Classical Aspects of Quantum Spin Chains

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We suggest a new variational approach for quantum spin chains, based on the stochastic behavior of the quantization axes, which describes a chain in terms of a classical and a quantum contribution to the free energy. For an easy-plane ferromagnetic chain with the external field in the plane it reveals that the nonlinear excitations are predominantly described by the classical degrees of freedom. Hence it offers a fundamental basis for the description of the elementary excitations of such systems in terms of classical solitons and quantum spin waves, as suggested by various experiments.

Considerable effort has been devoted to the theoretical description[1] and experimental verification of the existence of nonlinear (soliton) excitations. In this area of research magnetic chain systems have played an important role. In particular, chain systems with an easy-plane anisotropy, such as $CsNiF_3$ and $(C_6H_{11}NH_3)$-$CuBr_3$,[2] which are subjected to a symmetry-breaking field, were found to be soliton bearing. Theoretically, the description of the nonlinear excitations is based on the mapping[3] of the spin dynamics on that of a sine-Gordon model. Further research[4] indicated that the interpretation of the thermodynamic properties of *real* systems in terms of the sine-Gordon model is generally far beyond the validity range of the mapping, since it asserts a large spin and an extreme easy-plane anisotropy. Several attempts have been made to relax these conditions. However, the extension of the sine-Gordon model, in which out-of-plane components are taken into account, predicts instabilities for a single nonlinear "in-plane" excitation.[5]

On the other hand, the inclusion of quantum corrections seems to cancel the effect of out-of-plane components.[6,7] Moreover, attempts to include more than one soliton in such an approach are faced with the "theoretical" fact that the solitons go equidistant and form a lattice.[8]

In this Letter we will present a variation approach for the quantum spin chain, which is based on the stochastic behavior of the quantization axis of the individual spins. We will show that the free energy of such a system can be separated, in a straightforward way, into a quantum part and a classical part. For easy-plane ferromagnetic chains, the nonlinear excitations are contained in the classical part, whereas the quantum part contains predominantly linear excitations.

Our starting point is the model Hamiltonian H for a general XYZ spin chain, which contains four types of contributions: the external field, specified by its components B^x and B^z, the isotropic part of the exchange interaction J, and ΔJ and J_a, which specify an orthorhombic exchange anisotropy:

$$H = \sum_n \left[-\frac{J}{2}(S_n^+ S_{n+1}^- + S_n^- S_{n+1}^+) - (J - \Delta J)S_n^z S_{n+1}^z - \frac{J_a}{2}(S_n^+ S_{n+1}^+ + S_n^- S_{n+1}^-) - g\mu_B \frac{B^x}{2}(S_n^+ + S_n^-) - g\mu_B B^z S_n^z \right].$$

$$(1)$$

The dipolar interactions are considered not to be important, and therefore the direction of the spin chain in configuration space with respect to any preferred direction in spin space does not enter the model explicitly. The external field which interacts with a preferred spin component defines the spatial orientation: It relates the directions in spin space with those in configuration space. For a given chain all the directions are specified by the anisotropy and the field. In a quantum treatment of the model, the spin operators are usually written as a S_n^z component and ladder operators S_n^+ and S_n^-. It is possible to define a site-dependent z direction in spin space at

an angle (θ_n, ϕ_n) with the z direction in configuration space. The model Hamiltonian can then be written in terms of the spin operators defined with respect to the site-dependent z axis of the spin space. In the following we will call this axis the quantization axis. Of course, the model Hamiltonian (1) is written in a representation where the axis is the same for all sites. Different quantization axes at each site imply a rotation in spin space. The unitary transformation given by $\mathcal{U} = \exp[\sum_n U_n^z]$ $\times \exp[\sum_n U_n]$, with $U_n^z = i\phi_n S_n^z$ and $U_n = \frac{1}{2}\theta_n[S_n^+ - S_n^-]$, generates this rotation. The model Hamiltonian

in the new representation contains the angles (θ_n, ϕ_n) as parameters and it is obtained using the following transformation properties:

$$\mathcal{U}^{-1} S_n^z \mathcal{U} = \{\cos\theta_n\} S_n^z + \tfrac{1}{2}\sin\theta_n\{S_n^+ + S_n^-\} ,$$

$$\mathcal{U}^{-1} S_n^+ \exp(-i\phi_n)\mathcal{U} = \tfrac{1}{2}[\{\cos\theta_n + 1\} S_n^+ \{\cos\theta_n - 1\} S_n^-] - \{\sin\theta_n\} S_n , \qquad (2)$$

$$\mathcal{U}^{-1} S_n^- \exp(i\phi_n)\mathcal{U} = \tfrac{1}{2}[\{\cos\theta_n - 1\} S_n^+ + \{\cos\theta_n + 1\} S_n^-] - \{\sin\theta_n\} S_n^z .$$

In the following we will treat the angles (θ_n, ϕ_n) as random variables (Θ_n, Φ_n), since preliminary calculations indicated that searching for an optimal quantization axis per site is only useful for the calculation of the energy and the wave function of a few low-lying excited states. The partition function that we will consider is given by

$$Z = \mathrm{Tr}\exp(-\beta H) = E\{\mathrm{Tr}\exp(-\beta\mathcal{H})\} ,$$

where $\mathcal{H} = \mathcal{U}^{-1} H \mathcal{U}$. The symbol E denotes the expectation value over the random variables with a joint probability distribution which will optimize the free energy and Tr denotes the trace over the quantum states. Using the invariance of a trace operator with respect to cyclic permutations it is easy to show that this Z is also equal to the partition function of the spin chain described by the Hamiltonian (1). Our aim is now to find a reasonable approximation for the new partition function. For

$S = \tfrac{1}{2}$ chains it is well known that the S_n^z component can be eliminated from the Hamiltonian using the kinematical relation between the z component and the ladder operators, $S_n^z = \tfrac{1}{2} - S_n^+ S_n^-$. Doing so, we find that $\mathcal{H} = V + H_{\mathrm{qm}}$, where V contains only random variables. Defining the following average,

$$\langle A \rangle = \frac{E\{A\exp(-\beta V)\}}{E\{\exp(-\beta V)\}} , \qquad (3)$$

we split H_{qm} into $\langle H_{\mathrm{qm}}\rangle$ and $H_{\mathrm{qm}} - \langle H_{\mathrm{qm}}\rangle$, where the last term is treated as a perturbation. It should be noted that $\langle H_{\mathrm{qm}}\rangle$ is a quantum operator without random variables. The zeroth-order problem is defined by $\mathcal{H}^0 = V + \langle H_{\mathrm{qm}}\rangle$. In that case the partition function Z^0 equals

$$Z^0 = E\{\exp(-\beta V)\}\mathrm{Tr}\{\exp(-\beta\langle H_{\mathrm{qm}}\rangle)\} ,$$

where

$$E\{\exp(-\beta V)\} = \left\{ \prod_n \int d\phi_n\, d\theta_n \right\} \rho(\ldots, \phi_n\theta_n, \ldots)\exp\{-\beta V(\ldots, \phi_n\theta_n, \ldots)\} . \qquad (4)$$

Independent of our choice for the probability distribution $\rho(\ldots, \phi_n\theta_n, \ldots)$, the separation into a stochastic part and a quantum part is such that the first cumulant of the expansion of the free energy with respect to $H_{\mathrm{qm}} - \langle H_{\mathrm{qm}}\rangle$ disappears and the free energy obtained from Z^0 is an upper bound.[7,9] The free energy F of the chain is then approximated by

$$F < F_{\mathrm{cl}} + F_{\mathrm{qm}} ,$$

where

$$\beta F_{\mathrm{cl}} = -\ln[E\{\exp(-\beta V)\}] ,$$

$$\beta F_{\mathrm{qm}} = -\ln[\mathrm{Tr}\{\exp(-\beta\langle H_{\mathrm{qm}}\rangle)\}] . \qquad (5)$$

It is clear that all thermodynamic quantities are to the same extent a sum of a classical part and a quantum part. From Eq. (5) it is obvious that the introduction of site-dependent quantization axes in a random direction allows us to calculate an upper bound for the free energy of the chain which consists of two contributions. The first one is a configurational classical free energy, depending on the choice of the probability distribution for the quantization axes. The second contribution is the free energy of a modified quantum chain, whose parameters are classical averages and can be obtained from the configurational classical free energy.

We will confine ourselves now to the case of easy-plane anisotropy $(\Delta J > 0, J_a \approx 0)$, in which the quantization axes can be restricted to the easy plane. For convenience we choose a δ function $\delta(\theta_n - \pi/2)$ as the probability density for all Θ_n and the uniform distribution $\mathcal{F}\Phi_n$ for ϕ_n; $\mathcal{F}\Phi_n(\phi_n) = \phi_n/2\pi$, with $\phi_n \in [-\pi, +\pi]$. This specific choice leads directly to the classical partition function of a discrete sine-Gordon system, if we limit the expansion of $\cos(\phi_n - \phi_{n+1})$ to the first two terms. The "classical" free energy F_{cl} corresponds to the following sine-Gordon chain:

$$V_{\mathrm{sG}} = -\frac{JN}{4} + \frac{J}{4}\sum_n \left\{ \frac{1}{2}(\phi_n - \phi_{n+1})^2 \right.$$

$$\left. - \frac{2g\mu_B B^X}{J}\cos(\phi_n) \right\} . \qquad (6)$$

One should note that the present choice for the distribution $\mathcal{F}\Phi_n$ implies that there is no a priori correlation between the quantization axes of the spins (high-temperature limit). However, the functional form of Eq. (6) is preserved if we include some correlations between the quantization axes by a bivariate Gaussian distribution. The corresponding free energy, characterizing the degrees of freedom of the quantization axes, which are re-

stricted to the easy plane by the choice of our distribution, has been calculated by several authors.[10] In these calculations the free energy can be split into two parts, one originating from the classical oscillatory behavior of the quantization axis and another one describing the tun-

neling between the potential wells. The latter is generally attributed to solitons in the so-called ideal-gas phenomenology.[11]

Our next step is the calculation of F_{qm}, related to the partition function of the spin system defined by $\langle H_{qm}\rangle$. For an easy-plane system this Hamiltonian reads

$$\langle H_{qm}\rangle = J\sum_n \left\{\langle\cos(\phi_n - \phi_{n+1})\rangle + \frac{g\mu_B B^x}{J}\langle\cos(\phi_n)\rangle\right\}S_n^+ S_n^-$$

$$-\frac{J}{4}\sum_n \left\{\langle\cos(\phi_n - \phi_{n+1})\rangle - 1 - \frac{\Delta J}{J}\right\}\{S_n^+ S_{n+1}^+ + \text{H.c.}\}$$

$$-\frac{J}{4}\sum_n \left\{\langle\cos(\phi_n - \phi_{n+1})\rangle + 1 - \frac{\Delta J}{J}\right\}\{S_n^+ S_{n+1}^- + \text{H.c.}\}$$

$$-J\sum_n \langle\cos(\phi_n - \phi_{n+1})\rangle S_n^+ S_n^- S_{n+1}^+ S_{n+1}^- - \tfrac{1}{2}g\mu_B B^z\sum_n(S_n^+ + S_n^-). \tag{7}$$

Because the averages in this equation are the same for each site, they are related to derivatives of the free energy $F_{cl} = \beta^{-1}\ln[E\{\exp(-\beta V_{sG})\}]$. It is easy to show that

$$\langle\cos(\phi_n - \phi_{n+1})\rangle = -4\frac{\partial}{\partial J}\left[\frac{F_{cl}}{N}\right], \tag{8}$$

$$\langle\cos(\phi_n)\rangle = -\frac{2}{g\mu_B}\frac{\partial}{\partial B^x}\left[\frac{F_{cl}}{N}\right]. \tag{9}$$

The parameters for the *modified* quantum chain can now be interpreted: The averaged isotropic exchange interaction is given by $J\langle\cos(\phi_n - \phi_{n+1})\rangle$ and the in-plane field is modified by the average magnetization of the classical nonlinear excitations.

A few remarks seem to be appropriate: First, our

choice of the probability distribution for the angles of the quantization axes implies that the anisotropy of the exchange integral only manifests itself in the pure quantum part $\langle H_{qm}\rangle$. Apart from this, it is clear that in the low-temperature limit the perfect correlation between the quantization axes freezes out the classical degrees of freedom, because in that limit the Gaussian distribution becomes δ-function-like. With respect to the quantum part, one should note that the translation invariance of $\langle H_{qm}\rangle$ allows us to treat the wave number of the spin waves as a "good" quantum number, irrespective the presence of nonlinear excitations.

For those thermodynamic quantities that are insensitive to the contribution of the quantum excitations, the
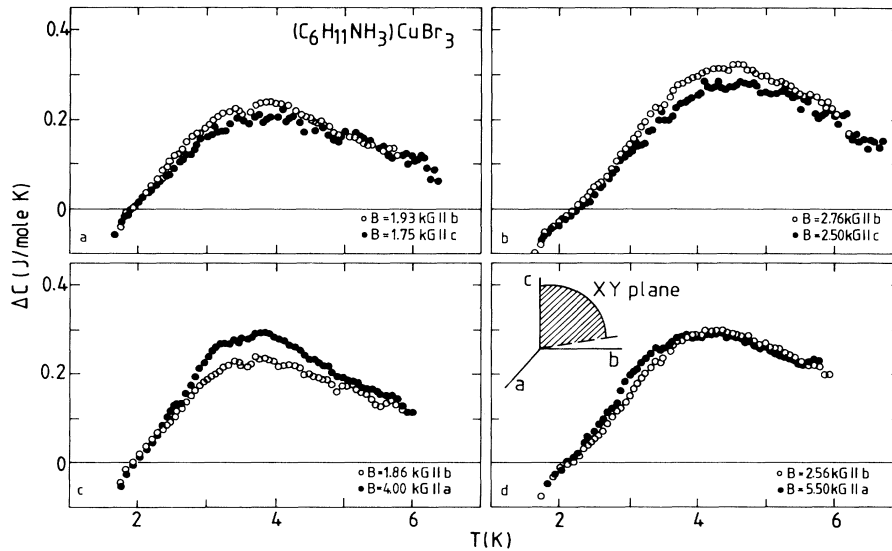

FIG. 1. Excess heat capacity ΔC of $(C_6H_{11}NH_3)CuBr_3$ obtained by subtracting the data collected in zero field from those collected in an applied field **B**. Each figure panel contains the results of two measurements performed in applied fields with a different magnitude and direction, but with the same component within the easy (XY) plane. The c axis is located within the easy plane; the angles of this plane with the a and b axes are 65° and 25°, respectively (see inset).

chain behaves as a classical sine-Gordon system (without out-of-plane corrections) with the soliton mass solely depending on the in-plane component of the external field. This behavior is corroborated experimentally by measurement of the excess heat capacity $\Delta C = C(\mathbf{B}) - C(0)$ of $(C_6H_{11}NH_3)CuBr_3$ for different magnetic fields $\mathbf{B}$ with the same in-plane component. According to the present approach, the free energy of these field configurations is given by the same classical behavior of the quantization axes and a different quantum-chain Hamiltonian $\langle H_{qm} \rangle$. Since it has been observed that the contribution of linear excitations to ΔC is small,[2] we expect the results for various fields to be quantitatively very similar. In Fig. 1 we have plotted the excess heat capacity of $(C_6H_{11}NH_3)CuBr_3$ for various fields with the same in-plane component. This experimental result, hard to understand by the traditional theory, is explained straightforwardly in our approach.

To conclude, a variety of experiments on easy-plane ferromagnetic chain systems[12] suggested that their behavior can be interpreted by assuming that the dominant elementary excitations are solitons and magnons. The success of this heuristic model, that characterizes such spin chains by two independent types of excitations, required a reformulation of the relation between the free energy of these spin chains and that of a sine-Gordon chain. In this Letter this reformulation is done on the basis of a variational approach for the distribution of the direction of the quantization axes. It is found that in general a simple distribution is sufficient to obtain a theoretical free energy consisting of a classical and a quantum part. In the case of an easy-plane system the classical free energy is described by a sine-Gordon model, with a mass related to the in-plane component of the external field. Secondly, the quantum free energy is described by a modified spin-chain Hamiltonian. As far as the magnon properties are concerned, our results show a renormalization induced by the presence of classical excitations. As a consequence, magnon excitation energies calculated with the modified spin-chain Hamiltonian have a term proportional to the soliton density.

The validity of the present approach is not restricted to easy-plane ferromagnetic chains. Also for more complex systems with, for example, an orthorhombic or helical symmetry, the introduction of stochastic quantization axes may contribute to the understanding of some of the thermodynamic properties of these quantum systems in terms of their classical equivalent.

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