High-temperature series expansion of the Helmholtz free energy of the quantum spin-*S* *XYZ* chain

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We consider the *XYZ* chain model of arbitrary spin S in the high-temperature region, with external magnetic field and single-ion anisotropy term. Our high-temperature expansion of the Helmholtz free energy is analytic in the parameters of the model for S, which may range from $1/2$ to the classical limit of infinite spin ($S\to\infty$). Our expansion is carried out up to order $(J\beta)^5$. Our results agree with numerical results of the specific heat per site for $S=1/2$, obtained by the Bethe ansatz, with $h=0$ and $D=0$. Finally, we show that the magnetic susceptibility and magnetization of the quantum model can be well approximated by their classical analog in this region of temperature.

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The one-dimensional Heisenberg model describing the exchange interaction of spins is intensively applied to study the magnetic properties of quantum spin chains. The *XXZ* spin-1/2 chain with external magnetic field along the z direction is exactly integrable, consequently its thermodynamics has been investigated since very early works.[1,2] The existence of higher-spin quasi-one-dimensional magnetic systems such as $CsVCl_3$ and $CsVBr_3$ ($S=3/2$),[3,4] $(C_{10}H_8N_2)MnCl_3$ ($S=2$),[5] and $(CD_3)_4NMnCl_3$ ($S=5/2$) has also been verified.[6,7] All these antiferromagnetic structures exhibit nearly ideal one-dimensional behavior over a considerable range of temperature. Motivated by these features, magnetic and thermodynamical properties for higher-spin chains were first investigated numerically.[8] More recently, we obtained in Ref. 9 the β expansion of the Helmholtz free energy (HFE) of the *XXZ* model, for arbitrary spin-S, up to order $(J\beta)^6$, where $\beta=1/kT$ (k is the Boltzmann constant and T is the absolute temperature), in the presence of an external magnetic field and a single-ion anisotropy term. We showed that in the high-temperature region, the magnetization and the magnetic susceptibility, even for low values of spin such as $S=3/2$, can be properly approximated by the classical results within a percental error of less than 4%.

Quasi-one-dimensional magnetic systems have been synthesized experimentally such as the $(C_6H_{11}NH_3)CuBr_3$ and the $(C_6H_{11}NH_3)CuCl_3$, known as CHAB and CHAC, respectively,[10] both exhibiting small anisotropy in the easy plane. They are described by the spin-1/2 *XYZ* spin model. By the appropriate design of molecules, it is possible to obtain a variety of spin systems, including those with spin larger than 1/2.

The thermodynamics of the *XYZ* model has been solved exactly for the spin-1/2 case without external magnetic fields; in this case, the model is integrable and its HFE is obtained from the Bethe ansatz through a couple of integral equations[2] and an infinite nonlinear coupled equation.[11]

The model is no longer integrable, though, if an external magnetic field in any direction is introduced. This is the case of the *XXZ* spin-1/2 spin chain with transverse external magnetic field; so far, only its phase diagram at zero temperature has been investigated,[12] since the external magnetic field does not commute with the Hamiltonian. However, an analytic high temperature series of its HFE has not been obtained so far.

In this Brief Report, we present the high-temperature thermodynamics of the spin-S *XYZ* model, for arbitrary value of S, in the presence of an external magnetic field and a single-ion anisotropy term. We also investigate if the anisotropy in the *XY* plane avoids or does not avoid the classical behavior of the magnetic susceptibility and magnetization in this region of temperature, even for $S=3/2$, as was shown in Ref. 9 for the spin-S *XXZ* model.

The Hamiltonian of the spin-S *XYZ* quantum periodic chain with N sites reads

$$\mathbf{H}=\sum_{i=1}^{N}\left[J_x'S_i^xS_{i+1}^x+J_y'S_i^yS_{i+1}^y+J_z'S_i^zS_{i+1}^z-h'S_i^z+D'(S_i^z)^2\right], \tag{1}$$

where $S_i^\alpha, \alpha\in\{x,y,z\}$, are the spin matrices at the ith site, the J_α' are the exchange interaction couplings between first neighbors, and h' is the external magnetic field along the z axis. We also include the single-ion anisotropy D' parallel to the external magnetic field. The periodic boundary condition $S_{N+1}^\alpha=S_1^\alpha$ is used.

In order to render the thermodynamic functions to be finite, even in the classical limit ($S\to\infty$), we define a scaled spin operator $\mathbf{s}$ with unitary norm[9] as $\mathbf{s}\equiv\mathbf{S}/\sqrt{S(S+1)}$. In order to write explicitly the effect of the anisotropy in the x and y directions in relation to the *XXZ* model,[9] we rewrite the Hamiltonian (1) in terms of the spin operators s_i^z and $s_j^\pm\equiv\frac{1}{\sqrt{2}}(s_j^x\pm is_j^y)$, with $j=1,\ldots,N$,

$$\mathbf{H} = \sum_{i=1}^{N} \{ J[s_i^- s_{i+1}^+ + s_i^+ s_{i+1}^- + \delta(s_i^+ s_{i+1}^+ + s_i^- s_{i+1}^-) + \Delta s_i^z s_{i+1}^z] - h s_i^z + D(s_i^z)^2 \}. \tag{2}$$

The relations among the constants in Hamiltonians (1) and (2) are: $J \equiv (S/2)(S+1)(J'_x + J'_y)$, $\delta \equiv (J'_x - J'_y)/(J'_x + J'_y)$, $\Delta \equiv 2J'_z/(J'_x + J'_y)$, $h \equiv \sqrt{S(S+1)}h'$, and $D \equiv S(S+1)D'$.

In Ref. 13, we presented a closed version of the cummulant expansion for any chain (any one-dimensional classical or quantum model) with periodic boundary condition and interaction between first neighbors. A survey with the main results of Ref. 13 is presented in Refs. 14 and 15. In this work, we apply that method to compute the high-temperature expansion of the HFE of the *XYZ* model ($\mathcal{W}_s$), for a fixed value of the spin (with unitary norm). Like in the case of the *XXZ* model, this high-temperature expansion is written as a series in powers of $[S(S+1)]^{-1}$. We use the interpolation method described in Ref. 9 to calculate the high-temperature expansion of $\mathcal{W}_s$, for arbitrary values of S, J, δ, Δ, h, and D, up to order $(J\beta)^5$. The whole expression is too large, so we present it here only up to order $(J\beta)^3$,

$$\begin{aligned}
\frac{\mathcal{W}_s(\beta)}{J} ={}& -\frac{\ln(2S+1)}{(J\beta)} + \frac{\tilde{D}}{3} + \Bigg(-\frac{\delta^2}{9} - \frac{\Delta^2}{18} - \frac{\tilde{h}^2}{6} - \frac{1}{9} + \left(\frac{1}{30\,S(S+1)} - \frac{2}{45}\right)\tilde{D}^2 \Bigg)(J\beta) \\
&+ \Bigg(-\frac{\Delta}{36\,S(S+1)} + \left(-\frac{1}{30\,S(S+1)} + \frac{2}{45}\right)\tilde{D}\tilde{h}^2 + \left(\frac{1}{45\,S(S+1)} - \frac{4}{135}\right)\tilde{D} + \frac{\Delta\,\delta^2}{36\,S(S+1)} + \frac{\Delta\tilde{h}^2}{9} \\
&+ \left(\frac{1}{126\,S^2(S+1)^2} - \frac{4}{315\,S(S+1)} + \frac{8}{2835}\right)\tilde{D}^3 + \left(-\frac{1}{45\,S(S+1)} + \frac{4}{135}\right)\Delta^2\tilde{D} + \left(\frac{1}{45\,S(S+1)} - \frac{4}{135}\right)\tilde{D}\delta^2 \Bigg) \\
&\times (J\beta)^2 + \Bigg(\left(-\frac{1}{5400\,S^2(S+1)^2} + \frac{2}{675\,S(S+1)} - \frac{7}{2700}\right)\Delta^4 + \left(-\frac{1}{300\,S^2(S+1)^2} + \frac{8}{2025\,S(S+1)} + \frac{2}{225}\right)\Delta^2 \\
&+ \left(\frac{1}{900\,S^2(S+1)^2} + \frac{64}{2025\,S(S+1)} - \frac{1}{25}\right)\delta^2 + \left(-\frac{11}{5400\,S^2(S+1)^2} + \frac{16}{2025\,S(S+1)} - \frac{1}{1350}\right)\delta^4 \\
&+ \left(\frac{1}{60\,S(S+1)} + \frac{2}{135}\right)\tilde{h}^2 + \left(-\frac{1}{84\,S^2(S+1)^2} + \frac{2}{105\,S(S+1)} - \frac{4}{945}\right)\tilde{h}^2\tilde{D}^2 + \Bigg(-\frac{3}{700\,S^2(S+1)^2} + \frac{8}{1575\,S(S+1)} \\
&+ \frac{4}{4725}\Bigg)\tilde{D}^2 + \left(-\frac{1}{540\,S(S+1)} + \frac{2}{135}\right)\delta^2\tilde{h}^2 + \left(\frac{1}{90\,S(S+1)} - \frac{7}{135}\right)\Delta^2\tilde{h}^2 + \Bigg(-\frac{1}{300\,S^2(S+1)^2} + \frac{8}{2025\,S(S+1)} \\
&+ \frac{2}{225}\Bigg)\Delta^2\delta^2 + \left(\frac{1}{360\,S(S+1)} + \frac{1}{180}\right)\tilde{h}^4 - \frac{11}{5400\,S^2(S+1)^2} + \frac{16}{2025\,S(S+1)} - \frac{1}{1350} + \Bigg(\frac{2}{45\,S(S+1)} \\
&- \frac{8}{135}\Bigg)\Delta\tilde{h}^2\tilde{D} + \left(\frac{1}{360\,S^3(S+1)^3} - \frac{97}{18900\,S^2(S+1)^2} + \frac{8}{4725\,S(S+1)} + \frac{4}{14175}\right)\tilde{D}^4 + \Bigg(-\frac{3}{700\,S^2(S+1)^2} \\
&+ \frac{8}{1575\,S(S+1)} + \frac{4}{4725}\Bigg)\delta^2\tilde{D}^2 + \left(-\frac{16}{1575\,S^2(S+1)^2} + \frac{88}{4725\,S(S+1)} - \frac{32}{4725}\right)\Delta^2\tilde{D}^2 \Bigg)(J\beta)^3 + \mathrm{O}((J\beta)^4),
\end{aligned} \tag{3}$$

where $\tilde{h} \equiv h/J$ and $\tilde{D} \equiv D/J$.

We point out that these coefficients of the HFE, calculated up to order $(J\beta)^5$, are exact and valid for $S=1/2$, 1, 3/2, 2, …. The dependence of the HFE on even powers of δ comes from the symmetry on the x and y directions. Letting $\mathcal{W}_S$ be the HFE of the *XYZ* model of spin with norm $S(S+1)$, we have that

$$\mathcal{W}_s(J,\delta,\Delta,h,D;\beta) \equiv \mathcal{W}_S\big(\sigma J,\delta,\Delta,\sqrt{\sigma}h,\sigma D;\beta\big), \tag{4}$$

where $\sigma = [S(S+1)]^{-1}$. The HFE is an homogeneous function of first degree, so it is simple to obtain the β expansion of $\mathcal{W}_S(J,\delta,\Delta,h,D;\beta)$ from Eq. (3). For $\delta=0$, we recover the results of Ref. 9. The full expression of the expansion, up to order $(J\beta)^5$, can be obtained upon request to the authors.

It is simple to derive from (3), the high-temperature expansion of the specific heat per site of the spin-S of the *XYZ* model, with unitary norm $C_s = -(\beta^2[\partial^2(\beta\mathcal{W}_s)/\partial\beta^2])$. We obtain $C_s = -(-(4D^2/45) - (h^2/3) + [D^2/15S(S+1)] - (\Delta^2/9) - \frac{2}{9} - (2\delta^2/9))\beta^2 + \mathcal{O}(\beta^3)$, which shows that in the high temperature region, the *XYZ* model also presents a tail of the Schottky peak[16] ($C_{Sch} \propto \beta^2$), for all values of S.

As a check of our β expansion of the HFE (3), valid for arbitrary spin-S, we compare the specific heat per site for $S=1/2$ derived from it to the numerical result obtained from

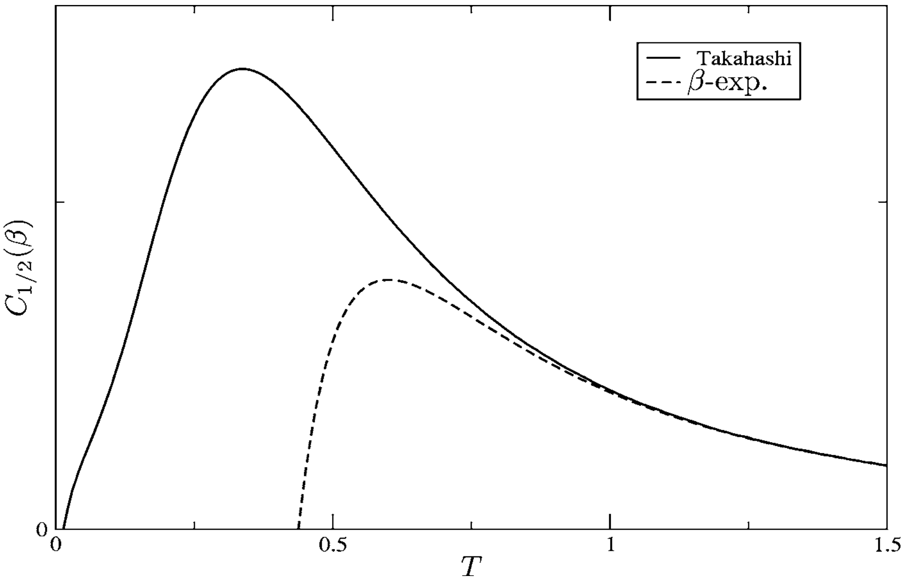

FIG. 1. Specif heat of spin-1/2 XYZ chain with $h=0$, $D=0$, $J_x=-1.0$, $J_y=1.2$, and $J_z=2.0$. The solid line corresponds to the numerical solution of Takahashi and the dashed line represents the β expansion of this function derived from (3).

the coupled equations by Takahashi.[11] In Fig. 1, we plot the specific heat for $S=1/2$ with $J_x=-1.0$, $J_y=1.2$, and $J_z=2.0$ (which corresponds to $J=(3/4)\times 0.1$, $\Delta=20$, and $\delta=-11$) in the absence of an external magnetic field ($h=0$) and no single-ion anisotropy term ($D=0$). At $T=0.90$, the difference of the solution is 2.9%.

One difficulty about the spin-S XYZ chain model is that it is no longer exactly soluble in the presence of an external magnetic field, even for $S=1/2$; moreover, the absence of symmetry in the x,y, and z directions makes numerical calculations much more involved. However, its classical limit, in the high-temperature region, can be easily obtained from Eq. (3) by taking $S\rightarrow\infty$.

In Fig. 2, we show that the magnetic susceptibility per site of this model can be approximated by their classical behavior even for $S=3/2$, in the high-temperature region, with a percent error smaller than 2%.

Figure 3 shows the comparision of the classical magnetization per site of the model to its quantum version for several values of spin, in the region of high temperatures. We verify that this thermodynamical function can be well approximated, in the high-temperature region, by its classical result up to $S=1$; the percent error, in this case, is smaller than 3% [see Fig. 3(b)].

In summary, we have presented the high-temperature expansion of the HFE of the XYZ model, for arbitrary values of spin, in the presence of an external magnetic field and single-ion anisotropy term, up to order $(J\beta)^5$. The thermodynamic functions derived from Eq. (3) can be used to fit experimental data to determine the value of the constants that describe the material under interest. As a check, we show that our expansion of the specific heat coincides with the numerical solution of Takahashi's coupled equations[11] up to $T\approx 1$ for $h=0$, $D=0$, $J_x=-1.0$, $J_y=1.2$, and $J_z=2.0$.

We easily obtain the β expansion of the classical behavior of the model in this region of temperature. Finally, we showed that the magnetic susceptibility and magnetization of the quantum XYZ model can be approximated by their clas-

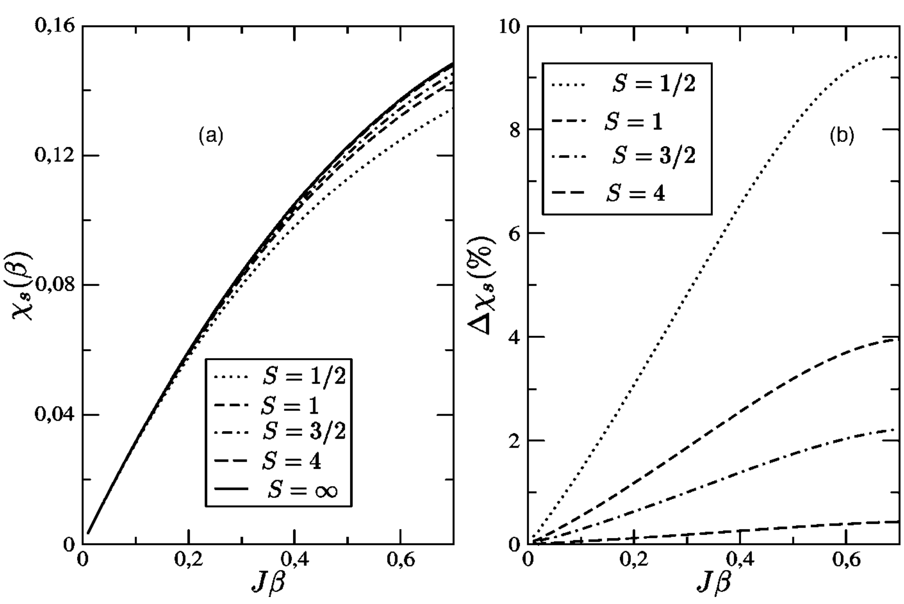

FIG. 2. In (a), we compare the classical ($S\rightarrow\infty$) and the quantum ($S=1/2$, 1, 3/2 and 4) magnetic susceptibility per site as a function of ($J\beta$). In (b), we present the relative percent difference between the quantum and classical results. We let $\Delta=1$, $\delta=1$, $h/J=0.3$, and $D/J=-0.5$.

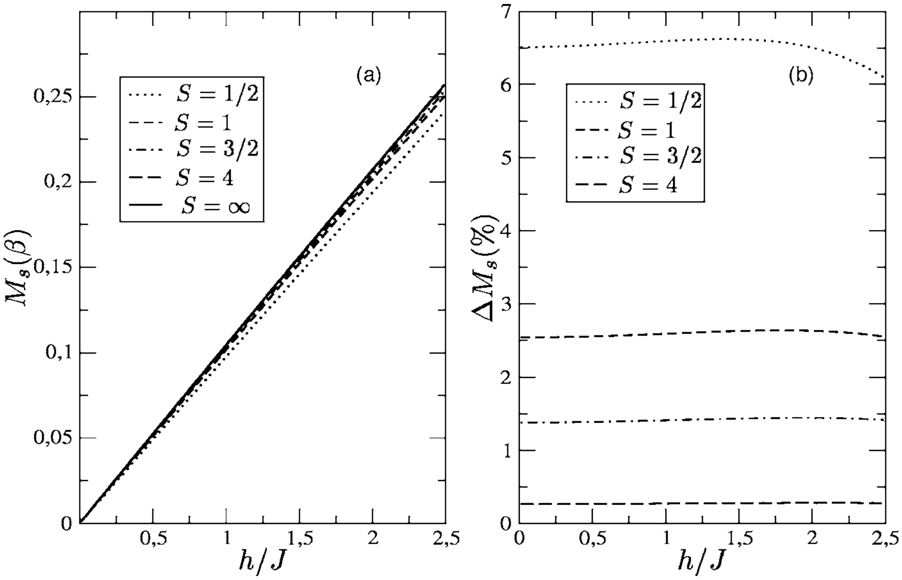

FIG. 3. The magnetization versus h/J at $J\beta=0.4$ is presented in (a) for $S=1/2$, 1, 3/2, 4 and $S\to\infty$. (b) shows the percent difference of those quantum magnetization curves with respect to the classical one. We let $\Delta=1$, $\delta=1$, and $D/J=-0.5$.

sical analog for $S\geqslant 3/2$ and $S\geqslant 1$, respectively. Our result allows the determination of the relative percent error between classical and quantum solutions, for any value of spin, for those thermodynamical functions, although this is not true for other functions like the specific heat per site.

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