Electron spin resonance in $S=\frac{1}{2}$ antiferromagnets at high temperature

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We study the electron spin resonance of low-dimensional spin systems at high temperature and test the Kubo-Tomita theory of exchange narrowing. In finite-size systems (molecular magnets), we found a double-peak resonance which strongly differs from the usual Lorentzian. For infinite systems, we have predictions for the linewidth and line shape as a function of the anisotropy strength. For this, we have used an interpolation between a nonperturbative calculation of the memory function at short times (exact diagonalization) and the hydrodynamic spin diffusion at long times. We show that the Dzyaloshinskii-Moriya anisotropies generally induce a much larger linewidth than the exchange anisotropies in two dimensions, contrary to the one-dimensional case.

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I. INTRODUCTION

The paramagnetic resonance is a well-known phenomenon resulting from the collective precession of the total magnetization about an external magnetic field. For spin systems with interactions of the standard SU(2) Heisenberg form, the total magnetization is conserved and there is no relaxation of the magnetization, regardless of the strength of the interaction. It is no longer true when anisotropic interactions are present and the magnetization relaxes with a characteristic time scale. A theoretical issue is to relate this time scale (or the width of the resonance) to the anisotropy strength in a many-body system. In strongly interacting systems, small anisotropies (as in transition-metal compounds) lead to an exchange-narrowed Lorentzian resonance.[1] The linewidth is given, generically, by the theory of Kubo-Tomita,[2] and cast into a more general formalism by Mori[3] and Zwanzig.[4] However, the Markovian assumption used by Kubo-Tomita was later argued to break down in low-dimensional systems. For one-dimensional systems, deviations from the Lorentzian line shape were indeed observed experimentally and attributed to spin diffusion,[5,6] which was not taken into account in the first place. Recently, Oshikawa and Affleck[7] have developed a direct approach in one-dimensional $S=\frac{1}{2}$ systems, based on an effective-field theory, which is valid at low temperatures and could account successfully for the (low-) temperature dependence of the measured linewidths. It is, however, clear that a theory of the high-temperature linewidth would be very useful to extract the anisotropies experimentally. The Kubo-Tomita formula has been widely used in this regime but not thoroughly tested.

It is nonetheless known that, even in the high-temperature regime, a direct application of the Kubo-Tomita formula fails in the case of Dzyaloshinskii-Moriya anisotropy in one dimension,[8,9] which is first order in the spin-orbit coupling in $S=\frac{1}{2}$ systems. It predicts indeed a linewidth varying like D^2/J, which was originally argued to be responsible for the large linewidth observed, in particular, in $CuGeO_3$.[10,11] It is in fact incompatible with a general argument in one dimension, which leads to predict a smaller D^4/J^3.[8,9] It is then of the same order of magnitude as the contribution of the exchange anisotropy (as also happens for other observables[12]), i.e., fourth order in the spin-orbit coupling and, hence, small. As alternatives, unconventional superexchange[13] or dynamical Dzyaloshinskii-Moriya interactions[14] were invoked to explain the strong broadening. Nonetheless, it is expected, on general grounds, that one-dimensional systems may possess an inherent strong broadening because of spin diffusion at high temperatures. One issue is to obtain a reliable quantitative estimation of the effect. Approximations, such as the random-phase approximation (RPA),[5] perturbative expansions,[15] or self-consistent RPA,[16] suggested, in particular, departures from the Lorentzian line shape, but it is difficult to judge how quantitative these theories are.

In contrast, in two spatial dimensions, it is surprising to notice (empirically) that applying the Kubo-Tomita's formula seems to give rather accurate results at high temperatures. For instance, in the Shastry-Sutherland compound, $SrCu_2(BO_3)_2$, this gives an out-of-plane Dzyaloshinskii-Moriya interaction $D=2.4$ K,[17] while neutron scattering gives 2.1 K.[18]

In the following, we will give a quantitative estimation of the linewidth in one and two dimensions and the corresponding line shapes. We predict an enhancement of the linewidth with respect to the perturbative Kubo-Tomita formula, particularly strong when the diffusive motion is assumed at long times. Moreover, while we agree that the linewidth induced by the Dzyaloshinskii-Moriya anisotropy or the exchange anisotropy are of the same order in one dimension (or more generally for the *reducible*[19] Dzyaloshinskii-Moriya interactions), we claim that, in two dimensions, the *irreducible* Dzyaloshinskii-Moriya interactions lead to a linewidth essentially varying like D^2/J, i.e., like in Kubo-Tomita, with a prefactor that we shall estimate.

An approach consists of exact numerical diagonalizations of the Hamiltonian and a calculation of the dynamics using the Kubo formula.[20] The approach is interesting not only because there is no approximation made but also because it provides information on the whole electron spin resonance

(ESR) spectrum and tells us whether there are more resonances than the paramagnetic resonance. It is of course limited by the system size and especially at finite temperatures where one needs to calculate all eigenstates. As we shall see, a direct computation of the Kubo formula gives results which are difficult to extrapolate to the thermodynamic limit. Since, however, the calculation is exact for small sizes, the prediction for the line shape may be interesting for molecular magnets, in particular, to disentangle different mechanisms. However, to obtain information for bulk systems, we suggest that it is more interesting to calculate the memory function by exact diagonalization, in the Mori-Zwanzig framework. While the calculation of the memory function is exact only at short times for finite-size systems, its validity goes beyond the perturbative short-time expansion developed earlier.[2,15] We find a clear slowing down of the memory function compared to Kubo-Tomita in one dimension (but not in two dimensions), possibly indicative of a crossover to spin diffusion. We can then test the spin-diffusion assumption for the long-time behavior. It is indeed reasonable to assume that the short-time behavior depends on the microscopic details of the lattice (and hence needs a precise calculation) while the long time may be more universal (and depends primarily on the spatial dimension). This allows to obtain a quantitative idea of how accurate the Kubo-Tomita's result is in one and two dimensions.

II. KUBO FORMULA AND FINITE-SIZE SYSTEMS

The linear response of the spin system to a long-wavelength oscillating magnetic field along, say, an x axis is given by the Kubo formula (or susceptibility),

$$\chi(\omega) = i\int_0^{+\infty} dt e^{i\omega t}\langle[S^x(t),S^x(0)]\rangle, \tag{1}$$

where $S^x=\Sigma_i S_i^x$ is the total magnetization along the x axis. The absorption cross section of the incident electromagnetic wave is proportional to $\omega\chi''(\omega)$, and

$$\chi''(\omega) = \pi(1-e^{-\beta\omega})S^{xx}(\omega), \tag{2}$$

where

$$S^{xx}(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t}\langle S^x(t)S^x(0)\rangle$$

$$= \frac{1}{\mathcal{Z}}\sum_{n,p} e^{-\beta E_n}|\langle n|S^x|p\rangle|^2\delta(\omega - E_p + E_n) \tag{3}$$

with a sum over the eigenstates $|n\rangle$ and $|p\rangle$ of the Hamiltonian ($\mathcal{Z}$ is the partition function). At high temperatures ($T\gg J$), $\omega\chi''(\omega)=(\omega^2/T)S^{xx}(\omega)$ and we show only $S^{xx}(\omega)$ in the following. Furthermore, all the states have the same weight (we now take $e^{-\beta E_n}=1$ which is valid for $T\gg J$) and $S^{xx}(\omega)$ is an even function of ω [$S^{xx}(\omega)=S^{xx}(-\omega)$]. To compute Eq. (3), we have calculated all eigenenergies and eigenstates of the Hamiltonian by exact numerical diagonalization. We have first considered the Heisenberg Hamiltonian for one-dimensional spin rings (with periodic boundary conditions) with two types of SU(2)-symmetry-breaking anisotropies, one is the Dzyaloshinskii-Moriya interaction (first order in spin-orbit coupling),

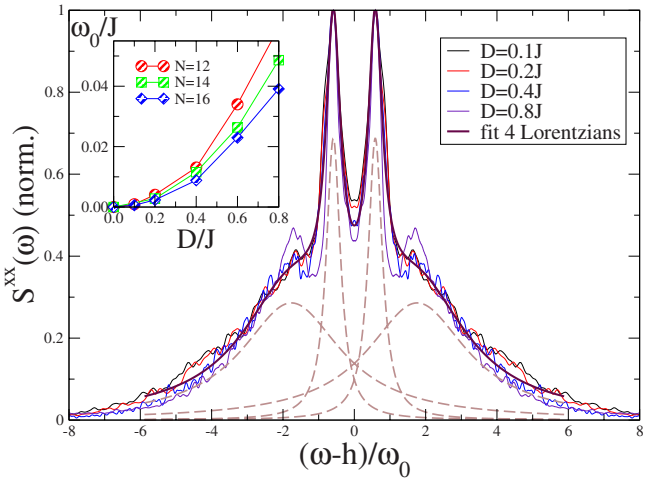

FIG. 1. (Color online) ESR line shape of a one-dimensional chain of $N=16$ spins ($T\gg J$). The curves are rescaled with the half width at half maximum, ω_0/J (shown in the inset as a function of D/J for three sizes).

$$\mathcal{H} = \sum_i J\mathbf{S}_i\cdot\mathbf{S}_{i+1} + \mathbf{D}_i\cdot(\mathbf{S}_i\times\mathbf{S}_{i+1}), \tag{4}$$

where $\mathbf{D}_i$ is a staggered vector from bond to bond (strength D) and taken along the z axis. The second is the XXZ exchange anisotropy (second order in spin-orbit coupling),

$$\mathcal{H}' = \sum_i J\mathbf{S}_i\cdot\mathbf{S}_{i+1} - \delta J S_i^z S_{i+1}^z \tag{5}$$

with an easy-plane anisotropy ($\delta>0$). Importantly, $\mathcal{H}$ can be mapped onto $\mathcal{H}'$ by rotating the spin operators, $\tilde{S}_i^+ = e^{i(-1)^i\theta}S_i^+$ with $\theta=D/2J$, giving $\delta\equiv D^2/2J^2$ at the lowest order.[8,9,12] In this mapping, the long-wavelength oscillating magnetic field acquires a staggered component. In the following, we restrict ourselves to an external field h along z. In this case, the z component of the total magnetization, S^z, is conserved and the magnetic field splits the excited states according to $-hS^z$ but does not change the matrix elements in Eq. (3). In addition, the operator S^x changes S^z by ±1 so that E_p-E_n is shifted by $\pm h$. As soon as h is larger than the linewidth, the $h\neq0$ line shape is the same as for $h=0$ shifted by $\pm h$.

The result of the calculation of the Kubo formula (3) for $N=16$ spins interacting with Hamiltonian (4) is shown in Fig. 1 [the delta peaks in Eq. (3) are slightly broadened by a Gaussian form[21]]. We find a broad resonance centered at the magnetic field h (there is no finite shift). Since we are at high temperatures, we stress that $S^{xx}(\omega)$ is the same around $\omega=-h$. The calculation being exact, this is the line shape we predict for molecular magnets of the ring geometry, at high temperature, would the mechanism giving the linewidth be purely magnetic in origin. In Fig. 1, the different curves correspond to different strengths of Dzyaloshinskii-Moriya coupling. They are normalized in intensity and rescaled in fre-

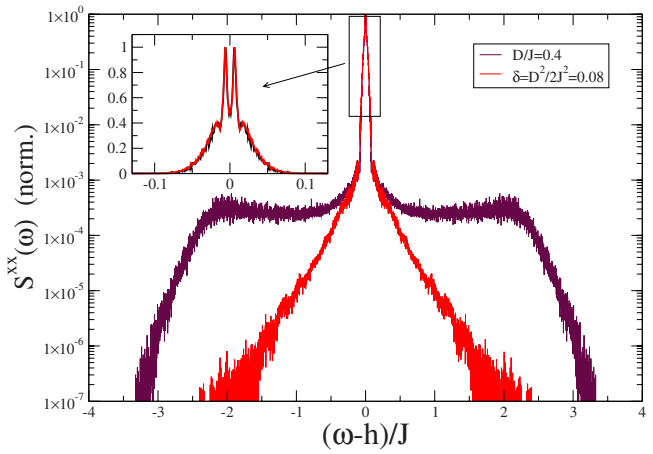

FIG. 2. (Color online) ESR line shape (high-energy tail) for a one-dimensional chain ($T \gg J$) for the Dzyaloshinskii-Moriya and XXZ models (using $2\delta=D^2/J^2$). The response is identical only at low energy (inset).

quency using the linewidth, noted ω_0, and defined as the half width at half maximum of the full line. They all collapse onto a single (quasi)-universal line shape with a double-peak structure, in a wide range of anisotropy strengths, $D \sim 0.1-0.8J$ and sizes. If we consider the special case $h=0$, the double-peak structure can be seen as a pseudogap. The prediction of this line shape seems at odds with the conventional exchange-narrowing theory which, in general, predicts a single Lorentzian. We will discuss the origin of these differences below. In addition to the double-peak structure, there is an additional weight in the wing. In fact, the line shape can be fitted by four Lorentzians, two centered at $\pm 0.59\omega_0$ and two at $\pm 3(0.59\omega_0)$ (each component is given by a dashed line in Fig. 1 and the fit by a solid thick line).

The linewidth ω_0 increases basically like $\alpha D^2/J$ (inset of Fig. 1) with a rather small prefactor, α. The prefactor is size dependent and is difficult to extrapolate to the thermodynamic limit. For this reason (and following the discussion of Sec. III), the special double-peak line shape may or may not survive in the thermodynamic limit. For molecular rings, this should be relevant and the prefactor is found to be $\alpha = 0.090(N=12)$, $0.071(N=14)$, and $0.059(N=16)$.

We now emphasize the difference between the Dzyaloshinskii-Moriya model and the XXZ model, as far as the response is concerned. In Fig. 2, we show the resonance line in absolute values for the two models with coupling strengths related by the mapping $2\delta=(D/J)^2$. The two resonance lines are undistinguishable at low energies (inset of Fig. 2) but differ at high energy in the background (Fig. 2). The difference comes from the small oscillating staggered field (or umklapp contribution from the spin fluctuations at $q=\pi$) that the mapping induces,[8,9]

$$S^{xx}(\omega) = \cos^2\theta\, \tilde{S}^{xx}(\omega) + \sin^2\,\theta \tilde{S}_u^{xx}(\omega), \tag{6}$$

where S^{xx} and $\tilde{S}^{xx}$ correspond to the Dzyaloshinskii-Moriya and XXZ model, respectively, and $\tilde{S}_u^{xx}(\omega)$ is the $q=\pi$ response. The second term gives extra "forbidden" resonances (or "satellite" lines) at low temperatures.[22] These resonances have disappeared at high temperatures. Instead, this contribution gives a broad background, covering the whole energy range. This is the origin of the difference of the two curves at high energy. To summarize, the resonance line shape as shown in Fig. 1 is the same for both the Dzyaloshinskii-Moriya and the XXZ models as long as we use the correspondence $2\delta=(D/J)^2$ (and not too small intensities).

Note that we have found deviations about the universality of the low-energy line shape at strong anisotropies (either Dzyaloshinskii-Moriya or XXZ). This is expected because, for $\delta=1$, the model is XY and the line shape is known to be exactly Gaussian.[23] We have recovered this result numerically: we have found no difference with a Gaussian at $\delta=1$ (no finite-size effects). The way it crossovers from a Gaussian function to four Lorentzians (by reducing δ from 1) is to depress the response at $\omega=h$ and let side peaks appear, which decrease in height. It is therefore clear that in the range of strong anisotropies ($D \gtrsim J$ or $\delta \gtrsim 0.5$), the line shape is not universal at all. It is worth noting that the line shape can also be calculated in exact soluble models which are extensions of the XY model.[24]

III. KUBO-TOMITA THEORY, EXACT CALCULATION OF THE MEMORY FUNCTION

We now discuss the Kubo-Tomita theory in order to understand why the line shape is not a single Lorentzian in such finite-size systems and go beyond the limitations imposed by finite-size calculations. A way to clarify the assumptions is to start with the more general Mori-Zwanzig formalism.[3,4] In this framework, the spin fluctuations (those that do not depend on time through the magnetization function) are viewed as a random noise (the bath) that forces the magnetization to equilibrate. The system is then governed by a Langevin equation,

$$\frac{d}{dt}S^x(t) = -\int_0^t d\tau \Sigma(t-\tau)S^x(\tau) + \eta(t) \equiv F(t), \tag{7}$$

where the "memory function" (or self-energy) $\Sigma(t)$ is related to the correlation function of the random force $\eta(t)$ by the fluctuation-dissipation theorem. However, neither $\Sigma(t)$ nor $\eta(t)$ are easily expressed in terms of the original spin Hamiltonian because of unknown projection operators.[3,4] It is only at second order in perturbation theory (here in the anisotropy),[4] that $\Sigma(t)$ is given by the total force correlation function

$$\Sigma(t) = \langle F(t)F^\dagger(0)\rangle, \tag{8}$$

where the total force (or torque) is given by $F(t) = ie^{i\mathcal{H}t}[\mathcal{H}, S^x]e^{-i\mathcal{H}t}$. Since $F(t)$ is linear in the anisotropy, $\Sigma(t)$ is second order, and perturbation theory holds for small anisotropies. Equation (8) is precisely what Kubo and Tomita have obtained directly by perturbation theory.

The second assumption is that $S^x(t)$ is slow compared to the relaxation time of the force (local equilibrium).[4] It is true that the force F is not conserved by the dynamics [whereas $S^x(t)$ is nearly conserved] and evolves on a short time scale

of order $1/J$,[1,2] but the absence of memory at long times is an assumption. If it is true (the system is Markovian), Eq. (7) simply defines a relaxation time, τ_c (or Onsager's transport coefficient)

$$\frac{1}{\tau_c} = \int_0^{+\infty} d\tau \Sigma(\tau). \tag{9}$$

In this "fast" regime, the line shape is therefore always Lorentzian with half width at half maximum (linewidth) given by $1/\tau_c$. In contrast, if slow hydrodynamic modes are present, the spin motion may be diffusive.[5,6] In this case, the memory function has a power-law tail $\Sigma(t) \sim 1/t^{d/2}$ and Eq. (9) diverges for $d \leq 2$. In fact, this signals a change in line shape and the general solution of Eq. (7) for the correlation function is

$$S^{xx}(\omega) = \frac{1}{4\pi} \frac{\Sigma''(\omega)}{[\omega + \Sigma'(\omega)]^2 + \Sigma''(\omega)^2} \tag{10}$$

with $\Sigma(\omega) = i\int_0^{+\infty} \Sigma(t) e^{i\omega t} dt$ the Laplace transform of the memory function, and $\Sigma'(\omega)$, $\Sigma''(\omega)$ are its real and imaginary parts. If "slow" processes are present, $\Sigma(\omega)$ varies considerably near $\omega = 0$ and the line shape deviates from a Lorentzian. The form of $\Sigma(t)$ is therefore of importance and various assumptions have been used. The original (third) assumption of Kubo-Tomita was to use a Gaussian decay for $\Sigma(t)$, based on the short-time evolution given by perturbation theory,

$$\Sigma(t) = \sum_n \frac{(it)^n}{n!} M_{n+2}, \tag{11}$$

where M_{n+2} are the moments, $M_2 = \Sigma(0) = \langle F^2 \rangle$, $M_3 = \langle [\mathcal{H}, F]F \rangle$, $M_4 = \langle [\mathcal{H}, F][F, \mathcal{H}] \rangle$, etc. They can be calculated exactly at high temperatures. For the XXZ model (5), $M_2/J^2 = \delta^2/4$, $M_3 = 0$, and $M_4/J^4 = 3\delta^2/8 - \delta^3/4 + \delta^4/4$. So at short times, $\Sigma(t)/\Sigma(0) = 1 - \frac{1}{2!}\omega_e^2 t^2$ with the definition $\omega_e^2 \equiv \frac{M_4}{M_2}$. Kubo and Tomita have postulated that

$$\Sigma(t) = \Sigma(0) \exp(-\omega_e^2 t^2/2) \tag{12}$$

with ω_e^2 matching that of the short-time expansion, Eq. (11), at second order, $\omega_e^2 \equiv M_4/M_2 = 3J^2/2 - \delta J^2 + \delta^2 J^2$. Equation (12) then basically corresponds to assuming a resummation of an infinite number of terms. The Kubo-Tomita formula for the linewidth is then at high temperature,

$$\frac{1}{\tau_c} = \sqrt{\frac{\pi}{2}} \frac{M_2}{\omega_e} \approx \sqrt{\frac{\pi}{3}} \frac{\delta^2}{4} J. \tag{13}$$

To summarize, the assumptions that lead to Eq. (13) are (i) perturbation theory in $\delta \ll 1$, (ii) Markovian behavior, and (iii) perturbation theory in time $t \ll 1/J$.

In order to go beyond perturbation theory and test these assumptions, we have calculated

$$\Sigma(t) = \frac{1}{\mathcal{Z}} \sum_{n,p} e^{-\beta E_n} |\langle n|[\mathcal{H}, S^x]|p\rangle|^2 e^{i(E_n - E_p)t} \tag{14}$$

by exact diagonalization of the Hamiltonian [see Eq. (3) for the definitions]. We restrict ourselves again to high temperatures ($e^{-\beta E_n} = 1$) and have computed all matrix elements. Here we calculate quantities for the model (5) which makes no difference as we mentioned. At short times (Fig. 3), $\Sigma(t)$ decreases indeed on a time scale $\sim 1/J$ and the Kubo-Tomita Gaussian decay holds for $tJ \lesssim 1.5$ (perturbative regime). For $tJ > 1.5$, $\Sigma(t)$ decreases slowly and by comparing the results for different sizes, we see no difference between the $N = 16$ and $N = 18$ curves for $tJ \lesssim 6.5$. We can therefore be confident that for $tJ \lesssim 6.5$, $\Sigma(t)$ is representative of the thermodynamic limit. The result is different from the Gaussian decay and there is a considerable slowing down for $1.5 \lesssim t \lesssim 6.5$. We have here access to a regime that would be difficult to access by perturbation theory. We will come back on this nonperturbative regime in the next section. Above $tJ \gtrsim 6.5$, finite-size effects dominate. In particular, at longer times (Fig. 4), $\Sigma(t)$ acquires an additional broad peak at about $t_a J \sim 10$–17. t_a increases almost linearly with the length of the chain N and its amplitude decreases with $\sim 1/N^{3/2}$ (as shown by the fit in the inset of Fig. 4). A possible interpretation is that this

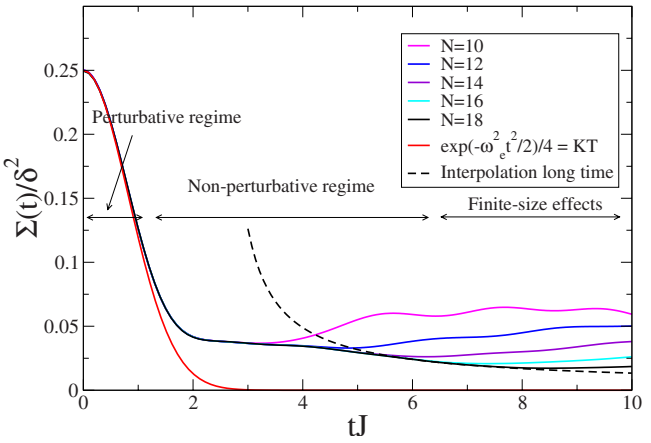

FIG. 3. (Color online) Memory function $\Sigma(t)$ at short times (N is the system size, $\delta = 0.08$). Convergence to $N = \infty$ is obtained for $tJ \lesssim 6.5$. The Kubo-Tomita Gaussian holds for $tJ \lesssim 1.5$. The interpolation to the long-time spin diffusion $1/t^{1/2}$ is shown (dashed line).

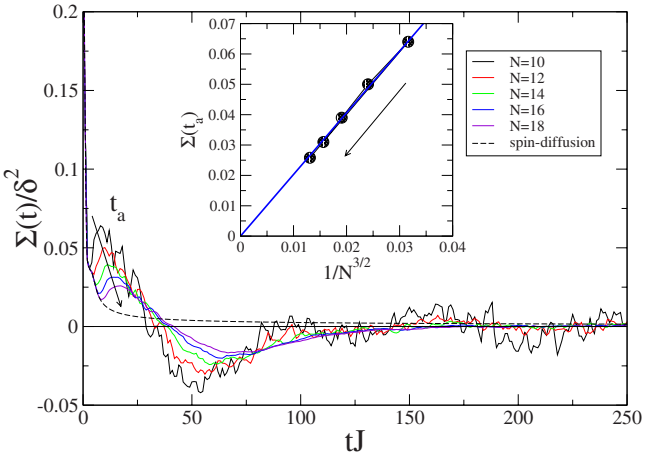

FIG. 4. (Color online) Memory function $\Sigma(t)$ at long times (system size N, $\delta = 0.08$). There is a peak at $t_a J \sim 10$–17 whose amplitude decreases with N (inset). The assumed long-time spin-diffusion tail is also shown (dashed line).

additional peak is related to the torque traveling around the ring. In this case, indeed the arrival time is expected to be controlled by J and weakly sensitive to the anisotropy, which is what we found. In fact if we take the des Cloizeaux-Pearson speed of the hydrodynamic excitation, the arrival time is $t_a=N/c=2N/\pi\sim 6-11$. This additional peak together with the long-time decay should be at the origin of the "double-peak" structure observed in Fig. 1. A simple way to see the effect of a long-time decay of $\Sigma(t)$ is to consider the Gaussian memory function of Eq. (12) with a long-time scale $1/\omega_e \gg 1/J$. The Laplace transform, $\Sigma(\omega)$, is a sum of a Gaussian function (imaginary part) and a Dawson function (real part), and $S^{xx}(\omega)$ [Eq. (10)] acquires a double-peak structure.[25] This occurs when the time scale of the memory function becomes comparable to that of the spin motion $1/\omega_e \geq \tau_c\sqrt{2\pi}/(2+\sqrt{\pi})$. For a general $\Sigma(t)$, the change in sign of the curvature of Eq. (10) at $\omega=0$ signals the occurrence of a double-peak structure. This happens when $\tau_c \leq \langle t\rangle + \langle t^2\rangle^{1/2}$, where $\langle t^n\rangle = (1/n!)\int_0^{+\infty}\Sigma(t)t^n dt/\int_0^{+\infty}\Sigma(t)dt$. As a consequence, there may be a critical size above which the double-peak structure disappears. These long-memory processes (non-Markovian) explain why deviations from a Lorentzian line shape take place in finite-size systems.

IV. RESONANCE IN ONE-DIMENSIONAL THERMODYNAMIC SYSTEMS

In the previous sections, we have given the exact line shape of a finite-size system. As we have explained, it is difficult to extrapolate it in the thermodynamic limit. We now discuss a way to obtain the resonance line in the thermodynamic limit by using some additional assumptions. The crucial point is to obtain the memory function $\Sigma(t)$ but exact diagonalization suffers from finite-size effects at long times. It is therefore interesting to assume a long-time behavior and test its consequences on the resonance line, which can then be compared to experiments. For this, we will interpolate between the exact result at short times [up to the time where $\Sigma(t)$ has converged for $N\to\infty$, i.e., $tJ=6.5$ in Fig. 3] and the assumed hydrodynamic behavior at long times.

First we note that the slowing down obtained in the nonperturbative regime ($1.5\lesssim tJ\lesssim 6.5$) already leads to increase the linewidth compared with Kubo-Tomita. If we assume, for instance, an abrupt cutoff at $tJ=6.5$ [remember that for $tJ>6.5$, $\Sigma(t)$ is dominated by finite-size effects], Eq. (9) defines a lower bound for the linewidth. The lower bound, fitted by $\sim 0.41\delta^2$, is yet larger than the Kubo-Tomita formula, $0.26\delta^2$ [Eq. (13)] (both shown in Fig. 5).

We now consider the idea that the long-time behavior may be universal and governed by a spin-diffusion equation. We recall that the diffusion of $\Sigma(t)$ is obtained assuming a RPA decoupling of the four-spin correlations in $\Sigma(t)$,[5,6] $\langle S_q^+(t)S_q^z(t)S_{q'}^z(0)S_{q'}^-(0)\rangle \sim \langle S_q^+(t)S_{q'}^-(0)\rangle\langle S_q^z(t)S_{q'}^z(0)\rangle$. Since S^z is conserved, the long-wavelength modes are supposed to be diffusive with $\langle S_q^z(t)S_{-q}^z(0)\rangle \sim e^{-Dq^2t}$. On the other hand, $\langle S_q^+(t)S_{-q}^-(0)\rangle \sim e^{-Dq^2t}e^{-t/\tau_c}$ is cutoff by the anisotropy, where τ_c is precisely the characteristic time scale we are looking for, as emphasized by Reiter and Boucher.[16] When summed over q, this leads at long times ($t\gg 1/J$) to

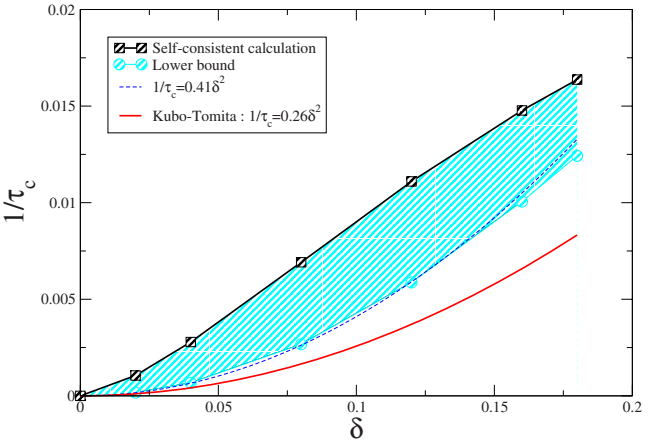

FIG. 5. (Color online) Linewidth vs anisotropy for infinite one-dimensional chains (lower bound, Kubo-Tomita and self-consistent calculation).

$$\Sigma(t) \sim \frac{e^{-t/\tau_0}}{t^{d/2}}, \tag{15}$$

where τ_0 is the cutoff time of the memory function: within the self-consistent RPA, $\tau_0=\tau_c$. As explained above, we cannot test this behavior quantitatively by exact diagonalization, although the slowing down for $1.5\lesssim tJ\lesssim 6.5$ seems to indicate a crossover regime. To test the idea of spin diffusion, Fabricius and McCoy have examined directly the two-spin autocorrelation function for the $N=16$ chain at high temperatures and concluded that the exponent may be closer to 0.7 in one dimension and increases with δ.[26] So the exponent 1/2 may be underestimated, thus leading to overestimate the linewidth. Since τ_c now explicitly enters in Eq. (15), Eq. (9) is a self-consistent equation. This is precisely the equation that Reiter and Boucher solved.[16] Instead of relying on RPA to obtain the prefactors, here we shall assume a long time tail of the form (15) and interpolate to the short-time behavior we have obtained by exact diagonalization. The idea of interpolating the two types of behavior was used by Gulley *et al.*,[15] together with perturbative short-time expansion. The interpolation provides a "variational" function $\Sigma(t,\tau_c)$ and we solve (in a similar spirit as in Ref. 16) the (now) self-consistent Eq. (9) with the new $\Sigma(t,\tau_c)$. In fact the long-tailed $\Sigma(t)$ changes the line shape according to Eq. (10). In this case, Eq. (9) does not hold anymore and we calculate the linewidth using instead the self-consistent equation, $S^{xx}(1/\tau_c)=S^{xx}(0)/2$, where $S^{xx}(\omega)$ is the solution given by Eq. (10). The difference between the two procedures is in fact quite small (from 4% to 7% depending on δ), and we show only the full self-consistent result in Fig. 5 (squares). This provides an estimation of the linewidth for a pure one-dimensional model within the spin-diffusion assumption.

It is now possible to relax the assumption that the cutoff $\tau_0=\tau_c$ in Eq. (15). It does not seem to be physically reasonable to take $\tau_0>\tau_c$ at high temperatures because it would mean having finite torque-torque correlations but no spin-spin correlation after a certain time.[27] In this case, Eq. (9) leads to a divergence of the linewidth $\sim\sqrt{\tau_0}$ whereas the use of the correct line shape provides a less diverging result

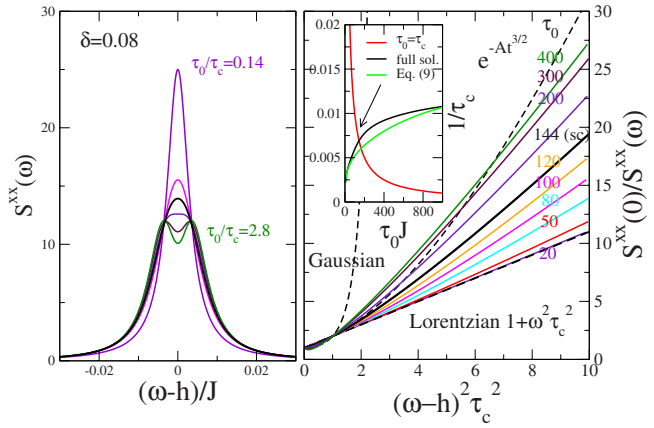

FIG. 6. (Color online) ESR line shape for infinite one-dimensional chains, assuming different cutoffs τ_0 of the diffusive tail. The arrow (inset) indicates the self-consistent τ_c.

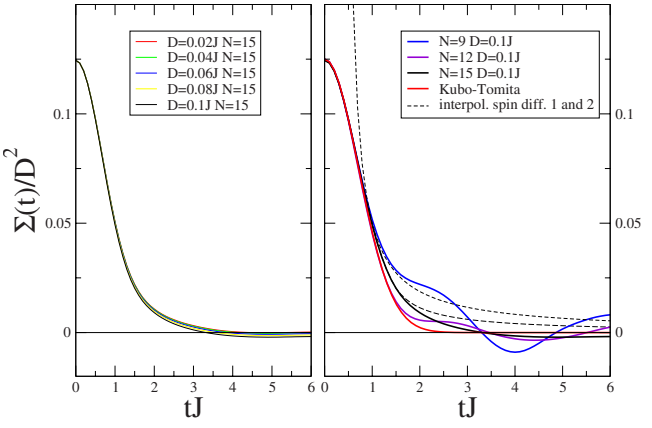

FIG. 7. (Color online) Memory function for the two-dimensional $S=\frac{1}{2}$ kagome antiferromagnet: effect of the Dzyaloshinskii-Moriya strength (left) and finite-size effects (right).

(shown in the inset of Fig. 6). The other assumption $\tau_0 < \tau_c$ is physically more relevant for two reasons. First τ_0 may be an intrinsic characteristic time of the one-dimensional model that terminates the spin diffusion before the anisotropy cutoff: $\tau_0 = \tau_c$ is valid only at the RPA level. Second, τ_0 may be an extrinsic "noise:" there are additional interactions, such as interchain couplings, that also tend to terminate the diffusion.[28–30] In fact it was argued that $\tau_0 J$ depends on the interchain coupling J' through $(J'/J)^{-4/3}$, which may indeed be a shorter time scale.[28] On the other hand, following the exact result at short times, the cutoff cannot be chosen smaller than $\tau_0 J = 6.5$ (but of course if J'/J becomes very strong, then one has to recalculate the short-time behavior as well). The linewidth decreases when τ_0 decreases; as a consequence, we regard the region represented in Fig. 5 by a hatched area as possibly relevant for experiments (we consider τ_0 as an unknown parameter). As we now explain, in this region, the line shape is a function of τ_0, thus giving the possibility to say how long the motion is diffusive and if it is diffusive at all.

In Fig. 6, we give the line shapes (normalized by the area), computed from Eq. (10), for different cutoffs of spin diffusion, τ_0. At small $\tau_0 \ll \tau_c$, the line shape is always Lorentzian (straight dashed line in the inverse representation on the right). For the self-consistent cutoff $\tau_0 = \tau_c$, the line shape strongly deviates from a Lorentzian. The deviation is less than that found by using the RPA calculation with a spin-diffusion tail [which is given by the Fourier transform of $\exp(-At^{3/2})$ (see intermediate dashed line)] (Ref. 5) and still far from the Gaussian profile (upper dashed line). For $\tau_0 > \tau_c$ we find a double-peak structure similar to that found in finite-size chains. We have therefore two possibilities for the double-peak structure as a function of the system size: either it survives in the thermodynamic limit (which means that for some reasons τ_0 could remain larger than τ_c) or it disappears. For a general τ_0, the inverse line shape changes smoothly as function of τ_0 and therefore a comparison of the line shape with experiment would provide a measure of the cutoff time, τ_0.

The linewidth (Fig. 5), together with the line shape (Fig. 6), can therefore be used to extract the anisotropy strength and test the spin-diffusion assumption. Note that in one dimension, because of the mapping we have discussed, it is not possible to tell whether the linewidth is due to the Dzyaloshinskii-Moriya or exchange anisotropies:[8,9] both contribute to an equal amount, using the replacement $2\delta \equiv (D/J)^2$.

V. RESONANCE IN TWO-DIMENSIONAL THERMODYNAMIC SYSTEMS

In two dimensions, the pattern of Dzyaloshinskii-Moriya vectors may generally be more complicated, depending on the symmetries of the crystal structure. In particular, it is not always possible to perform the mapping onto an exchange anisotropy because of the frustration that the closed loops of the lattice introduce (*irreducible components*). In this case, there seems to be no reason why the Dzyaloshinskii-Moriya term should contribute to the linewidth by an equal amount as the exchange anisotropy, and we shall see that it does not.

We have considered the example of the kagome antiferromagnet where the pattern of Dzyaloshinskii-Moriya vectors precisely have irreducible components.[31] These are the z component of the Dzyaloshinskii-Moriya field. We have calculated the memory function $\Sigma(t)$ by exact diagonalizations of clusters of up to 15 spins. We see that the result is weakly dependent on the strength of the Dzyaloshinskii-Moriya coupling, D (Fig. 7, left), except through $\Sigma(0) = D^2/8$ (at high temperatures). As a consequence, the linewidth should vary essentially like D^2/J. We now proceed like in one dimension to obtain a quantitative estimation of the prefactor. In fact finite-size effects are somehow more difficult to handle because we have less sizes available. In addition, we see a parity effect between clusters of odd and even sizes (Fig. 7, right). If we had only the $N=12$ cluster, it would be tempting to conclude that Kubo-Tomita is essentially exact in two dimensions. However, the $N=15$ cluster deviates from Kubo-Tomita. It is not clear whether this is an artifact due to the odd size of the cluster. We now proceed with the interpolation to the spin-diffusion assumption (which is in $1/t$ in two dimensions). Since we see no clear slowing down in the

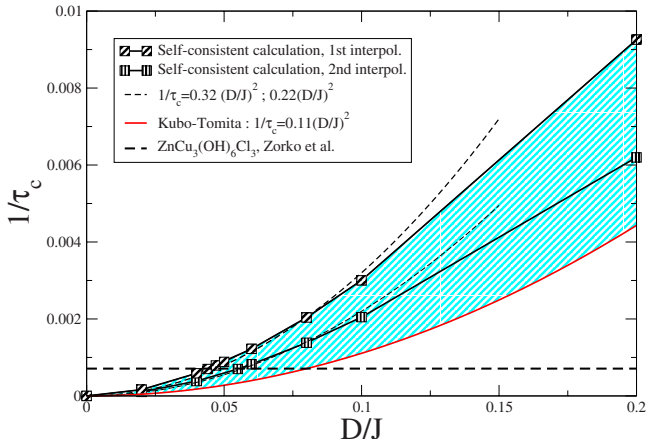

FIG. 8. (Color online) Linewidth vs anisotropy for the $S=\frac{1}{2}$ kagome antiferromagnet (Kubo-Tomita and self-consistent calculation). The horizontal line shows the experimental linewidth of $ZnCu_3(OH)_6Cl_3$ (Ref. 32).

present case, we have used two different times for the interpolation, $tJ=1$ (which certainly gives an upper bound) or $tJ=1.5$ (see the two dashed lines in Fig. 7).

The two results of the self-consistent calculation are shown in Fig. 8 (squares) and are fitted by $1/\tau_c=0.32(D/J)^2$ and $0.22(D/J)^2$ for small anisotropy. The linewidth is therefore larger than in one dimension. To put numbers, if we take $D=0.2J$, the linewidth is $6.0\times10^{-3}J$ (Fig. 8), whereas for the same D in one dimension, we have to take $\delta=(D/J)^2/2=0.02$, and the linewidth is $1.0\times10^{-3}J$ (Fig. 5). Now, as in one dimension, the area below the self-consistent result in Fig. 8 could be experimentally relevant (because of interplane couplings, for instance). Away from the Kubo-Tomita line (lower bound in Fig. 8), we can see in Fig. 9 that the line shape starts to deviate from a Lorentzian (but less than in one dimension).

We now apply this to the $S=\frac{1}{2}$ kagome compound $ZnCu_3(OH)_6Cl_3$.[33] The analysis of the linewidth using the Kubo-Tomita formula provided $D/J=0.08$.[32] If we assume that spin diffusion takes place, the self-consistent calculation

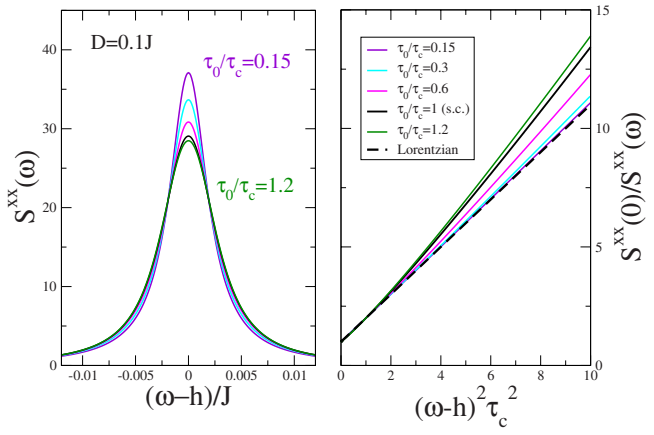

FIG. 9. (Color online) ESR line shape for the two-dimensional kagome antiferromagnet, assuming different cutoffs τ_0 of the $1/t$ diffusive tail.

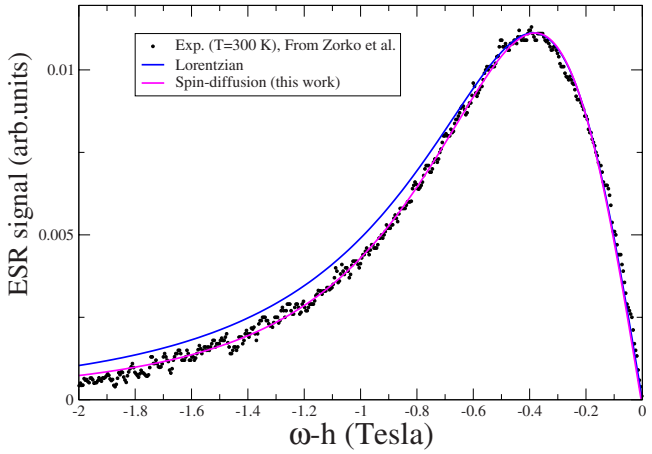

FIG. 10. (Color online) ESR signal (derivative of the resonance line at $\omega<h$): theory and experiment on the kagome $S=\frac{1}{2}$ $ZnCu_3(OH_3)Cl_2$ (from Ref. 32).

reproduces the same experimental linewidth providing $0.044\leq D/J\leq0.08$ (see dashed line in Fig. 8). It is difficult to compare directly with the ESR line shape of $ZnCu_3(OH)_6Cl_3$ because the experiment was done on powder samples.[32] One needs to average over all directions of the field and we have assumed a single direction here. Nonetheless, Fig. 10 shows that the deviations from a Lorentzian in the wings (here we restrict to $\omega<h$, which is not spoiled by an impurity line) can be accounted for by the spin-diffusion assumption and $D/J\sim0.05$. The result may be partly coincidental because there are other sources of deviations, such as the chemical disorder and the polycrystalline nature of the sample. Still we note that this coupling strength is not incompatible with the analysis of NMR which stated that $D/J\gtrsim0.05$.[34] In any case, from the ESR linewidth alone, we can conclude that $0.044\leq D/J\leq0.08$.

VI. CONCLUSION

First, for finite-size chains (zero dimension), we have found a special (and exact) double-peak line shape (Fig. 1) which may be interesting in molecular magnets having the geometry of a ring, especially because the line shape seems insensitive to the strength anisotropy (up to a rescaling) and size (in the limit of small size). We have stressed that such a line shape usually results from non-Markovian correlations in the memory function, which we did find in the calculation of $\Sigma(t)$ in this case.

In the thermodynamic limit, we have obtained the electron spin resonance in one and two dimensions for the anisotropies relevant to $S=\frac{1}{2}$ systems, by computing the memory function. We have provided the exact numerical result for $\Sigma(t)$ at short times and used it as an initial condition for a long-time spin-diffusion tail, which was taken as an assumption. We have then calculated the characteristic relaxation time (or linewidth) self-consistently, as well as the line shape.

In one dimension, the spin-diffusion assumption leads to enhance the linewidth by a factor that we have quantitatively

estimated (see Fig. 5 [squares]). It is about four times larger than the perturbative Kubo-Tomita's result. When this is true, the line shape strongly differs from a Lorentzian. To compare with experiments, it is interesting to consider another time scale, τ_0 which is the cutoff of the memory function (the physical reason may be intrinsic or extrinsic; for instance, because of interchain couplings). When τ_0 is reduced from its self-consistent value, the linewidth decreases and the line shape crossovers to a Lorentzian. A comparison of both the linewidth and line shape should therefore allow experimentally to determine the anisotropy strength and τ_0 (with a better accuracy than the use of the Kubo-Tomita formula). Note that, given a resonance line, we can extract the anisotropy parameter δ but we cannot tell whether δ is due to the exchange anisotropy or the Dzyaloshinskii-Moriya field (unless the later is forbidden by symmetry): both contribute at the same order of magnitude in one dimension.[8,9]

In two dimensions, the situation is different and there are two distinct cases: (1) *irreducible case* (the Dzyaloshinskii-Moriya vectors do not sum to zero while going around closed loops of the lattice). We have argued that the linewidth should vary essentially like D^2/J. (2) *Reducible case* (the Dzyaloshinskii-Moriya vectors do sum to zero). An exact transformation maps again the model onto an exchange anisotropy and, as in one dimension, both contribute at the same order ($\delta^2 J \sim D^4/J^3$).

The result in the irreducible case is in fact what the Kubo-Tomita formula gives, qualitatively. Quantitatively, the prefactor is bounded below by the Kubo-Tomita result. In fact if we restrict to the cluster of even size ($N=12$), we see an excellent agreement with the Gaussian decay and we would be tempted to conclude that we see no *quantitative* difference with Kubo-Tomita. By computing the next cluster ($N=15$), however, the difference turns out to be larger. While it is difficult to know if the difference comes from the odd size of the cluster, we have given in the later case the interpolation to the $1/t^{d/2}(d=2)$. The self-consistently calculated linewidth is in this case close to $0.22D^2/J$ or $0.32D^2/J$ (Fig. 8) depending on the interpolation time, but still larger than the Kubo-Tomita's formula, $0.11D^2/J$ (and in between, if interplane couplings are present).

We have applied the present theory to the two-dimensional kagome $ZnCu_3(OH_3)Cl_2$,[33] and concluded that $0.044 \leq D/J \leq 0.08$ from the ESR linewidth. In addition, the spin-diffusion assumption seems to account for the deviations of the line shape from a Lorentzian (Fig. 10) but single crystals are needed to avoid additional averaging effects. In this compound, the out-of-plane Dzyaloshinskii-Moriya component is irreducible while the in plane is reducible.[31] For single crystals, we therefore predict a much larger linewidth when the field is perpendicular to the plane.

We also note that, in absolute values, the irreducible Dzyaloshinskii-Moriya interactions in two dimensions induce a linewidth larger than in one dimension (where the Dzyaloshinskii-Moriya interactions are always reducible). The essential factor that governs the linewidth in low-dimensional $S=\frac{1}{2}$ systems is not the strength of the divergence $1/t^{1/2}$ versus $1/t$ of the spin diffusion (assuming it exists) but rather the reducible versus irreducible character of the Dzyaloshinskii-Moriya interaction. We have illustrated this on the kagome lattice but, at high temperatures, the shape of the lattice should not matter (as long as there are closed loops with Dzyaloshinskii-Moriya vectors not summing to zero).

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given. In fact there are many additional sources of natural broadening. Even if these were absent, experimentalists usually modulates the external field by a (very) small-frequency component, thus artificially broadening each peak.

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