a complete mode-coupling treatment of the dynamics. When the nonsecular terms are neglected in our formalism, our theory of the ideal one-dimensional magnetic system is equivalent to the theory of Reiter and Boucher.[2] In addition, we will include the effect on the dynamics of interchain exchange interaction and we will discuss interchain dipolar interaction.

Recently, Boucher *et al.*[9] interpreted their excellent experimental data regarding diffusion cutoff effects in NMR and the $\theta = 0°$ EPR line shape in terms of the so-called "total-spin-torque" (TST) correlation function. We will show that their approach contains several inconsistencies and cannot be considered to be an alternative to the mode-coupling approach. Some spectacular effects, which were recently predicted to be observable in the NMR spectra of one-dimensional magnetic systems[10] will be shown to be incorrect or of academic interest only.

The continued-fraction-expansion method, even in sophisticated forms[11] cannot be applied to the magnetic resonance problem in one-dimensional systems. In one-dimensional magnetic systems the long-time behavior of correlation functions is studied with magnetic resonance, whereas continued fraction expansions or other expansions based on moments are essentially short-time expansions. The continued-fraction method can describe dynamic properties of model systems satisfactorily when simply one time scale is present. When more time scales are present, this method can deal with them only if the time scales can be separated, as in the case of magnetic resonance in three-dimensional paramagnets, where the broadening mechanism and exchange interaction can be separated.

The most important conclusion of this paper will not only be that the mode-mode coupling theory can successfully explain magnetic resonance phenomena in one-dimensional systems, but rather that the mode-mode coupling theory is also the only theory yet explored for which this is true. This does not exclude better theories being developed in the future but it does exclude some existing theories.

In many real quasi-one-dimensional magnetic systems, the influence of the interchain coupling cannot be neglected. A treatment of this effect has been given by Hennessy, McElwee, and Richards[12] using a Kubo-Tomita-type calculation. Such a treatment can only be used for the normal EPR resonance, and is inapplicable for other resonances. We will extend our theory in such a way that the effect of interchain exchange coupling can be incorporated. It is the first time that a mode-coupling solution is given in the frequency domain which includes the effect of interchain exchange coupling. The influence of interchain exchange coupling on the satellites will be shown to be dramatic. We will indicate that the inclusion of the interchain dipolar coupling is straightforward. Incorporation of both interchain interactions is also possible within our theory.

It will be shown that the new observable EPR

resonances are only present when the magnetic field is swept and are not present, or at least are strongly suppressed, when the frequency is varied. It is a general feature of the theory that there is a large difference between scanning the frequency and scanning the magnetic field in a magnetic-resonance experiment on a one-dimensional magnetic system.

In Sec. II the general theory is presented. In Sec. III the theory will be applied to the EPR in one-dimensional magnetic systems. Section IV is devoted to the NMR, including cutoff effects. In Sec. V interchain coupling will be discussed. Section VI contains comparison with other theories. In Sec. VII the concluding remarks will be presented.

II. GENERAL THEORY

A. Method

The total Liouville operator of the electronic spin system is

$$\mathcal{L} = \mathcal{L}_{EZ} + \mathcal{L}_D + \mathcal{L}_H , \tag{2.1}$$

where $\mathcal{L}_{EZ}$ is the Liouville operator of the electronic Zeeman interaction, $\mathcal{L}_D$ is the Liouville operator of the dipolar interaction, and $\mathcal{L}_H$ is the Liouville operator associated with the exchange interaction. Our main interest lies in the $k \approx 0$ region, and exactly in this region the dipolar interaction has to be included in the total Liouville operator (2.1). To take advantage of the translational invariance of the interactions, spin operators will be defined in k space

$$\vec{S}(k,t) = N^{-1/2} \sum_j \vec{S}_j(t) e^{-ikr_j} . \tag{2.2}$$

The Kubo relaxation function will be written[13,14]

$$\langle S^\alpha(k,t) \,|\, S^{\alpha'}(k)\rangle = \int_0^\beta d\lambda \, \langle\langle S^{-\alpha}(-k,t) \times e^{-\hbar\mathcal{L}\lambda} S^{\alpha'}(k)\rangle\rangle , \tag{2.3}$$

where $\alpha = 0$, $(+)$, or $(-)$ depending on which spin operator is involved. The double angular brackets denote thermal averaging. The scalar product (2.3) has several important symmetry properties in the time domain. They will be discussed later on when we will investigate the symmetry properties in the frequency domain. The Mori projection operator method will be used[13,14] to calculate the relaxation function (2.3) in the long-wavelength limit. We will show that the relaxation functions we are seeking usually possess several resonances. For this reason the calculations will be performed in the frequency domain.

The Mori projection operator, which should project onto the "slow" variables, is defined to project onto single operators. In our spin system the projection operator P^α projects onto the single spin-fluctuations states

$$P^\alpha = \sum_k |S^\alpha(k)\rangle [\chi^\alpha(k)]^{-1} \langle S^\alpha(k)| , \tag{2.4}$$

in which $\chi^\alpha(k)$ is the susceptibility

$$\langle S^\alpha(k) \,|\, S^\alpha(k)\rangle .$$

Q^α projects onto the complementary space

$$Q^\alpha = I - P^\alpha . \tag{2.5}$$

The one-sided Fourier transform of the equation of motion of the relaxation function can be written[13,14]

$$\langle S^\alpha(k) \,|\, (z - \mathcal{L})^{-1} S^\alpha(k)\rangle = \chi^\alpha(k) [z - \omega^\alpha(k) - \Gamma^\alpha(k,z)]^{-1} , \tag{2.6}$$

where the self-energy

$$\Gamma^\alpha(k,z) = \langle Q^\alpha \mathcal{L} S^\alpha(k) \,|\, (z - Q^\alpha \mathcal{L} Q^\alpha)^{-1} Q^\alpha \mathcal{L} S^\alpha(k)\rangle \times [\chi^\alpha(k)]^{-1} , \tag{2.7}$$

and where we have the frequency

$$\omega^\alpha(k) = [\hbar \chi^\alpha(k)]^{-1} \langle\langle [S^{-\alpha}(-k), S^\alpha(k)]\rangle\rangle . \tag{2.8}$$

We are interested in the $k = 0$ mode, and for this mode the self-energy can be simplified considerably

$$\Gamma^\alpha(k=0,z) = \langle \mathcal{L}_D S^\alpha(k=0) \,|\, (z - Q^\alpha \mathcal{L} Q^\alpha)^{-1} \mathcal{L}_D S^\alpha(k=0)\rangle \times [\chi^\alpha(k=0)]^{-1} . \tag{2.9}$$

The fluctuation-dissipation theorem connects relaxation functions and correlation functions. One can make a high-temperature expansion of the fluctuation-dissipation theorem. As long as the frequencies of interest are much smaller than k_B, the high-temperature form of the fluctuation-dissipation theorem can be used

$$\langle A \,|\, B\rangle = \beta \langle\langle A^\dagger B\rangle\rangle , \tag{2.10}$$

where A and B are operators. The frequencies we are concerned with are, in temperature units, about 0.5 K, which is much smaller than the temperatures of interest here. Consequently, we will assume that Eq. (2.10) can be used for the dynamic $k = 0$ properties. If necessary one can use the symmetrized product of $A^\dagger$ and B in (2.10).

Reiter and Boucher[2] used mode-coupling arguments to treat the EPR spectrum of a one-dimensional paramagnet with only the secular part of the dipole-dipole interaction as the broadening mechanism. We will include the nonsecular terms of the dipole-dipole interaction in the calculation. In the spirit of the mode-coupling formalism all

four-spin correlations in $\Gamma^{\alpha}(k,z)$ will be decoupled according to

$$\langle\langle ABCD\rangle\rangle = \langle\langle AB\rangle\rangle\langle\langle CD\rangle\rangle + \langle\langle AC\rangle\rangle\langle\langle BD\rangle\rangle + \langle\langle AD\rangle\rangle\langle\langle BC\rangle\rangle, \quad (2.11)$$

where, in the decoupled correlation functions, the projection operator should of course be neglected. This decoupling is well known, and has been discussed several times.[15] If we include the nonsecular terms in the dipolar interaction and apply decoupling (2.11) in expression (2.9), we are left with many products of two-spin correlation functions. We will retain only those products which would possess frequency poles in a perturbation calculation. That is to say, we only keep correlations for which the total component of spin angular momentum vanishes. These terms force us to do the whole calculation self-consistently. The neglect of the nonspherical terms will be discussed at some length at the end of this section. The self-energies can now be expressed as

$$\Gamma^{+}(k=0,z) = -i\beta\hbar^{-2}[\chi^{+}(k=0)N]^{-1}\int_0^{\infty} e^{izt}\sum_k [9|A(k)|^2\Sigma^0(k,t)\Sigma^{+}(k,t) + 8|B(k)|^2\Sigma^{+}(k,t)^2 + 32|B(k)|^2\Sigma^0(k,t)^2 + 4|B(k)|^2\Sigma^{+}(k,t)\Sigma^{-}(k,t) + 16|C(k)|^2\Sigma^{-}(k,t)\Sigma^0(k,t)]\,dt\,, \quad \mathrm{Im}z>0 \quad (2.12a)$$

and

$$\Gamma^0(k=0,z) = -i\beta\hbar^{-2}[\chi^0(k=0)N]^{-1}\int_0^{\infty} e^{izt}\sum_k [4|B(k)|^2\Sigma^0(k,t)\Sigma^{+}(k,t) + 8|C(k)|^2\Sigma^{+}(k,t)^2 + \text{c.c.}]\,dt\,, \quad \mathrm{Im}z>0, \quad (2.12b)$$

where $A(k)$ is given by

$$A(k) = \sum_j e^{-ikr_{ij}}A(r_{ij}), \quad (2.13)$$

in which

$$A(r_{ij}) = -\tfrac{1}{2}g^2_e\beta^2_e r^{-3}_{ij}(3\cos^2\theta - 1), \quad (2.14a)$$

and the other coefficients $B(r_{ij})$ and $C(r_{ij})$ are given by

$$B(r_{ij}) = -\tfrac{3}{4}g^2_e\beta^2_e r^{-3}_{ij}\sin\theta\cos\theta \quad (2.14b)$$

and

$$C(r_{ij}) = -\tfrac{3}{8}g^2_e\beta^2_e r^{-3}_{ij}\sin^2\theta. \quad (2.14c)$$

In Eqs. (2.12), $\Sigma^{\alpha}(k,t)$ denotes

$$\Sigma^{\alpha}(k,t) = \langle\langle S^{-\alpha}(-k)e^{-i(\mathcal{L}_H+\mathcal{L}_{EZ}+\mathcal{L}_D)t}S^{\alpha}(k)\rangle\rangle, \quad (2.15)$$

and θ represents the angle between the magnetic field direction and the chain direction. Equations (2.12) can be readily generalized to nonzero k. These generalized equations should be solved self-consistently. This is a problem of extreme complexity and we will use a simpler approach. The approximate solution we will obtain is estimated to differ from the full mode-coupling solution by less than 10%.

The magnetization is a conserved quantity in a Heisenberg model. This is a manifestation of the high symmetry of a Heisenberg model. The conservation leads to a slow decay of the $k\approx 0$ modes, and of course to no decay at all for the $k=0$ mode. When we introduce an anisotropy term in the Hamiltonian (for instance, the dipole-dipole interaction), the magnetization is not conserved any more. This additional term has lowered the symmetry of the Hamiltonian. As a result of this the $k=0$ mode has a finite lifetime and the $k\approx 0$ modes decay faster. The modes we are discussing here enter in the mode-coupling equations (2.12). The mode-coupling structure of these equations indicates that all modes participate in the damping of the $k=0$ mode. Neglecting $\mathcal{L}_D$ in expression (2.15) would have dramatic consequences in (2.12). The slow decay of the $k\approx 0$ modes results in a very inefficient damping of the $k=0$ mode. As a result the self-energies $\Gamma^{\alpha}(k=0,z)$ would have several poles on the real axis, and the spectral functions associated with these self-energies would possess unphysical characteristics. The retention of $\mathcal{L}_D$ in (2.15) removes the singularities. The $k\approx 0$ modes decay faster due to $\mathcal{L}_D$ and their friction on the $k=0$ mode is effective enough to result in a suppression of the poles in the frequency domain.

The damping of a mode with wave vector k is described by the imaginary part of the self-energy $\Gamma^{\alpha}(k,z)$. The real part of $\Gamma^{\alpha}(k,z)$ gives rise to frequency shifts and could be interpreted in magnetic systems as "internal dynamic magnetic fields." The mode-coupling equations (2.12) indicate that these internal dynamic fields damp the $k=0$ mode. In other words, the real parts of the self-energies of the $k\approx 0$ modes effect the imagin-

ary part of the self-energy of the $k=0$ mode. Of course, this holds for all modes, demonstrating the need for a self-consistent solution of the generalization of Eqs. (2.12). We have emphasized this point for the $k=0$ mode, because we will only solve (2.12), and not its generalization to nonzero k. An approximate solution should take into account these dynamic internal fields.

Before we will turn to the solution of Eqs. (2.12), we will investigate the symmetry of $\Gamma^{\alpha}(k,z)$. The symmetry of $\Gamma^{\alpha}(k,z)$ allows us to reduce the number of independent self-energies from three to two, and exploitation of this symmetry simplifies the calculations considerably. To find the symmetry of $\Gamma^{\alpha}(k,z)$ we will follow closely Götze and Michel,[16] who discuss the symmetry of dynamic succeptibilities. First of all, we will introduce the spectral representation of $\Gamma^{\alpha}(k,z)$, which will be denoted by $\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega)$,

$$\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega) = -\frac{1}{2}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \times \langle Q^{\alpha}\mathfrak{L}S^{\alpha}(k)| e^{-iQ^{\alpha}\mathfrak{L}Q^{\alpha}t} Q^{\alpha}\mathfrak{L}S^{\alpha}(k)\rangle \times [\chi^{\alpha}(k)]^{-1} . \tag{2.16}$$

The connection between $\Gamma^{\alpha}(k,z)$ and $\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega)$ is given by

$$\Gamma^{\alpha}(k,z) = \int_{-\infty}^{+\infty} d\omega \frac{\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega)}{\pi(\omega - z)} . \tag{2.17}$$

When $z = \omega \pm i\epsilon$,

$$\Gamma^{\alpha}(k,\omega \pm i\epsilon) = \tilde{\Gamma}^{\alpha\prime}(k,\omega) \pm i\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega) , \tag{2.18}$$

where $\tilde{\Gamma}^{\alpha\prime}(k,\omega)$ and $\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega)$ are related to each other by the Kramers-Kronig-type relation

$$\tilde{\Gamma}^{\alpha\prime}(k,\omega) = \mathrm{P}\int_{-\infty}^{+\infty} d\omega' \frac{\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega')}{\pi(\omega' - \omega)} , \tag{2.19}$$

in which P indicates principle-value integration.

From (2.16) we conclude that

$$\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega) = \tilde{\Gamma}^{-\alpha\prime\prime}(-k,-\omega) . \tag{2.20a}$$

The time-reversal symmetry can only be indicated properly if the dependence of $\Gamma^{\alpha\prime\prime}(k,\omega)$ on the magnetic field is shown explicitly. We obtain

$$\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega,\omega_0) = \tilde{\Gamma}^{-\alpha\prime\prime}(-k,\omega,-\omega_0) , \tag{2.20b}$$

in which ω_0 denotes the Larmor frequency. Consequently, the imaginary parts of the $k=0$ self-energies of the longitudinal magnetization ($\alpha=0$) are even in frequency and even in ω_0. The self-energies of the transverse magnetization modes ($\alpha=\pm1$) do not possess a well-defined symmetry on their own, but they pass into each other as the result of frequency reflection or as the result of reversal of the magnetic field. The symmetry of $\tilde{\Gamma}^{\alpha\prime}(k,\omega)$ can now be determined with the aid of Eq. (2.19) and the result reads

$$\tilde{\Gamma}^{\alpha\prime}(k,\omega) = -\tilde{\Gamma}^{-\alpha\prime}(-k,-\omega) \tag{2.21a}$$

and

$$\tilde{\Gamma}^{\alpha\prime}(k,\omega,\omega_0) = \tilde{\Gamma}^{-\alpha\prime}(-k,\omega,-\omega_0) . \tag{2.21b}$$

The stability of the system in time is reflected by the fact that

$$\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega) \leqslant 0 .$$

The symmetry of $\Gamma^{\alpha}(k,z)$ can also be established and we find

$$\Gamma^{\alpha}(k,z) = -\Gamma^{-\alpha}(k,-z), \tag{2.22a}$$

$$\Gamma^{\alpha}(k,z)^* = -\Gamma^{-\alpha}(-k,-z^*) , \tag{2.22b}$$

and

$$\Gamma^{\alpha}(k,z,\omega_0) = \Gamma^{-\alpha}(-k,z,-\omega_0) . \tag{2.22c}$$

Having determined the symmetry of $\Gamma^{\alpha}(k,z)$ and of $\tilde{\Gamma}^{\alpha}(k,\omega)$, we will now turn to the solution of Eqs. (2.12). For this purpose we will look in some detail at the functions $\Sigma^{\alpha}(k,t)$, which act as damping kernels. In Eqs. (2.12) the functions $\Sigma^{\alpha}(k,t)$ always occur in pairs. This is a consequence of the mode-coupling approach. Since we are seeking a solution in the frequency domain, we would have to express these pairs of $\Sigma^{\alpha}(k,t)$ in terms of convolution integrals in the frequency domain. The resulting equations would be hopelessly complicated and would probably better be solved in the time domain. A numerical solution in the time domain, however, would very likely lose the pronounced resonance structure of the self-energies. We suggest an approximation which enables us to evaluate the convolution integrals analytically. This approximation can be tested afterwards and will be shown to be good, in some cases even excellent. The justification of our approximation with the help of the convolution integrals is straightforward but somewhat involved, and will only be sketched. Actually, two approximations are quite sensible, resulting in a "simple" solution and in an "improved" solution. Both will be discussed.

Suppose we omit the dipolar propagator from the evolution operator of $\Sigma^{\alpha}(k,t)$. In that case we are dealing with a "pure" Heisenberg two-spin correlation function. The self-energy in the low frequency and small k limit is known,[14] and given by

$$\lim_{k\to 0}\lim_{z\to 0+i\epsilon}\langle Q^\alpha \mathcal{L}_H S^\alpha(k)|(z-Q^\alpha\mathcal{L}_H Q^\alpha)^{-1}Q^\alpha\mathcal{L}_H S^\alpha(k)\rangle \times[\chi^\alpha(k)]^{-1}=-iDk^2\ , \quad (2.23)$$

in which D is the spin-diffusion coefficient. The occurence of spin diffusion is connected with the conservation of the magnetization. Let us introduce the dipolar and Zeeman propagator next. In the strongly exchange-coupled system we want to describe $\omega_0, \omega_D \ll J/\hbar$, where ω_D is a typical dipolar frequency. Making use of this inequality in the generalization of (2.12) to nonzero k, it can be argued that[2]

$$\Gamma^\alpha(k,z)=\Gamma^\alpha(k=0,z)-iDk^2\ , \quad (2.24)$$

for those wave vectors for which the diffusion law holds. Fortunately, in the one-dimensional wave-vector sums we will perform, only those wave vectors contribute significantly. Inserting (2.24) in (2.6), and taking the high-temperature limit ($T \gg J/k_B$) results in

$$\langle S^\alpha(k)|(\omega+i\epsilon-\mathcal{L})^{-1}S^\alpha(k)\rangle = [\tfrac{1}{3}(|\alpha|+1)]S(S+1) \times\beta[\omega-\alpha\omega_0+i\epsilon+iDk^2 -\Gamma^\alpha(k=0,\omega+i\epsilon)]^{-1}\ , \quad (2.25)$$

which, apart from the factor β, is the one-sided Fourier transform of $\Sigma^\alpha(k,t)$. The principal action of $\Gamma^\alpha(k=0,\omega+i\epsilon)$ in (2.25) is to produce a finite width for this spectral function when k is small and when $\omega=\alpha\omega_0$. If k differs considerably from zero, the influence of $\Gamma^\alpha(k=0,\omega+i\epsilon)$ is small. This illustrates the fact that only the long-wavelength dynamics is influenced noticeably by the dipolar interaction. It can be demonstrated that even if k is small (but if ω differs considerably from ω_0) the retention of $\Gamma^\alpha(k=0,\omega+i\epsilon)$ in the spectral function (2.25) is unnecessary to obtain meaningful results when these functions are used for the damping kernels $\Sigma^\alpha(k,t)$ in order to calculate $\Gamma^\alpha(k=0,\omega+i\epsilon)$. To verify this fact, one should write all $\Sigma^\alpha(k,t)$ in Eqs. (2.12) in their Fourier representation. Neglect of all self-energies then gives always nondiverging results except when the complication $\omega\approx\alpha\omega_0$ occurs in the various terms. This argument indicates that the simplest possible description of the spin dynamics is to set the self-energy in (2.25) equal to a constant

$$\Gamma^\alpha(k=0,\omega+i\epsilon)=\Gamma^\alpha(k=0,\alpha\omega_0+i\epsilon)\equiv-i\Gamma^\alpha\ , \quad (2.26)$$

when Eq. (2.25) is used for the damping kernels $\Sigma^\alpha(k,t)$ *of (2.12).* Whenever one would like to introduce a constant self-energy, it is simple to show that choice (2.26) is the only reasonable one. In the first place, it is only in the neighborhood of $\omega=\alpha\omega_0$ that the influence of $\Gamma^\alpha(k=0,\omega+i\epsilon)$ is important. In the second place, the derivative with respect to frequency of the imaginary part of the self-energy is very small, sometimes even zero, when $\omega=\alpha\omega_0$. This can be checked *a posteriori*. Furthermore, at those orientations of the magnetic field for which the secular part of the dipole-dipole interaction dominates, the spectral functions should be independent of ω_0. Our choice (2.26) has precisely this effect. Consequently, choice (2.26) is the only consistent choice which can be made within this approximation scheme.

There are now two ways to proceed. Using Eq. (2.26) in Eq. (2.25) enables one to transform this equation into the time domain, resulting in damped cosines for the damping kernels $\Sigma^\alpha(k,t)$. The "simple" solution for the $k=0$ dynamics consists of replacing all $\Sigma^\alpha(k,t)$ in (2.12) by

$$\Sigma^\alpha(k,t)=\tfrac{1}{3}(|\alpha|+1)S(S+1)e^{-Dk^2t-\Gamma^\alpha t-i\alpha\omega_0 t}\ . \quad (2.27)$$

The integrations in Eqs. (2.12) can be performed analytically, and the constants Γ^α are determined self-consistently with the help of Eq. (2.26). The "improved" solution can be obtained by replacing in Eqs. (2.12) only one $\Sigma^\alpha(k,t)$ by expression (2.27) in a pair of $\Sigma^\alpha(k,t)$. Which one should be replaced in products like $\Sigma^\alpha(k,t)\Sigma^{\alpha\prime}(k,t)$ will be extracted from the simple solution.

B. Simple solution

Substitution of (2.27) in (2.12) for all functions $\Sigma^\alpha(k,t)$ gives

$$\Gamma^+(k=0,\omega+i\epsilon)=-i\hbar^{-2}c\tfrac{1}{3}S(S+1)(2D)^{-1/2}[\tfrac{9}{2}A^2(0)(-i\omega+i\omega_0+\epsilon+\Gamma^0+\Gamma^+)^{-1/2}+8B^2(0)(-i\omega+2i\omega_0+\epsilon+2\Gamma^+)^{-1/2} +6B^2(0)(-i\omega+\epsilon+2\Gamma^0)^{-1/2}+4B^2(0)(-i\omega+\epsilon+\Gamma^++\Gamma^{+*})^{-1/2}+8C^2(0) \times(-i\omega-i\omega_0+\epsilon+\Gamma^0+\Gamma^{+*})^{-1/2}]\ , \quad (2.28a)$$

and

$$\Gamma^0(k=0,\omega+i\epsilon)=-i\hbar^{-2}c\tfrac{1}{3}S(S+1)(2D)^{-1/2}[4B^2(0)(-i\omega+i\omega_0+\epsilon+\Gamma^0+\Gamma^+)^{-1/2}+4B^2(0)(-i\omega-i\omega_0+\epsilon+\Gamma^0+\Gamma^{+*})^{-1/2} +16C^2(0)(-i\omega+2i\omega_0+\epsilon+2\Gamma^+)^{-1/2} +16C^2(0)(-i\omega-2i\omega_0+\epsilon+2\Gamma^{+*})^{-1/2}]\ , \quad (2.28b)$$

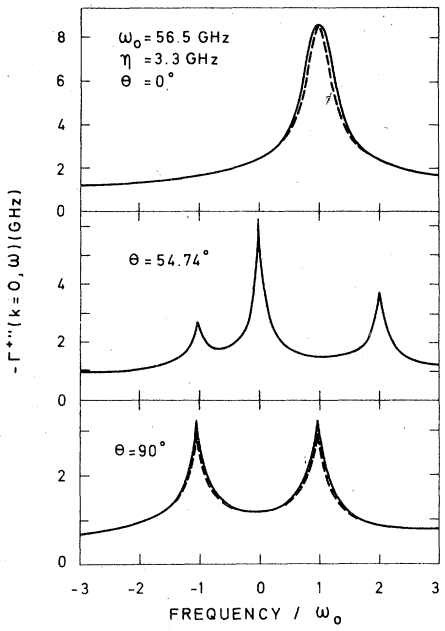

FIG. 1. Self-energy $\tilde{\Gamma}^{+''}(k=0,\omega)$ as a function of frequency. Dashed line: simple theory; solid line: improved theory. The three figures correspond to three different orientations of the magnetic field.

in which c is the lattice constant of the Heisenberg chain. The complex constants Γ^{α} are to be determined self-consistently by introducing (2.26) into (2.28). The three equations one obtains for Γ^{0} and Γ^{+} can be solved very easily numerically. In Figs. 1 and 2 results have been displayed, showing $\tilde{\Gamma}^{\alpha''}(k=0,\omega)$ for three characteristic orientations of the magnetic field as a function of ω: (i) $\theta=0^0$ (no nonsecular terms), (ii) $\theta=54.7^0$ (no secular terms), and (iii) $\theta=90^0$ (only half of the nonsecular terms present). Clearly visible is the resonance structure of $\Gamma^{\alpha''}(k=0,\omega)$ induced by the dipolar interaction. The self-energies depend on both ω and ω_0. From a theoretical point of view the ω dependence is more fundamental, but from an experimental point of view the ω_0 dependence is more interesting. In Figs. 3 and 4 the results of the simple solution are shown as a function of ω_0. The $\theta=0°$ results depend only on $\omega-\omega_0$ and Fig. 1 can also be used for variation of the magnetic field. As expected, the resonance structure is still visible and the connection between the two types of experiments is that the resonance at $2\omega_0$ in the frequency domain should be visible at "half-field" ($\frac{1}{2}\omega$) in a plot in which the magnetic field is varied. Note that the self-energy $\Gamma^{+''}(k=0,\omega)$ does not show a resonance at

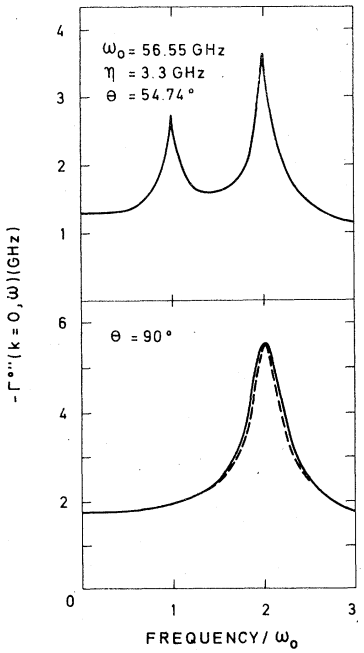

FIG. 2. Self-energy $\tilde{\Gamma}^{0''}(k=0,\omega)$ as a function of frequency. Dashed line: simple theory; solid line, improved theory. The two figures correspond to two different orientations of the magnetic field. When the dashed line is not present, the two theories give the same results. The $\theta=0°$ result has not been presented because $\tilde{\Gamma}^{0''}$ $(k=0,\ \omega)$ is then zero.

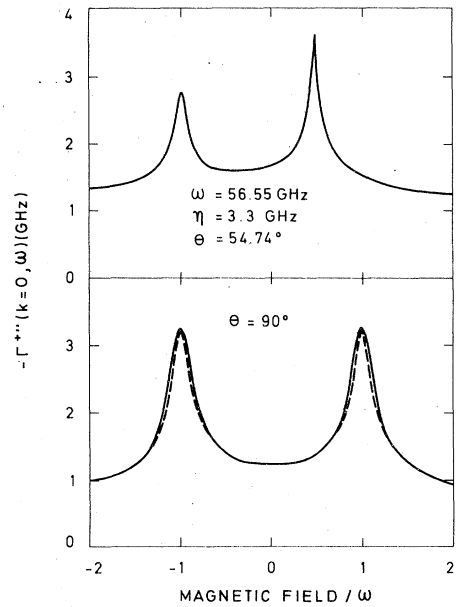

FIG. 3. Self-energy $\tilde{\Gamma}^{+''}(k=0,\omega)$ as a function of the magnitude of the magnetic field. Dashed line: simple theory; solid line: improved theory. The two figures correspond to two different orientations of the magnetic field. When the dashed line is not present, the two theories give the same results.

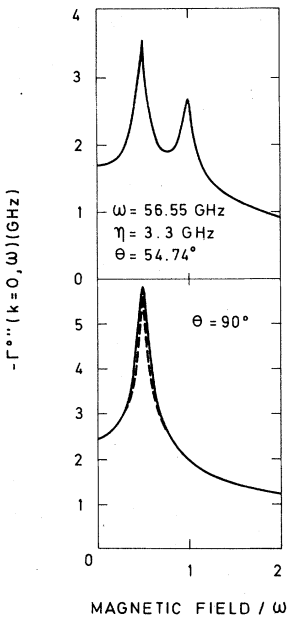

FIG. 4. Self-energy $\tilde{\Gamma}^{0\prime\prime}(k=0,\omega)$ as a function of the magnitude of the magnetic field. Dashed line: simple theory; solid line: improved theory. The two figures correspond to two different orientations of the magnetic field. When the dashed line is not present the two theories give the same results.

the Larmor frequency when $\theta = 54.7°$, which points to a Lorentzian line shape for the spectral function at this orientation. The results in the neighborhood of zero magnetic field should be considered with some reservation if the corrections due to the nonsecular terms are large because the neglect of the nonspherical correlations cannot be justified in this magnetic field region. The parameters Γ^0 and Γ^+ depend on ω_0 through the nonsecular terms and consequently, the calculation of the ω_0 dependence is considerably more time consuming than the ω dependence. Nevertheless, the solution is still simple. In principle, the simple solution can be presented with the help of reduced variables. This feature is lost in the improved solution. For this reason, and because reduced variables usually do not add to the readibility of results, we will not use these reduced variables. The parameters which determine the solution of (2.28) are the orientation of the magnetic field, the magnitude of the magnetic field, the frequency ω, and the value of the anisotropy parameter η,

$$\eta^{3/2} = S(S+1)\left(\frac{D}{c^2}\right)^{-1/2}\omega_D^2\left(\sum_{j=1}^{\infty} j^{-3}\right)^2, \qquad (2.29)$$

in which the dipolar frequency $\omega_D = g_e^2\beta_e^2/c^3\hbar$. The numerical solution of (2.28) is simple and fast and can be obtained easily for all values of the parameters. In Figs. 1–4 some characteristic values have been used for the parameters.

C. Improved solution

Inspection of Fig. 2 shows that the approximation to take $\Gamma^0(k=0,\omega+i\epsilon)$, constant around zero frequency, is indeed an excellent approximation. The approximation regarding $\Gamma^+(k=0,\omega+i\epsilon)$ is good when θ is close to 54° but becomes less so at orientations far away from this orientation. $\Gamma^+(k=0,\omega+i\epsilon)$ is clearly frequency dependent, and the approximation to replace it by a constant in the memory kernels of Eqs. (2.12) is not so good. The improvement consists of setting only $\Gamma^0(k=0,\omega+i\epsilon)$ equal to a constant in pairs of $\Sigma^\alpha(k,t)$. Several pairs do not contain $\Sigma^0(k,t)$; in that case, we still use the same kind of approximation. That is to say, for the product $\Sigma^+(k,t)\Sigma^+(k,t)$ we use Eq. (2.27) for only one $\Sigma^+(k,t)$. Let us now calculate one of the terms in Eqs. (2.12), for instance

$$\int_0^\infty e^{izt}\,\Sigma^+(k,t)\Sigma^0(k,t)\,dt$$

$$= i\tfrac{2}{9}S^2(S+1)^2\,[z-\omega_0+i\Gamma^0+2iDk^2 - \Gamma^+(k=0,z+iDk^2+i\Gamma^0)]^{-1}. \qquad (2.30)$$

The simple solution (2.28) can be recovered if $z=\omega+i\epsilon$ and if we put

$$\Gamma^+(k=0,\omega+i\epsilon+i\Gamma^0+iDk^2) = \Gamma^+(k=0,\omega_0+i\epsilon).$$

A considerable improvement will be to set

$$\Gamma^+(k=0,\omega+i\epsilon+i\Gamma^0+iDk^2) = \Gamma^+(k=0,\omega+i\epsilon-\mathrm{Im}\Gamma^0). \qquad (2.31)$$

A similar procedure has been followed by Reiter and Boucher.[2] This type of approximation will be used for *all* terms in Eqs. (2.12). In (2.31), $\mathrm{Im}\Gamma^0$ is of course equal to zero, but it has been retained there because in the analogous equations for other pairs of $\Sigma^\alpha(k,t)$, $\mathrm{Im}\Gamma^+$, and $\mathrm{Im}\Gamma^-$ occur and they do not vanish. The resultant equations which should be solved self-consistently are

$$\Gamma^{+}(k=0,\omega+i\epsilon) = -i\hbar^{-2}c\tfrac{1}{3}S(S+1)(2D)^{-1/2}\{\tfrac{9}{2}A^2(0)[-i\omega+i\omega_0+\epsilon+i\Gamma^0(k=0,i\epsilon)+i\Gamma^{+}(k=0,\omega+i\epsilon)]^{-1/2}$$

$$+8B^2(0)[-i\omega+2i\omega_0+\epsilon+i\Gamma^{+}(k=0,\omega_0+i\epsilon)+i\Gamma^{+}(k=0,\omega-\omega_0+i\epsilon-\mathrm{Re}\Gamma^{+}(k=0,\omega_0+i\epsilon))]^{-1/2}$$

$$+8B^2(0)[-i\omega+\epsilon+i\Gamma^0(k=0,i\epsilon)+i\Gamma^0(k=0,\omega+i\epsilon)]^{-1/2}$$

$$+4B^2(0)[-i\omega+\epsilon-i\Gamma^{+}(k=0,\omega_0+i\epsilon)^{*}+i\Gamma^{+}(k=0,\omega+\omega_0+i\epsilon+\mathrm{Re}\Gamma^{+}(k=0,\omega_0+i\epsilon))]^{-1/2}$$

$$+8C^2(0)[-i\omega-i\omega_0+\epsilon+i\Gamma^0(k=0,i\epsilon)-i\Gamma^{+*}(k=0,-\omega+i\epsilon)]^{-1/2}] \tag{2.32a}$$

and

$$\Gamma^0(k=0,\omega+i\epsilon) = -i\hbar^{-2}c(1/3)S(S+1)(2D)^{-1/2}[4B^2(0)[-i\omega+i\omega_0+\epsilon+i\Gamma^0(k=0,i\epsilon)+i\Gamma^{+}(k=0,\omega+i\epsilon)]^{-1/2}$$

$$+4B^2(0)[-i\omega-i\omega_0+\epsilon+i\Gamma^0(k=0,i\epsilon)-i\Gamma^{+*}(k=0,-\omega+i\epsilon)]^{-1/2}$$

$$+16C^2(0)[-i\omega+2\omega_0+\epsilon+i\Gamma^{+}(k=0,\omega_0+i\epsilon)+i\Gamma^{+}(k=0,\omega-\omega_0+i\epsilon-\mathrm{Re}\Gamma^{+}(k=0,\omega_0+i\epsilon))]^{-1/2}$$

$$+16C^2(0)[-i\omega-2\omega_0+\epsilon-i\Gamma^{+*}(k=0,\omega_0+i\epsilon)$$

$$-i\Gamma^{+*}(k=0,-\omega-\omega_0+i\epsilon+\mathrm{Re}\Gamma^{+}(k=0,\omega_0+i\epsilon))]^{-1/2}]. \tag{2.32b}$$

Equations (2.32) form a set of four coupled equations. The principal difference between the structure of (2.28) and of (2.32) is that in the latter, self-energies at different frequencies are coupled. This means that numerical determination at each frequency is required. To determine the effect of varying ω_0 one needs to solve Eqs. (2.32) in the complete frequency domain for each ω_0. In Figs. 1 and 2 we have displayed the results of the frequency dependence of $\tilde{\Gamma}^{\alpha\prime\prime}(k=0,\omega)$. In Figs. 3 and 4 the ω_0 dependence has been presented. Since in these figures the results of the simple solution have also been shown, one can compare both calculations easily. As expected, the largest difference occurs at $\theta=0°$, and the smallest difference at $\theta=54°$. As could be anticipated, the improved solution has the effect of broadening the resonances in the self-energies.

In the section on EPR in one-dimensional magnetic systems (Sec. III) we will discuss in detail the spectral functions which are associated with the self-energies calculated in this section.

D. Local properties

In some cases, for instance in an NMR experiment on one-dimensional systems, one is more interested in local properties than in wave-vector-dependent correlations. It is not difficult to calculate the low-frequency behavior of these local properties, like pair spin correlations because the influence of the $k\approx 0$ modes dominate these correlations also. In other words, Eq. (2.24) can be used for the wave-vector dependence of the self-energies. We obtain

$$\langle S_i^{\alpha}|(\omega+i\epsilon-\mathcal{L})^{-1}S_j^{\alpha}\rangle = N^{-1}\sum_k[e^{ikr_{ij}}\langle S^{\alpha}(k)|(\omega+i\epsilon-\mathcal{L})^{-1}S^{\alpha}(k)\rangle]$$

$$= -i\beta\frac{|\alpha|+1}{6}S(S+1)D^{-1/2}c[-i\omega+i\alpha\omega_0+\epsilon+i\Gamma^{\alpha}(k=0,\omega+i\epsilon)]^{-1/2}. \tag{2.33}$$

$\Gamma^{\alpha}(k=0,\omega+i\epsilon)$ has been calculated [solution of (2.28) or of (2.32)].

E. Note

Before turning to the spectral functions, there are two things which should be clarified. Actually, the self-energy is a second-rank tensor, and we have only calculated its diagonal part. As long as we keep only the secular part of the dipolar interaction, this is exact. However, the nonsecular terms introduce a coupling between correlations of different angular momenta. What is the reason that our exact formalism did not yield equations

for the nondiagonal part of the self-energies? We introduced three projection operators, viz., P^+, P^-, and P^0, but in doing so we did not allow a coupling between the slow variables. This can be done easily through defining a more general projection operator, which would couple the three slow variables and would introduce the necessity of considering correlations like

$$\langle S^+(k)(z-\mathcal{L})^{-1}S^-(k)\rangle . \tag{2.34}$$

The study of these terms introduce a tremendous increase in complexity to the problem. To our knowledge, no dynamic solution is available in which the dipolar interaction has been taken into account fully, that is to say, without separation of secular and nonsecular terms, and taking into account correlations like (2.34). It is the magnetic field which allows us to introduce the partioning in a secular and nonsecular terms, and it is the Heisenberg interaction which makes correlations like (2.34) less important. As long as the nonsecular terms are small, correlations like (2.34) can be neglected. A justification can be given in our case *a posteriori*. If the resulting self-energies have pronounced resonances at positions determined by the magnetic field and widths determined by the dipolar interactions, the neglect of the nonspherical correlations can be justified.

The second point which needs a clarification is the importance of the short-time behavior of the correlation functions. This part of the correlation functions is not at all important in the neighborhood of resonances in the self-energies. However, far away from these resonances, the short-time dependence becomes somewhat more important. The importance of the initial time dependence of the correlation functions increases if the Larmor frequency increases. The result is that some linewidths (for instance the magic-angle EPR linewidth) will be underestimated a little using large Larmor frequencies. We will not correct for this effect because it would introduce an extra parameter in the theory of which no serious estimate can be made. Luckily, the correction is small, and in the majority of experimental linewidth determinations, one can correct experimentally for this effect by studying the dependence of the linewidths on the resonance frequency.

III. SPECTRAL FUNCTIONS AND EPR

The formalism developed in Sec. II is very well suited to treat the EPR absorption in one-dimensional paramagnets. The reason for introducing the particular scalar product (2.3) in the foregoing section is that this product is closely related to the linear response of the system. Absorption of radiation is usually described in terms of the complex susceptibility tensor

$$\chi_{ij}(k,\omega)=\chi'_{ij}(k,\omega)+i\chi''_{ij}(k,\omega) , \tag{3.1}$$

where i and j are Cartesian components or combinations of them. The fluctuation-dissipation theorem connects the imaginary part of the susceptibility with the spectral representation of $\langle S^\alpha(k)|(z-\mathcal{L})^{-1}S^\alpha(k)\rangle$. In an EPR experiment the $k=0$ susceptibility is measured. From now on, the label k will be removed from the susceptibility in this section and $k=0$ is implied.

When the microwave field is polarized circularly and perpendicular to the static magnetic field (whose direction is z by definition), the rate of absorption per volume is[7]

$$P^\perp_{\rm cp}(\omega)=\tfrac{1}{2}\omega H_1^2[\chi'_{xy}(\omega)-\chi'_{yx}(\omega)+\chi''_{xx}(\omega)+\chi''_{yy}(\omega)] . \tag{3.2}$$

The microwave-field x, y, and z components are $H_1\cos\omega t$, $H_1\sin\omega t$, and 0, respectively, in this case. It is advantageous to rewrite the tensor χ in the complex tetragonal axis system, in which $x+iy=+$, $x-iy=-$, and $z=0$. In this new axis system

$$p^\perp_{\rm cp}(\omega)=\tfrac{1}{2}\omega H_1^2\chi''_{++}(\omega) . \tag{3.3}$$

If the radiation is polarized linearly and perpendicular to the static magnetic field, the rate of absorption is given by

$$p^\perp_{\rm lp}(\omega)=\tfrac{1}{8}\omega H_1^2[\chi''_{++}(\omega)+\chi''_{--}(\omega)] , \tag{3.4}$$

where the nondiagonal parts have been neglected. The microwave components in this case are $H_1\cos\omega t$, 0, and 0 for x, y, and z, respectively. The nondiagonal parts of the susceptibility tensor are associated with correlations like (2.34), which were neglected. When the microwaves are polarized parallel to the static magnetic field, the absorption is calculated to be

$$p^\parallel(\omega)=\tfrac{1}{2}\omega H_1^2\chi''_{00}(\omega) . \tag{3.5}$$

It is clear from Eqs. (3.3)–(3.5) that we need to know $\chi''_{\alpha\alpha}(\omega)$. The fluctuation-dissipation theorem connects these dynamic susceptibilities with the spectral representation of $\langle S^\alpha(k=0)|(z-\mathcal{L})^{-1}S^\alpha(k=0)\rangle$, which will be denoted by $\tilde{S}^{\alpha\prime\prime}(\omega)$. The relation between $\tilde{S}^{\alpha\prime\prime}(\omega)$ and $\langle S^\alpha(k=0)|(z-\mathcal{L})^{-1}S^\alpha(k=0)\rangle$ is the same as the relation between $\Gamma^\alpha(k,z)$ and $\tilde{\Gamma}^{\alpha\prime\prime}(k,\omega)$ (see Sec. II). The fluctuation-dissipation theorem implies[14]

$$\chi''_{\alpha\alpha}(\omega)=-\omega\tilde{S}^{\alpha\prime\prime}(\omega) . \tag{3.6}$$

Combination of the fluctuation-dissipation theorem (3.6) with Eqs. (3.3)–(3.5) tells us that the spectral functions $\tilde{S}^{\alpha\prime\prime}(\omega)$ determine the EPR absorption.

We will investigate these spectral functions in detail. One should realize that in case of frequency variation, the widths of the spectral functions may be slightly different from the widths of the EPR absorption if the resonances are very broad due to the factor ω^2 in $P(\omega)$.

The symmetry properties of $\tilde{S}^{\alpha\prime\prime}(\omega)$ will not be considered here explicitly, because it is very easy to derive them from the symmetry properties of the self-energies $\Gamma^{\alpha}(k=0, \omega+i\epsilon)$ [see Eqs. (2.20) and (2.21)]. The functions $\tilde{S}^{\alpha\prime\prime}(\omega)$ depend on both ω and ω_0. Traditionally, in theoretical studies, ω_0 is being held constant, and ω is being varied. Forced by practical considerations, an experimentalist keeps ω constant and ω_0 is being swept. Under certain circumstances there is a one-to-one correspondence between the two situations. One of the conditions is that the resonance lines should be situated very close to the free-electron g value.

Varying the frequency, while keeping the magnetic field constant, is a more natural way of investigating the magnetic system. One is looking at the linear response of one-and-the-same system as a function of the frequency of the external perturbation. In a magnetic field swept experiment, one is looking at the linear response of different systems to one-and-the-same external perturbation. A magnetic field swept experiment cannot be interpreted as the linear response to the perturbation of the static magnetic field. In Sec. II the dependence of $\tilde{\Gamma}^{\alpha}(k=0, \omega)$ on both ω and ω_0 has been calculcated. Therefore it is possible to investigate both situations, (i) ω_0 constant and ω being varied, and (ii) ω constant and ω_0 being varied.

In Figs. 5 and 6 the spectral function $\tilde{S}^{\alpha\prime\prime}(\omega)$ have been displayed as a function of frequency and they correspond to the self-energies shown in Fig. 1 and 2. In Figs. 7 and 8 the spectral functions $\tilde{S}^{\alpha\prime\prime}(\omega)$ have been presented as a function of ω_0, and they correspond to the self-energies displayed in Figs. 3 and 4. As could be anticipated, the resonance structure of the self-energies manifests itself as the appearance of satellites in the spectral functions. Again, there is roughly the correspondence that the resonance at $2\omega_0$ in the frequency domain occurs at $\frac{1}{2}\omega$ in a magnetic field plot. The difference between frequency scanning and magnetic field variation is demonstrated by the pronounced resonance structure in $\tilde{S}^{0\prime\prime}(\omega)$ when ω_0

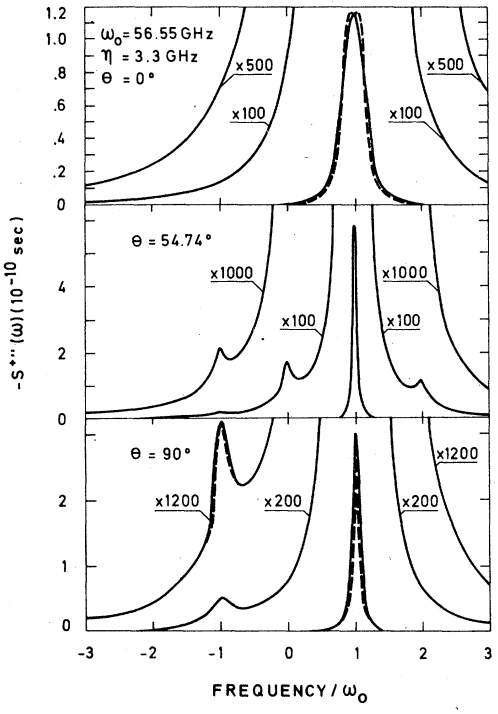

FIG. 5. Spectral function $\tilde{S}^{+\prime\prime}(\omega)$ as a function of frequency. Dashed line: simple theory; solid line: improved theory. The three figures correspond to three different orientations of the magnetic field. When the dashed line is not present, the two theories give the same results.

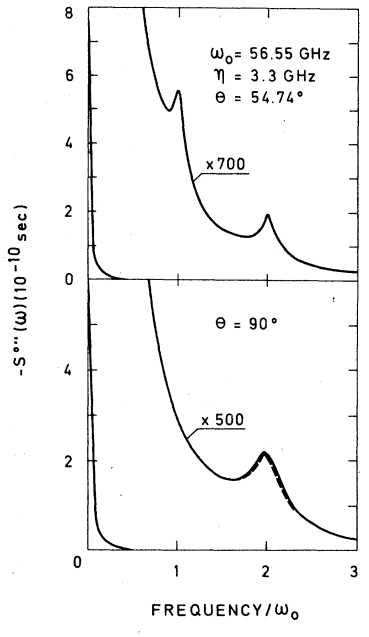

FIG. 6. Spectral function $\tilde{S}^{0\prime\prime}(\omega)$ as a function of frequency. Dashed line: simple theory; solid line: improved theory. The two figures correspond to two different orientations of the magnetic field. When the dashed line is not present, the two theories give the same results.

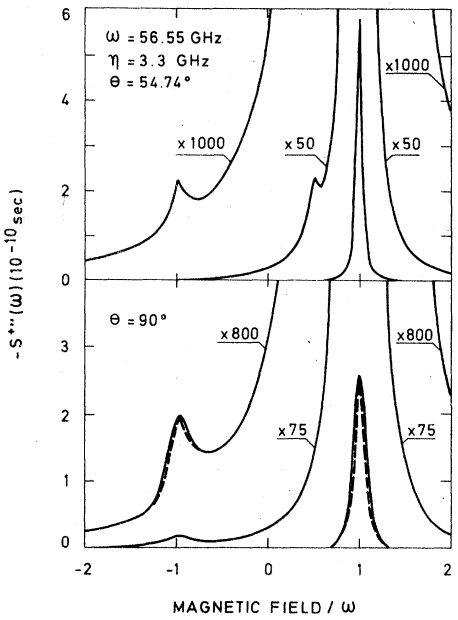

FIG. 7. Spectral function $\tilde{S}^{+''}(\omega)$ as a function of the magnitude of the magnetic field. Dashed line: simple theory; solid line: improved theory. The two figures correspond to two different orientations of the magnetic field. When the dashed line is not present, the two theories give the same results.

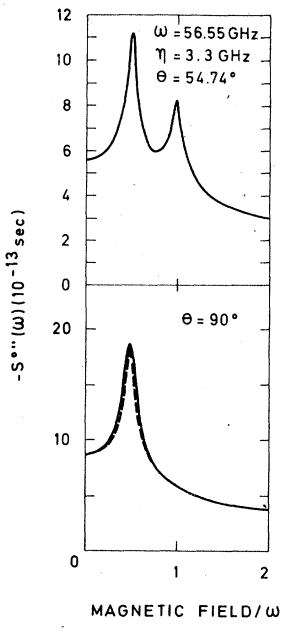

FIG. 8. Spectral function $\tilde{S}^{0''}(\omega)$ as a function of the magnitude of the magnetic field. Dashed line: simple theory; solid line: improved theory. The two figures correspond to two different orientations of the magnetic field. When the dashed line is not present, the two theories give the same results.

is varied. In a frequency swept experiment the satellites of both $\tilde{S}^{+''}$ and $\tilde{S}^{0''}(\omega)$ are suppressed by the fundamental resonance. On the other hand, in a field-swept experiment, only $\tilde{S}^{+''}(\omega)$ shows its fundamental resonance but $\tilde{S}^{0''}(\omega)$ does not, because its fundamental resonance is located at zero frequency in a frequency plot. Some limiting situations can be observed regarding the spectral functions. $\tilde{S}^{0''}(\omega)$ has a Lorentzian shape around zero frequency, and is constant around zero magnetic field. When $\theta = 0°$, $\tilde{S}^{0''}(\omega)$ is a δ function in frequency space. At this orientation, S_z commutes with the Hamiltonian and there is no decay channel for longitudinal magnetization. Of course the width of $\tilde{S}^{0''}(\omega)$ becomes finite when one introduces additional perturbation like interchain dipolar interaction. The fundamental resonance of $\tilde{S}^{+''}(\omega)$ has a Lorentzian shape near the magic angle, and its width exhibits the typical one-dimensional $\omega^{-1/2}$ or $\omega_0^{-1/2}$ dependence at this orientation. The difference between the improved solution and the simple solution can be ignored at the magic angle. At all other angles except in the $\theta = 0°$ region, the improvement consists of a slight broadening of the resonance. In the neighborhood of $\theta = 0°$ the simple solution differs qualitatively from the improved solution. When η is rather large (in the range which produces full half-widths $\geq \frac{1}{2}\omega_0$) the simple solution results in an unphysical double-peaked structure for $\tilde{S}^{+''}(\omega)$ which is caused by the fact that the resonance in the self-energy is too sharp at this orientation.

We will discuss, the some extent, the linewidths of the fundamental resonance of $\tilde{S}^{+''}(\omega)$, that is to say, we will focus on an ordinary EPR experiment. In Fig. 9 we have depicted the full half-width of the EPR linewidth (field scan) as a function of the orientation of the magnetic field. In addition, the experimental data on tetramethylammonium-manganese-trichloride (TMMC) obtained at X band are presented in the same figure. A full angular variation study at K band has been reported previously.[6] The parameter η was adjusted to the best fit. Dietz *et al.*[6] interpreted their results with only the secular part of the dipolar interaction as the broadening mode. Reiter and Boucher employed a completely different theory using the same broadening mechanism.[2] In both cases the linewidths exhibit a $(3\cos^2\theta - 1)^{4/3}$. An evident failure of this approach is a vanishing linewidth at the magic angle. This defect in the theory was clearly recognized by Dietz *et al.*,[6] and an estimation of the nonsecular contribution was given.[12] We have included in Fig. 9 the earlier theories also and scaled them to fit the $\theta = 0°$ linewidth. The improvement we get with our theory is very gratifying. The first ameliora-

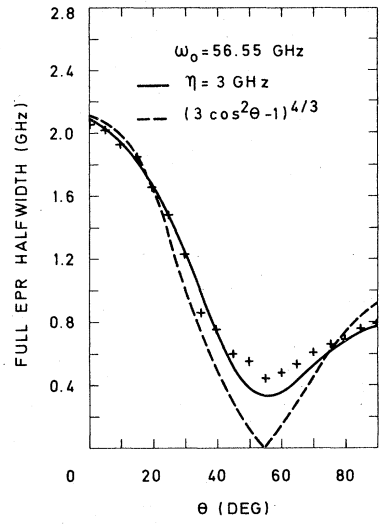

FIG. 9. Full half-width of the EPR line of TMMC as a function of the orientation of the magnetic field. Dashed line: $(3\cos^2\theta-1)^{4/3}$ theories; solid line: this work with $\eta=3$ GHz; crosses: experiment at X band.

tion is the finite linewidth at the magic angle. However, it is also in a different way that the nonsecular terms shine light on the problem. Leaving out the nonsecular part from the dipolar interaction, our theory would also possess the $(3\cos^2\theta-1)^{4/3}$ behavior. Introduction of the nonsecular terms, which is an additional *broadening* mechanism, results in a *narrowing* of the line when θ is near 90°, resulting in a less steep behavior of the linewidth as a function of θ when $\theta>60°$, in agreement with experiment. It is the first time that this pure one-dimensional effect has been reported. The explanation for this effect will be given now. One aspect of the addition of the nonsecular terms is an additional broadening because more damping kernels are inserted, which makes the damping of the $k=0$ mode more effective. Another aspect is that the correlation function connected with the secular broadening, which can be indicated schematically by $\langle\langle S_j^+(t)S_k^0(t)S_l^-(0)S_m^0(0)\rangle\rangle$, decays faster due to the presence of the nonsecular terms in the evolution operator. This causes a change in line shape and a less effective damping of the $k=0$ mode. The latter effect overwhelms the former at $\theta=90°$ and inclusion of the nonsecular terms results in a reduction of the linewidth of about 20% for this orientation. In three-dimensional systems the second effect can be neglected because the dipole-dipole interaction can be disregarded in the propagator, and the introduction of the nonsecular terms always gives rise to an additional broadening.

As far as possible satellites are concerned in $\tilde{S}^{+\prime\prime}(\omega)$, the only resonance which could be observed if linearly polarized microwaves are used is the half-field resonance. The intensity should scale with $\sin\theta\cos\theta$. Together with the request that the principal resonance should be as narrow as possible, the magic angle seems the most suitable orientation for this resonance. Using the value $\eta=3$ GHz, one calculates that this resonance is smaller than the normal resonance by a factor of 3000 for TMMC. Although this resonance has a very small intensity, it might still be observable. A handicap for the observation of this satellite is the impossibility to study the angular dependence due to the presence of the normal resonance. In TMMC this satellite was not observed. An additional complication is that the resonance at half-field in $\tilde{S}^{0\prime\prime}(\omega)$ might interfere due to inhomogeneity of the microwaves. Materials with much smaller linewidths probably do not improve on this situation because the intensity of the satellite will also decrease with decreasing dipolar interaction. Anyway, the resonance is very small and its observability remains an open question.[17]

It is clear that the linewidth of the Lorentzian $\tilde{S}^{0\prime\prime}(\omega)$ in the frequency domain near the origin is given by $\tilde{\Gamma}^{0\prime\prime}(0)$. This quantity shows roughly a $\sin^2\theta$ behavior due to the domination of the corresponding dipolar term. The well-defined resonance at half-field in $\tilde{S}^{0\prime\prime}(\omega)$ in a magnetic field plot has been treated in detail previously.[8] The improved solution increases the linewidths of the half-field resonance when $\theta=90°$ by about 10%. The resonance at the Larmor frequency in $\tilde{S}^{0\prime\prime}(\omega)$ has not been observed yet. Its major feature is the intensity factor $\sin\theta\cos\theta$. The observation of this satellite requires a very homogeneous microwave field in order to minimize the perturbation of the highly allowed resonance in $\tilde{S}^{+\prime\prime}(\omega)$. The simultaneous observation of both resonances in $\tilde{S}^{0\prime\prime}(\omega)$ would be of importance because the calculated relative intensity of both resonances could be checked with experiment. It is interesting to note that both resonances would be suppressed dramatically in a frequency variation study due to the resonance at zero frequency (see Fig. 6).

In the calculation of the linewidths in TMMC, we have adjusted η to get the best agreement, and this value was $\eta=3$ GHz. Calculation of η yields $\eta=6$ GHz.[18] This discrepancy has been found earlier, and several possible explanations have been put forward. One can seek the origin of the difference in the decoupling of the correlation functions. Another possibility is the introduction of single-ion anisotropy as a broadening mechanism, which could lead to a narrowing of the resonance because cross terms of single-ion anisotropy and dipole-dipole interactions occur. We will not

discuss this point further but we would like to stress the following point: without the nonsecular dipole-dipole terms the problem contains one parameter. Consequently, all results should scale with this parameter and a $3\cos^2\theta - 1$ behavior will always be found. Experimental data were interpreted by adjusting this scale parameter. Taking the nonsecular terms in consideration adds an extra parameter to the problem (for instance, the frequency of the microwaves). The results depend on both parameters and a simple scaling law is absent. It turns out that in the case of TMMC, the reduction of η is not only necessary to get absolute agreement with the linewidth for some specific orientation but is also necessary to get the relative angular variation correct. This is very pronounced for the half-field transition in $\tilde{S}^{0\prime\prime}(\omega)$ because at this low field, the nonsecular terms are very important.

We will not report comparisons between experimental and theoretical line shapes. The most important orientations are certainly $\theta = 0°$, $\theta = 54.7°$, and $\theta = 90°$. At $\theta = 0°$ our theory of the ideal chain is equivalent to the theory of Reiter and Boucher.[2] These workers compared their resulting lineshape with the Kubo and Tomita[7] theory. A surpringly good agreement was found between the two theories. The Kubo and Tomita theory is known to describe the $\theta = 0°$ EPR resonance well.[6] At $\theta = 54.7°$ our theory gives a Lorentzian line shape in agreement with experiment. The $\theta = 90°$ experiments are important for various reasons. We will wait with a comparison between experimental and theoretical line shapes until the EPR results are known for various frequencies of the microwaves for this orientation.[19]

IV. NMR IN ONE-DIMENSIONAL MAGNETIC SYSTEMS

Rather than using the expressions for the nuclear T_1 and T_2 of Moriya[20] immediately, the expressions will be derived using a different formalism. This formalism has as major advantage that the time dependence of correlation functions is defined precisely. This is important because small perturbations can have dramatic effects when they occur in evolution operators. The need for the precise description of this time dependence is illustrated by the fact that wrong conclusions have been drawn regarding the NMR spectra of one-dimensional systems due to the use of incorrect propagators.[10]

The NMR in magnetic systems is a clear-cut example of motional narrowing. Motional narrowing can be described as a special case of a weak coupling situation. The Liouville operator for the nuclear problem $\mathcal{L}_N$ can be written

$$\mathcal{L}_N = \mathcal{L}_{NZ} + \mathcal{L}_I + \mathcal{L}_L \,, \tag{4.1}$$

in which $\mathcal{L}_{NZ}$, $\mathcal{L}_I$ and $\mathcal{L}_L$ are the Liouville operators of the nuclear Zeeman interaction, the coupling of the nuclear spins to the lattice and the lattice, respectively. The lattice in this case is the electronic spin system and the coupling between the lattice and the nuclear spin system is via the contact and/or dipole-dipole hyperfine interaction. In three-dimensional systems the lattice can be represented by the Heisenberg exchange coupling and electronic Zeeman interaction. On the other hand, in one-dimensional magnetic systems the dipole-dipole interaction has to be kept in the Hamiltonian of the lattice. The reason is that the $k \approx 0$ modes are very important and would give rise to zero-frequency poles. Any term in the Hamiltonian which lowers the symmetry of the Hamiltonian will act so as to suppress this divergence. As a consequence, the largest of this low-symmetry term has to be kept in the lattice Hamiltonian. It is clear that in any real system such an interaction will always exist (dipole-dipole interaction or single-ion anisotropy). If we would leave out this term the hyperfine interaction would act as the diffusion cutoff. This academic problem is much more difficult to solve because there would be no large separation between the time-scales of the nuclear and electronic spins.[21]

In view of the above remark the Liouville operator of the lattice will be taken into account as

$$\mathcal{L}_L = \mathcal{L}_H + \mathcal{L}_D + \mathcal{L}_{EZ} \,. \tag{4.2}$$

The nuclear spins change very slowly compared to the electronic spins. One would like to have a projection operator P_N which projects onto the nuclear spin space. Oftentimes, one uses projection operators which in some well defined way take the lattice average of the operator on which they work.[22] However, our formalism is based on correlation functions rather than equations of motion for density matrices and a Mori-type projection operator is more suitable. The energies involved in an NMR experiment ($\sim 10^{-3}$ K) are much smaller than k_B in the majority of experiments, and one could immediately write down correlation functions rather than relaxation functions. This will not be done here because the relaxation functions are defined as scalar products and, taking advantage of some properties of scalar products, the resulting equations will look somewhat neater than in the case when they are written in terms of correlation functions.

The complete set of operators consists of nuclear spin operators, electronic spin operators, and combinations of them. The set of nuclear operators will be denoted by I_N. This is a complete

set in the nuclear subspace and contains all nuclear operators of all inequivalent nuclei coupled to the electronic spins. The operators P_N projects onto the subspace of the nuclear operators

$$P_N=\sum_{\alpha,\beta\subset I_N}|\alpha\rangle\langle\alpha|\beta\rangle_{-1}\langle\beta|\,, \tag{4.3}$$

where $\langle\alpha|\beta\rangle_{-1}$ is the $\alpha\beta$th element of the inverse of the matrix $\langle\alpha|\beta\rangle$. The scalar product is defined in the space spanned by all operators. This space is much larger than the space of the electronic spin operators or the space of nuclear spin operators only. The dynamics of the nuclear spins is of course irrelevant for the dynamics of the electronic spins and can be disregarded in the ESR problem. The reverse is obviously not true and the full space has to be used. Q_N projects on the complementary space of P_N

$$Q_N=I-P_N\,. \tag{4.4}$$

Application of the Mori projection-operator technique leads again to exact and useful equations. However, the scalar product of two different nuclear operators does not need to vanish in principle. It is a question of choosing a suitable basis set to minimize the mixing. Anyway, the result is that the evolution of all slow nuclear operators is coupled and the exact equation will be a matrix equation. This equation reads[14]

$$\sum_\beta[z\delta_{\alpha\beta}-\Omega_{\alpha\beta}-\Gamma^N_{\alpha\beta}(z)]\times\langle\beta|(z-\mathcal{L}_N)^{-1}\gamma\rangle=\langle\alpha|\gamma\rangle\,, \tag{4.5}$$

in which

$$\Omega_{\alpha\beta}=\hbar^{-1}\sum_\delta\langle\!\langle[\alpha^\dagger,\delta]]\!\rangle\langle\delta|\beta\rangle_{-1} \tag{4.6a}$$

and

$$\Gamma^N_{\alpha\beta}(z)=\sum_\delta\langle Q_N\mathcal{L}_N\alpha|(z-Q_N\mathcal{L}_NQ_N)^{-1}Q_N\mathcal{L}_N\delta\rangle\langle\delta|\beta\rangle_{-1}\,. \tag{4.6b}$$

All the summations in these equations are over the set I_N. The usefulness of these matrix equations depends on the possibility to expand the proagator $e^{iQ_N\mathcal{L}_NQ_Nt}$ into something more tractable. The way to proceed is to expand this propagator with $\mathcal{L}_I$ as a small parameter. It must be clear by now why the dipolar interaction had to be included. If it had not been included, the expansion with $\mathcal{L}_I$ as a small parameter would not have been very useful because the correlation $\langle\mathcal{L}_I\alpha|(z-\mathcal{L}_H)^{-1}\mathcal{L}_I\beta\rangle$ would diverge for zero frequency. The reason is that in this case one is essentially dealing with an electronic spin pair correlation function which has a zero-frequency pole in the case of one-dimensional diffusion. The expansion reads

$$(z-Q_N\mathcal{L}_NQ_N)^{-1}=(z-\mathcal{L}_{NZ}-\mathcal{L}_L)^{-1}+(z-\mathcal{L}_{NZ}-\mathcal{L}_L)^{-1}\times(-P_N\mathcal{L}_{NZ}+Q_N\mathcal{L}_I)\times(z-\mathcal{L}_{NZ}-\mathcal{L}_L)^{-1}+\cdots\,. \tag{4.7}$$

Inserting this expansion in the expression for the self-energy one calculates that the next nonzero term after the first is at least smaller than the first one by a factor of ω_I/ω_L, ω_I being a characteristic frequency of the hyperfine interaction, and ω_L a characteristic frequency of the lattice. The smallest value for ω_L occurs when it is determined by the dipolar propagator. In Sec. III ω_L has been calculated in this case and demonstrated to be of the order of several hundred Gauss, indeed much larger than ω_I, being of the order of several Gauss. Consequently, there is indeed a separation of time scales and as a result only the first term of expansion (4.7) needs to be used in the self-energy. The self-energies can still be simplified considerably if the proper nuclear operators are used. We will first consider the situation when only one nuclear spin is present. If only one nucleus is involved, a convenient set of nuclear operators is the irreducible spherical tensor operators like I^+, I^-, I^0, $(1/\sqrt{2})(I^+I^0+I^0I^+)$, etc. This set has the useful property that $\langle\!\langle\alpha^\dagger\beta\rangle\!\rangle$ is of order one if α and β are identical, and much smaller if α and β are different operators. Using this basis, the matrix equation can be simplified considerably. The succeptibility $\langle\alpha|\beta\rangle$, α and β being nuclear operators, is essentially a trace in spin space because Eq. (10) can be used, and this trace vanishes in the high-temperature limit when α and β are different nuclear operators. Consequently, the susceptibility matrix is diagonal and so is its inverse. One should realize that neglect of correlations having a ω/k_B term leading in a $1/k_B$ expansion where ω is any relevant frequency, is only correct if these quantities are compared with correlations having a leading term of order one in a $1/k_B$ expansion. Combination of Eq. (4.6b) with the approximation we made with respect to Eq. (4.7) shows that the self-energy of memory matrix is also diagonal. Because the frequency matrix is also diagonal, all slow nuclear operators are decoupled. Furthermore, the fact that the frequencies in an NMR experiment are much smaller than any relevant lattice frequency, can be used to simplify the self-energy even more. The lattice frequency is the frequency scale for

the self-energy $\Gamma^N_{\alpha\alpha}(z)$. The decay of nuclear magnetization is then determined completely by $\Gamma^N_{\alpha\alpha}(z=i\epsilon)\equiv -i\gamma_\alpha$.

After having made some well understood approximations, one arrives at decoupled dynamical equations for the nuclear magnetization

$$\langle I^\alpha \,|\, (z-\mathcal{L}_N)^{-1} I^\alpha\rangle = \tfrac{1}{3}(|\alpha|+1)(I)(I+1) \times (z+\alpha\omega_N+i\gamma)^{-1} , \tag{4.8}$$

in which ω_N denotes the nuclear Larmor frequency. One is only interested in the dynamics of the nuclear magnetization since the aim is to understand the NMR spectra. The presented formalism gives all nuclear correlations, for instance also $\langle (I^0I^+ + I^+I^0) \,|\, (z-\mathcal{L}_N)^{-1}(I^0I^+ + I^+I^0)\rangle$, which could be of use in other situations. In (4.8), I^α represents nuclear spin operators of one nucleus. The extension to include all nuclear operators of inequivalent nuclei is straightforward, leading to uncoupled equations for all of them. The resonance is thus described by a Lorentzian line shape or a sum of Lorentzians and the decay of nonequilibrium nuclear magnetization is being characterized by an exponential decay or a sum of exponentials. If more nuclei are involved with the same Larmor frequency, say protons, but with different linewidths, the resulting linewidth is still Lorentzian if the individual Lorentzians have almost the same linewidth. In that case the linewidth is the average of the individual linewidths. In many calculations this average is calculated, but it should be realized that this in only meaningful if the condition with respect to the individual linewidths if fulfilled. An important complication may occur when the nuclear positions are time dependent. In our language this means that we have to extend the Liouville operator of the lattice (4.2). The way one has included these effects is standard.

In all cases, γ_α is the important parameter and should be compared with experiment. γ_α is essentially a property of the electronic spin system with some geometrical coupling factors involving the nuclei. The calculation of these geometrical factors is rather technical and can be involved. However, the most important part of calculation of the self-energy

$$\langle \mathcal{L}_I I^\alpha \,|\, (i\epsilon - \mathcal{L}_{NZ} - \mathcal{L}_H - \mathcal{L}_D - \mathcal{L}_{EZ})^{-1} \mathcal{L}_I I^\alpha\rangle ,$$

in which α is 0, (+), or (−), consists of the calculation of

$$\langle S_i^\beta \,|\, (i\epsilon - \alpha'\omega_N - \mathcal{L}_H - \mathcal{L}_D - \mathcal{L}_{EZ})^{-1} S_j^\beta\rangle ,$$

in which $\beta = 0$, (+), or (−). The range of $|i-j|$ depends on the convergence of the dipolar part of the hyperfine interaction. Taking into account the relative magnitude of ω_0 compared to ω_N, the two important quantities to be calculated are

$$f^+_{i-j}(i\epsilon) = \langle S_i^+ \,|\, (i\epsilon - \mathcal{L}_H - \mathcal{L}_D - \mathcal{L}_{EZ})^{-1} S_j^+\rangle \tag{4.9a}$$

and

$$f^0_{i-j}(i\epsilon) = \langle S_i^0 \,|\, (i\epsilon - \mathcal{L}_H - \mathcal{L}_D - \mathcal{L}_{EZ})^{-1} S_j^0\rangle . \tag{4.9b}$$

These quantities have been calculated in Sec. II and the results were

$$f^+_{i-j}(i\epsilon) = -i\beta\tfrac{1}{3}S(S+1)D^{-1/2}c \times [\epsilon + i\omega_0 + i\Gamma^+(k=0, i\epsilon)]^{-1/2} , \tag{4.10a}$$

$$f^0_{i-j}(i\epsilon) = -i\beta\tfrac{1}{6}S(S+1)D^{-1/2}c \times [\epsilon + i\Gamma^0(k=0, i\epsilon)]^{-1/2} . \tag{4.10b}$$

It is conventional to write the NMR relaxation

$$\gamma_0 = T_1^{-1} = \frac{2S(S+1)}{3}\sum_j A_j f^0_j(i\epsilon) + B_j\, f^+_j(i\epsilon) , \tag{4.11}$$

in which essentially the real parts of expressions (4.9) are meant. In such a way the geometrical factors are separated. The largest problem is now that these geometrical factors are usually not known precisely because of the incertainty in the positions of the ions (for instance protons) subject to the coupling with the electron spin Even if the positions are known or quessed, the calculations of the dipolar factors need not converge very rapidly.

In the case of the TMMC, the $\theta = 0°$ and $\theta = 90°$ proton T_1's were measured very thoroughly.[9] Clément measured the complete angular dependence.[23] In Fig. 10 we present our calculation of T_1^{-1} and $T_{1\rho}^{-1}$. In a $T_{1\rho}$ experiment a different nuclear correlation is excited, and consequently, different geometrical factors are involved. We have used the geometrical factors of Clément referring to a simplified model of proton locations.[23] The parameter η has been adjusted. The experimental data in this figure are from Clément. The fit is more than satisfactory, and the value of η which would result from the used parameters is 4.75 GHz. This should be compared to $\eta = 3$ GHz obtained from the EPR data. The uncertainty in the proton locations should be recalled.[9,23]

We note that our theory gives only the diffusive contribution. Under those experimental conditions for which the damping is ineffective, for instance magic-angle experiments on $\tilde{S}^{+\prime}(\omega)$ or determination of the magnetic field dependence of $f^0_j(i\epsilon)$, one might reach a situation in which the short-time dependence of the correlations becomes

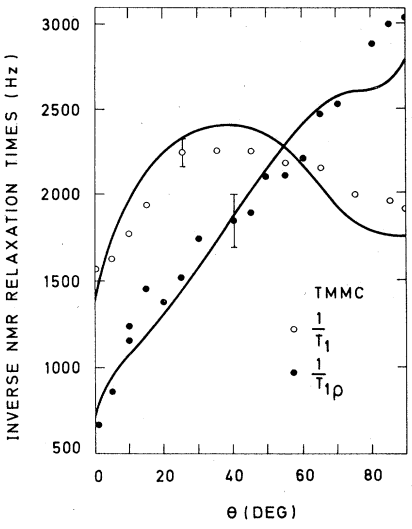

FIG. 10. T_1^{-1} and $T_{1\rho}^{-1}$ of protons in TMMC as a function of the orientation of the magnetic field. Solid line: this work using geometrical coupling coefficients of Ref. 23 with $\eta = 4.75$ GHz. Circles: experiment of Ref. 23.

important. We have discussed this point at the end of Sec. II.

The angular dependence of the nuclear spin lattice relaxation times is much less fundamental than the angular dependence of the electronic spin-relaxation times. The characteristic one-dimensional angular dependence of the spin dynamics is masked in an NMR experiment by the uninteresting angular dependence of the geometrical coupling factors. If the NMR of the magnetic ions could be observed, a situation would be present comparable to the EPR experiments, with an interesting nontrivial angular dependence of the linewidths.

V. INTERCHAIN INTERACTIONS

Two types of interchain interactions will be considered here. The first type does not commute with the total magnetization, like interchain dipole-dipole coupling, and this interaction adds a broadening mechanism to the problem. The line shape remains of pure one-dimensional character and the decoupling of correlation functions involving spins on different chains is correct. It might be surprising that a four-spin correlation function which is written as a combination of products of two-spin correlation functions having diffusion tails on their own, also decays according to a diffusion law. The key lies in the fact that one has to sum over all lattice sites. In fact the same effect occurs in the pure one-dimensional case. We would like to stress that solutions of the one-dimensional diffusion equations, expressed with the help of the imaginary Bessel functions, is very useful in this respect. For instance, the above-mentioned problem is dealt with very easily using Neumann's addition theorem of the Bessel functions.[24] The other type of interaction which will be considered, the interchain Heisenberg coupling, does commute with the total magnetization, and gives the damping process a three-dimensional character.

The influence of interchain dipolar interaction can be calculated easily. The most important work is the calculation of the second moments of the various terms of the interchain dipolar interaction and adding them to the $k=0$ second moment of the intrachain dipolar coupling. These second moments depend on the orientation of the magnetic field, although not as simple as the $k=0$ part of the intrachain dipolar interaction. The reason for this complication lies in the fact that the internuclear vectors of two interacting spins on different chains are not parallel in general. We will not go into details; however, the corrections are small and they can be easily calculated within our formalism. One exception is, of course, the linewidth of $\tilde{S}^{0\prime\prime}(\omega)$ when $\theta = 0°$; the line shape will change from a δ function to a Lorentzian with a width determined by the intrachain dipolar interaction. The incorporation of this effect is thus straightforward. The change compared to the ideal one-dimensional case is the inclusion of the second moments of the interchain dipolar interactions in the broadening terms. The calculation of these moments is straightforward, although in low-symmetry cases, they are certainly not simple. The rest of the calculation proceeds in the same way as for the ideal one-dimensional case.

The interchain exchange interaction is much more interesting. It is obvious that when the interchain exchange becomes comparable to the intrachain interaction, our approach breaks down completely. The self-energies would contain no pronounced resonance structure. When the interchain coupling is small, on the other hand, our calculation can be extended to include this term. We will soon be able to state more precisely what we mean by *small*. A small interchain interaction is extremely interesting because in many real materials this interaction cannot be neglected. In addition, the introduction of a small interchain Heisenberg exchange interaction shows beautifully the fading away of the resonance structure in the self-energy, and the decrease in magnitude of the self-energy (more effective narrowing). We will first treat the situation in which the Heisenberg interchain coupling is the only important inter-

chain term, and later on we will show how one can treat both interchain interactions (dipolar and Heisenberg) simultaneously.

The self-energies depend now on three wave-vector components: k_a, k_b, and k_c. This axis system is crystal fixed, and c is the chain direction by definition. The other reference frame x, y, and z is magnetic field fixed. The wave-vector dependence of the self-energy is only known in the long-wavelength limit. However, the wave-vector sums over k_a, k_b, and k_c, will also contain short-wavelength contributions from the a and b direction. We will have to make an approximation which is good throughout the whole Brillioun zone. In a situation where all modes contribute, the detailed dynamics of one mode is usually not so important. With this in mind the following approximation is made[25]:

$$\Gamma^{\alpha}(\vec{k}, \omega + i\epsilon) = \Gamma^{\alpha}(\vec{k}=0, \omega + i\epsilon) - 4i\frac{D_a}{a^2}\sin^2\left(\frac{k_a}{2}a\right) - 4i\frac{D_b}{b^2}\sin^2\left(\frac{k_b}{2}b\right) - 4i\frac{D_c}{c^2}\sin^2\left(\frac{k_c}{2}c\right) , \tag{5.1}$$

where D_a, D_b, and D_c are the diffusion coefficients. There are several theories which relate the off-chain diffusion coefficients to the off-chain exchange constants. The difference between these theories is at most a factor of 2 in the off-chain diffusion coefficients.[25,26] Actually, Eq. (5.1) can only be applied to an orthorombic magnetic lattice due to symmetry reasons. For instance, in hexagonal crystals cross terms would occur in k_a, k_b, and k_c. This case could be treated also, the only difference being that the wave-vector sums would be more involved. The implicit Markovian character of the Heisenberg dynamics as expressed by (5.1) obviously breaks down at short times and large wave vectors, but the corrections due to this effect will probably be small. We substitute Eq. (5.1) in the mode-coupling equations (2.12) and to show how the calculation proceeds we will pick out one term [the first term of $\Gamma^{+}(k=0, \omega + i\epsilon)$]. We integrate this term over the time using the approximation which we have used to obtain our improved solution. The result for this term of $\Gamma^{+}(k=0, \omega + i\epsilon)$ reads

$$N_a^{-1}N_b^{-1}N_c^{-1}\sum_{k_a}\sum_{k_b}\sum_{k_c}\left\{|A(k_c)|^2\left[-i\omega + i\omega_0 + \epsilon + i\Gamma^0(k=0, i\epsilon) + i\Gamma^{+}(k=0, \omega + i\epsilon) + \frac{8D_a}{a^2}\sin^2\left(\frac{k_a}{2}a\right) + \frac{8D_b}{b^2}\sin^2\left(\frac{k_b}{2}b\right) + \frac{8D_c}{c^2}\sin^2\left(\frac{k_c}{2}c\right)\right]^{-1}\right\} \equiv \Delta , \tag{5.2}$$

in which N_a, N_b, N_c denote the number of spins in the a, b, and c direction, respectively.

We will sum over k_c and assume $D_c/c^2 \gg D_a/a^2, D_b/b^2, \Gamma^{\alpha}$. One obtains

$$\Delta = N_a^{-1}N_b^{-1}\frac{|A(0)|^2}{2\sqrt{2D_c}}c\sum_{k_a}\sum_{k_b}\left[-i\omega + i\omega_0 + \epsilon + i\Gamma^0(k=0, i\epsilon) + i\Gamma^{+}(k=0, \omega + i\epsilon) + \frac{8D_a}{a^2}\sin^2\left(\frac{k_a}{2}a\right) + \frac{8D_b}{b^2}\sin^2\left(\frac{k_b}{2}b\right)\right]^{-1/2} . \tag{5.3}$$

When D_a or D_b is equal to zero, the remaining wave-vector sum can be done exactly. However, we would like to be able to trace the three-dimensional correction to the ideal one-dimensional solution in any stage of the calculation. In addition, when both D_a and D_b do not vanish, the remaining wave-vector sums cannot be done exactly. For these reasons we assume that $D_a/a^2, D_b/b^2 < \Gamma^{+}$ and expand the square root in powers of $D_{a,b}/\Gamma^{+}$. One finds after performing the residual wave-

vector sums

$$\Delta = c\frac{|A(0)|^2}{2\sqrt{2D_c}}[-i\omega + i\omega_0 + \epsilon + i\Gamma^0(k=0, i\epsilon) + i\Gamma^+(k=0, \omega + i\epsilon)]^{-1/2}$$
$$\times\left[1 - \left(\frac{2D_a}{a^2} + \frac{2D_b}{b^2}\right)[-i\omega + i\omega_0 + \epsilon + i\Gamma^0(k=0, i\epsilon) + i\Gamma^+(k=0, \omega + i\epsilon)]^{-1} + \cdots\right], \quad (5.4)$$

where the dots indicate higher-order terms. We will only consider the lowest-order corrections, although inclusion of higher-order terms is possible. If many higher-order terms need to be considered, the method becomes impractical. Our criterion for a small interchain coupling is clear whether or not many higher-order terms are to be included. The procedure followed here can only be used for materials which exhibit a qualitative one-dimensional behavior. When many terms are needed in Eq. (5.4), the dynamics are not describable anymore as perturbed one dimensional. It is not surprising that our formalism breaks down or becomes impracical for three-dimensional dynamics. In this region, other theories are preferable.[27]

The nice thing about Eq. (5.4) is that it can be separated into a one-dimensional contribution and three-dimensional corrections. We have used the approximation method as expressed by Eq. (5.4) for all terms in the mode-coupling equations; and, of course, the whole machinery of the self-consistent procedure can be started again. As indicated above, again a simple and an improved solution exists, and the calculation of Secs. II and III can be repeated again, but now with a finite interchain exchange coupling. We will only give some general results. Inspection of Eq. (5.4) shows that the self-energies with finite interchain exchange result in self-energies having resonances which are smaller and broader as has been anticipated. A practical consequence of this behavior is that the difference between the simple solution and the improved one becomes smaller. In Fig. 11 we present the results of a calculation of the self-energies with inclusion of interchain exchange. In Fig. 12 we present the results of a calculation of the angular dependence of the full halfwidth of the fundamental resonance of the transverse magnetization (EPR linewidth). We see that the influence of the interchain coupling is twofold. In the first place, the linewidth becomes smaller, and in the second place, the angular variation becomes less pronounced. Both features are inherent to the three-dimensional character of the narrowing process.

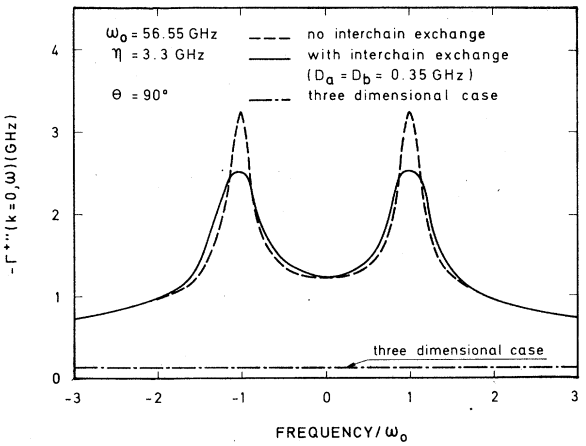

FIG. 11. Self-energy $\tilde{\Gamma}^{+\prime\prime}(k=0,\omega)$ as a function of frequency for the magnetic field perpendicular to the chain direction. Dashed line: no interchain exchange. Solid line: with perpendicular diffusion constants of 0.35 GHz. Dash-dot line gives the results when the Heisenberg system would have cubic symmetry.

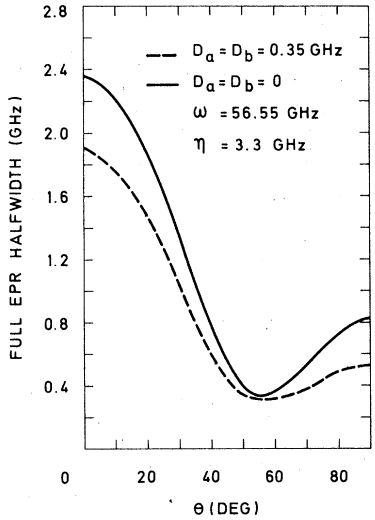

FIG. 12. Full half width of the EPR line as a function of the orientation of the magnetic field. Dashed line: η = 3.3 GHz and no interchain exchange. Solid line: η = 3.3 GHz and with perpendicular diffusion coefficients of 0.35 GHz.

For illustrative purposes we have also indicated in Fig. 11 the results in case the Heisenberg dynamics would be completely three dimensional (cubic).

One might wonder if it is possible to treat the corrections due to interchain dipolar and interchain exchange coupling both at the same time. If both corrections are small this is even simple. In this case when the broadening term, which consists of a one-dimensional dipolar and a three-dimensional dipolar part, is multiplied with narrowing terms like Eq. (5.4), one does not need to take into account the cross terms of both interchain interactions and the extension is trivial. If this is not allowed, the calculation becomes complicated. We will not go into detail because we do not think that this is of much practical value at present.

VI. COMPARISONS WITH OTHER THEORIES

Hennessy *et al.*[12] developed a theory within the Kubo and Tomita framework which was used to explain experimental data on one-dimensional systems. Interchain exchange coupling was included in their study. The theory of Kubo and Tomita[7] has some disadvantages which were discussed recently.[2] Apart from this point, the calculation of Hennessy *et al.*[12] is essentially a calculation in the time domain. In general, a calculation in the time domain is not suitable to treat extra resonances and, in particular, the Kubo and Tomita theory[7] cannot deal with the extra resonances at all. The reason is that in the Kubo and Tomita theory one deals with pure Heisenberg evolution operators and these cannot cut off the one-dimensional diffusion.

Furthermore, Hennessy *et al.*[12] included only the secular part of the dipolar interaction. In the neighborhood of $\theta = 0°$ both our theory and the theory of Hennessey *et al.*[12] will probably give similar results, and the use of either of them is a matter of taste or of calculation time. We note that in the neighborhood of $\theta = 0^0$ our theory is completely equivalent to the theory of Reiter and Boucher[2] if no interchain coupling is present.

Boucher *et al.*[9] presented a complete theory regarding long-wavelength dynamics in one-dimensional magnetic systems including interchain effects. The theory was used to explain EPR and rather extensive NMR data concerning TMMC. Their calculation was done in the frequency domain. There are principal differences with this work and they will be discussed now. Boucher *et al.*[9] interpret their data in terms of what they call the "total spin torque" (TST) correlation function. This function appears after calculating the spectral function of a two-spin correlation function. To compute the frequency dependence of a two-spin correlation function they essentially use the following identity:

$$(z - \mathcal{L})^{-1} = z^{-1} + \mathcal{L}z^{-2} + \mathcal{L}^2 z^{-2}(z - \mathcal{L})^{-1} . \tag{6.1}$$

This is a moment expansion and can be expected to be useful at high frequencies, where a simplification of $\mathcal{L}^2 z^{-2}(z - \mathcal{L})^{-1}$ might be possible. In one-dimensional systems the major difficulty lies in the low-frequency behavior. The use of identity (6.1) to describe the low-frequency properties does not seem profitable. One would like to have an equation which is able to treat low- and high-frequency behavior such as Mori's equations of motion. Boucher *et al.*[9] manipulate (6.1) incorrectly to get such an equation. This can be seen as follows: taking matrix elements of identity (6.1), the second term on the right-hand side causes the shift of the resonance. These shifts are small and can be neglected. The third term on the right-hand side was argued to be negligible compared to z^{-1}. The conclusion of this simplification should be $(z - \mathcal{L})^{-1} \sim z^{-1}$, which is not of any use because all information of the system is lost. The equation used by Boucher *et al.*[9] can be derived correctly within the Mori framework. One uses the expansion of $(z - Q^\alpha \mathcal{L} Q^\alpha)^{-1}$ in powers of the dipolar interaction. This expansion is very useful in describing the long-wavelength dynamics of three-dimensional magnetic systems. The obvious reason why it cannot be applied directly to one-dimensional systems, is that when $z \to i\epsilon$, divergencies will show up when matrix elements are taken. An expansion in diverging diagrams is very inconvenient; however, if one keeps z far away from $i\epsilon$, the expansion of $(z - Q^\alpha \mathcal{L} Q^\alpha)^{-1}$ in powers of the dipolar interaction might still be of value. This situation is present in the wings of the principal resonance of $\tilde{S}^{+-}(\omega)$, which is the normal EPR line. The wings of the EPR line are thus determined by pure four-spin correlation functions that is, without dipolar evolution operators. Analyzing the wings of the resonance line could yield information about the Heisenberg system without invoking any decoupling. The wings of a resonance line are of course difficult to study for intensity reasons. Boucher *et al.*[9] did not analyze the wing structure of the $\theta = 0°$ spectrum directly, but they scaled it with the central part of the resonance, which spoils the argument that information is gained regarding uncoupled pure correlation functions. The situation is much simpler at the magic angle ($\theta = 54.7°$), where the secular part of the dipole-dipole interaction vanishes. The expansion of $(z - Q^\alpha \mathcal{L} Q^\alpha)^{-1}$ can now be used for the central portion of the resonance and, con-

sequently, the central part reflects properties of pure four-spin correlation functions. The experimental data indicated unambigiously that the four-spin correlation functions involved in this experiment possess diffusive tails.[5] In some cases the pure four-spin correlation determine the NMR cut-off frequencies, and the diffusive character was also proven in this case.[3,4,9] However, if one wants to describe the resonance properties of one-dimensional magnetic systems without invoking decoupling procedures, it is impossible to extract the diffusion coefficient of the four-spin correlation functions from the experimental data. Boucher *et al.*[9] did infer the magnitude of the diffusion constant of the four-spin correlation functions (D_{TST}) from the experimental data. It will be demonstrated that such a procedure implies decoupling and cannot considered to be a way of finding D_{TST} independent of decoupling arguments.

The total-spin-torque correlation is connected with

$$\langle \mathcal{L}_D S^\alpha(k=0) \,|\, e^{-i\mathcal{L}_H t - i\mathcal{L}_E z t} \mathcal{L}_D S^\alpha(k=0)\rangle ,$$

which is a combination of pure four-spin correlation functions. The four-spin correlation functions which differ only in their spin components are linearly dependent.[28] This holds because the dipolar interaction is not present in the propagator. A typical term for $S^+(k=0)$ is proportional to

$$\phi(t) = N^{-1} 9 S^{-2} (S+1)^{-2} \times \sum_{i\neq j} \sum_{l\neq m} \left(\frac{c}{\gamma_{ij}}\right)^3 \left(\frac{c}{\gamma_{lm}}\right)^3 \langle\langle S_i^0 S_j^0 e^{-i\mathcal{L}_H t} S_l^0 S_m^0 \rangle\rangle . \tag{6.2}$$

If one assumes diffusive behavior for $\phi(t)$ we know that at long times $\phi(t)$ is proportional to $t^{-1/2}$. If $\phi(t)$ is diffusive, $2\phi(t)$ also is, and obviously one needs a normalization factor to be able to infer the complete time dependence of $\phi(t)$ from the assumption of diffusive behavior. This normalization should be found without invoking decoupling arguments because we investigate the possibility of extracting information from experiment without decoupling. Exact properties known of $\phi(t)$ concern the small time behavior. One could like to normalize $\phi(t)$ using its value at $t=0$. However, it is impossible to make a connection between $\phi(0)$ and $t^{-1/2}$ directly. A solution of the one-dimensional diffusion equation which has a finite short time behavior and shows the $t^{-1/2}$ tail is proportional to

$$e^{-2D_{\mathrm{TST}}c^{-2}t} I_0(2D_{\mathrm{TST}}c^{-2}t) ,$$

where $I_0(t)$ is the modified Bessel function of zero'th order and argument t, D_{TST} would be the diffusion coefficient of $\phi(t)$ and consequently, also of the TST correlation. Calculating $\phi(0)$ exactly gives the result $\phi(0) = 4\rho(6)$, where $\rho(n)$ is the Rieman ζ function of order n.[24] Using the Bessel function solution and $\phi(0)$ as normalization, we find for the long-time behavior

$$\phi(t) = 4\rho(6)(4\pi D_{\mathrm{TST}} c^{-2} t)^{-1/2} , \qquad \phi(t) \approx 4.08(4\pi D_{\mathrm{TST}} c^{-2} t)^{-1/2} . \tag{6.3}$$

It is interesting to investigate the long-time behavior of $\phi(t)$ introducing decoupling of the four-spin correlations. The decoupling gives

$$\phi_{\mathrm{dec}}(t) = 2N^{-1} \sum_k E^2(k) e^{-2Dk^2 t} , \tag{6.4}$$

in which

$$E(k) = \sum_j e^{ikr_{ij}} \,|\, r_{ij} \,|^{-3} ,$$

and where D is the diffusion coefficient of the two-spin correlation functions.

The long-time behavior of $\phi_{\mathrm{dec}}(t)$ is

$$\phi_{\mathrm{dec}}(t) = 8\rho^2(3)(8\pi D c^{-2} t)^{-1/2} \approx 11.56(8\pi D c^{-2}(t)^{-1/2} . \tag{6.5}$$

There is a large numerical difference between (6.3) and (6.5) if one realizes that D_{TST} will be of the order of $2D$. Using Eq. (6.3) in the analysis of experimental data, one would obtain values for D_{TST} which are much too small (~400%). Furthermore, the short-time normalization we sketched is arbitrary and other normalizations are equally good or bad. Boucher *et al.*[9] used

$$\phi(t) = 11.56(4\pi D_{\mathrm{TST}} c^{-2} t)^{-1/2} . \tag{6.6}$$

It is clear from the discussion above that such an assumption implies decoupling and consequently cannot be considered correct if one does not want to apply decoupling of four-spin correlation functions. In our opinion, at the present stage of the theory two possibilities exist for a diffusive $\phi(t)$: (i) Eq. (6.5) implying an independent mode approximation or (ii) $\phi(t) = Mt^{-1/2}$, in which M is an unknown normalization factor. Without decoupling D_{TST} cannot be obtained from experiment because it is not the only factor determining M.

In the formalism of this paper, no four-spin correlation functions are needed because they are decoupled directly. It is nevertheless easy to trace back the frequencies where the results could have been interpreted in terms of pure four-spin correlations. Whenever in the equations for $\Gamma^\alpha(k=0, \omega + i\epsilon)$ in the inverse complex

square-root terms like $\Gamma^{\alpha}(k=0, \omega+i\epsilon)$ can be neglected, the results could have been described using the pure four-spin correlation functions. This situation arises for instance in $\Gamma^{+}(k=0, \omega+i\epsilon)$ at the magic angle. In the major part of the frequency domain this simplification is invalid and even if the pure four-spin correlation functions can be used, one cannot extract the diffusion constant of these functions from experiment as has been outlined above. Consequently, the use of decoupling everywhere in the frequency domain is much more elegant, and that is why this procedure has been followed throughout this paper.

The way Boucher *et al.*[9] introduced the cutoff of the diffusion is arbitrary because it is applied essentially to a three-spin correlation function which is not suited for these purposes and, in addition, their argument is based on an order of magnitude estimate. For instance, the satellite in $\tilde{S}^{0\prime\prime}(2\omega_0 \approx \omega)$ would have a completely different angular behavior than the angular behavior predicted with our theory, which is in agreement with experiment.[8] There remains one thing which needs to be clarified. Boucher *et al.*[9] used for the $\theta=0°$ EPR experiments a theory which is mathematically similar to our simple solution. We have indicated that exactly in this region the value of the simple theory is doubtful because it can produce a two-peaked structure for the EPR line (see Fig. 5). Apart from this problem they get a much smaller width than we get, and their width is also much smaller than the calculated linewidths of other theories.[2,12] In our opinion the explanation for this discrepancy is that they used the wrong sign for the real part of the self-energy $\tilde{\Gamma}^{+\prime}(k=0, \omega)$. It is not difficult to show, with the help of the Kramers-Kronig relation (2.19), that if the imaginary part of the self-energy consists of a single symmetric resonance, the real part will always act so as to broaden the spectral function. A reversal of the sign of the real part in our case narrows the resonance and removes the double-peaked structure in most cases, although this is of course an invalid procedure.

Recently, some new spectacular effects were predicted to be observable with NMR experiments on one-dimensional systems.[10] These predictions are in contradiction with the excellent data obtained on TMMC.[3,4,9] We have obtained elsewhere that these new spectular effects were obtained by solving an unphysical model incorrectly.[21]

VII. CONCLUDING REMARKS

In this paper, a theory has been presented on high-temperature dynamics of one-dimensional magnetic systems in the presence of a magnetic field. The interactions which have been taken into account are the Heisenberg exchange interaction, the Zeeman interaction, and the intrachain dipole-dipole coupling (secular and nonsecular terms). In addition, corrections due to interchain effects have been incorporated. The basic assumption of the theory is the decoupling of certain four-spin correlation functions leading to equations which can be classified as mode-mode coupling equations. The qualitative aspects of our results do not depend on the decoupling, but of course the actual widths and magnitudes of resonances result from the decoupling approximation.

Many features were shown to be purely one dimensional. A striking feature of all the results is the appearance of well-defined resonances in the self-energies (memory functions) of the spectral functions. It is this resonance structure in the self-energies which gives rise to satellite lines in the spectral functions. The ultimate success of the theory is undoubtedly the observation of such a satellite line in the EPR spectrum of TMMC.[8] The three-dimensional systems behave quite differently. The self-energies have extremely broad resonances, and these resonances do not show up in any way in the spectral functions (see Fig. 11).

The theory is valid for all orientations of the magnetic field. An important result has been obtained when the magnetic field makes an angle of 90° with the chain axis. At this orientation the EPR linewidth is reduced when one introduces the nonsecular terms of the dipole-dipole coupling. In three-dimensional systems the introduction of the nonsecular terms always gives rise to an additional broadening of the resonance lines. An experimental determination of the dependence of line shape, linewidth, and line position on the frequency of the microwaves at this orientation would be very welcome. Such an experiment would constitute a critical test of the theory.

The spectral function which have been calculated in this work can also be used to evaluate NMR linewidths in one-dimensional magnetic systems. The complicated angular dependence of the geometrical factors masks somewhat the influence of the anisotropy of the dynamical properties on the NMR linewidths. In addition, these geometrical factors are not known to a high precision. We have obtained satisfactory agreement between experimental and theoretical T_1 and $T_{1\rho}$ data of protons in TMMC for all orientations of the magnetic field using a simplified model for the geometrical factors.

At some frequencies and at some specific orientations of the magnetic field, an interpretation is possible which does not rely on decoupling of four-

spin correlation functions. However, in contrast to conclusions of previous work,[9] the diffusion constant of the four-spin correlation functions cannot be inferred from experiment directly. Realizing, in addition, the limitations in frequency and orientation, the formalism without decoupling was not pursued. Although we have indicated where and how, one transforms the equations so as to let them apply to the case of no decoupling.

The influence of interchain exchange starts to become important if its magnitude cannot be neglected when it is compared with the (theoretical) EPR linewidth obtained without the interchain perturbation. Its effect is most dramatic when the magnetic field is parallel to the chain direction. At the magic angle ($\theta = 54.7°$) the influence of the interchain exchange is much less pronounced.

We hope that the theory will be applicable to the magnetic resonance of a variety of one-dimensional materials.[29] Because some controversy exists with respect to the EPR linewidth in TMMC,[2,5,12,30] more experiments are necessary to find out whether or not TMMC behaves somewhat pathologically. Throughout this paper we have used the dipole-dipole interaction as the broadening mechanism. The treatment of single-ion anisotropy or even both single-ion anisotropy and dipolar interaction as the broadening mechanisms is possible, and would only change the $k = 0$ second moments in our theory.[30]

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