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LETTER TO THE EDITOR

Calculation of the susceptibility of the $S = 1$ antiferromagnetic Heisenberg chain with single-ion anisotropy using the transfer matrix renormalization group method

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Abstract. Using an extension of the density matrix renormalization group method at finite temperature, we have calculated the magnetic susceptibility of the $S = 1$ antiferromagnetic Heisenberg chain with single-ion anisotropy. We investigate the dependence of the Haldane gap on the anisotropy energy. The results are compared with experimental data for the compound NENP.

Quantum spin chains have been the subject of many recent theoretical and experimental studies [1–12]. Here we present our calculations for the thermodynamics of the $S = 1$ antiferromagnetic Heisenberg model with single-ion anisotropy using a recent extension of the density matrix renormalization group (DMRG) method. We believe this to be the first application of this method to produce results which can be directly compared with experiment. This method allows us to calculate thermodynamic quantities at finite temperature. In addition the method may be used to estimate the properties of the system at zero temperature in the thermodynamic limit.

The system that we have considered is described by the Hamiltonian

$$H = J \sum_i \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} + D \sum_i (S_i^z)^2 \tag{1}$$

where the vectors $\boldsymbol{S}_i$ are quantum mechanical spin-one operators. This model is believed to describe quasi-one-dimensional magnets such as $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, NENP, in which magnetic ions form chains with negligible interchain interaction. The anisotropic term arises as a result of the crystal field. As such, a study of this system for various values of D/J is useful to compare with results from experiments on such materials. Also from a theoretical point of view, the system is believed to undergo a phase transition in the region $D \approx J$.

The study of quantum spin chains dates back to Bethe's solution for the spin-half Heisenberg antiferromagnet [1] which was shown to have a ground state with no long-range order and to have a gapless excitation spectrum. Higher-spin models, which are not analytically soluble by the Bethe *ansatz*, were believed to have qualitatively similar properties. Haldane's conjecture in 1983 [2], that systems with integral spin are gapped, was therefore met with some surprise. However, both numerical and experimental results

were forthcoming which supported this claim. Exact-diagonalization [3], quantum Monte Carlo [4], real-space renormalization group [5] and DMR [6] calculations give a value for the Haldane gap in the isotropic antiferromagnetic $S = 1$ Heisenberg model of $0.4101\,J$. The gap was also found experimentally in NENP by inelastic neutron scattering [7] and susceptibility measurements [8].

The ground state of this system is known to be a non-magnetic singlet, $S_T = 0$, while the first excited state is a triplet with $S_T = 1$. One qualitative explanation for the gap in the excitation spectrum is that proposed by Affleck *et al* [9] for the $S = 1$ chain with an additional biquadratic interaction. In this 'valence-bond solid' (VBS), each site on the chain is occupied by two spin-$1/2$ variables. The ground state has $S = 1$ spins formed by the bonding of two $S = 1/2$ spins from adjacent sites, thus forming dimers. These dimers must be broken in order to excite the system and Affleck *et al* rigorously showed that this leads to a non-zero energy gap between the ground and first excited states of the chain. The VBS model on a finite lattice leads to the formation of free spins with $S = 1/2$ at the ends and these have been experimentally observed in real systems [10] suggesting that this picture is also applicable at the Haldane point.

The effect of single-ion anisotropy on the Haldane gap has been studied by exact-diagonalization and quantum Monte Carlo methods by Golinelli *et al* [11] and the susceptibility by Yamamoto and Miyashita [12]. For small positive D, the triply degenerate first excited state is split into a lower-energy doublet with $S^z = \pm 1$ and a higher-energy state with $S^z = 0$. The gap is therefore split into two components, as observed by neutron scattering experiments on NENP, with the energy difference between the ground and first excited states decreasing with increasing D. A mean-field study by Chen *et al* predicted that the gap vanishes for $D = J$ [13]. For large D, the ground state is approximately that with all the spins in the $S^z = 0$ state. Perturbation theory [11] shows that the gap should increase with D within this region.

The transfer matrix renormalization group method (TMRG), introduced by Bursill, Xiang and Gehring [14] and then improved by Wang and Xiang [15], is a truncated-basis scheme for calculating the thermodynamics of one-dimensional interacting quantum lattice systems. It makes a Trotter–Suzuki decomposition of the Hamiltonian which allows Nishino's application of the DMRG algorithm to two-dimensional transfer matrices [16] to be applied. The method's first applications were in the study of exactly solvable $S = 1/2$ models and it proved itself to be an accurate and robust technique for calculating the free energy in the thermodynamic limit, giving encouraging results down to low temperatures. It was observed that the low-temperature region was most accurately reproduced when dealing with systems with an energy gap between the ground and first excited states. As well as calculating the free energy of the system, the TMRG can also be used to obtain thermal averages of other operators enabling the internal energy and magnetization to be calculated. Numerical differentiation then gives the specific heat and spin susceptibility.

As such the TMRG is a competitive computational method in two respects. Foremost, it allows the calculation of thermodynamic properties over the whole temperature range with an accuracy at least comparable to that of finite-temperature quantum Monte Carlo calculations and series expansions. Secondly, analysis of the low-temperature behaviour of the system can often be used to infer information about the ground state of the system. Whilst not being as accurate as the exact-diagonalization or zero-temperature QMC methods for this purpose, the TMRG method does have the advantage of dealing with an infinite chain rather than a finite one. Exact diagonalization, of course gives the exact energies of a finite system and errors are only introduced when attempting to extrapolate to the infinite system. The zero-temperature QMC method allows for larger systems but with reduced

accuracy. The TMRG method always works in the thermodynamic limit and this may be of significance when dealing with systems near a critical point where the correlation length of the system is diverging. Finite-lattice results may become unreliable as the correlation length becomes comparable with the size of the system. The TMRG method can also be used to calculate correlation lengths at finite temperature although this has not been done in the present case.

The TMRG method has been described in detail in references [14] and [15]. In going from an $S = 1/2$ to an $S = 1$ system, the main increase in difficulty is due to the increased size of the matrices which need to be stored and diagonalized. By making full use of the symmetries and sparcities of the matrices, we are able to retain $m = 70$ states in both the system and environment blocks used to the construct the transfer matrix, which is comparable to the number of states kept in the previous $S = 1/2$ calculations. The superblock transfer matrix is a large, asymmetric matrix whose maximal eigenvalue is obtained by application of the restarted Arnoldi algorithm.

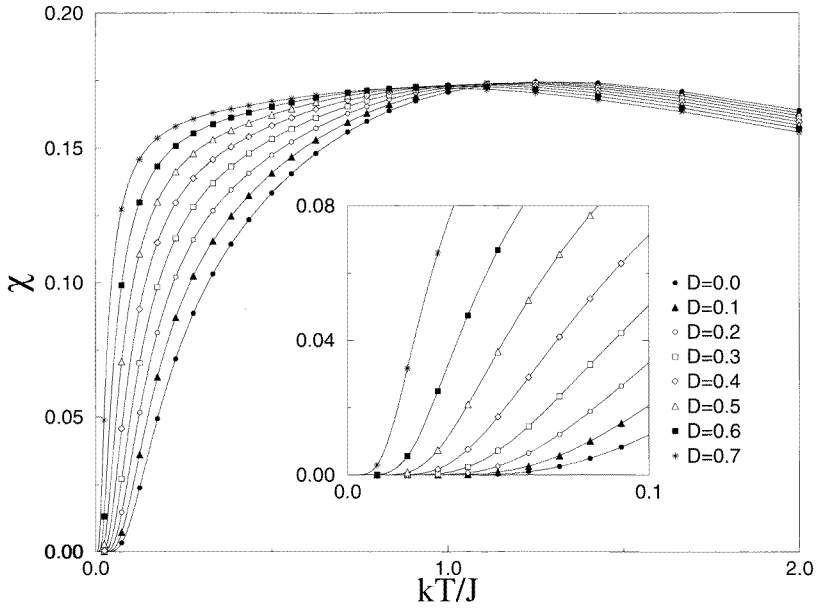

Figure 1. The magnetic susceptibility $\chi(T)$ for $0 \leqslant D \leqslant 0.7$. The inset shows the low-temperature region.

For the current model under consideration we have calculated the zero-field spin susceptibility, $\chi(T)$, for different values of D (J is set to 1 for all of the calculations). Figure 1 shows $\chi(T)$ over the region $0 \leqslant D \leqslant 0.7$. Each of the curves shows a peak at around $k_B T/J = 1$. Looking at the low-temperature behaviour, $\chi(T)$ shows an exponential rise, confirming the presence of an energy gap.

Sorensen and Affleck [17] treated the isotropic case by considering a dilute system of polarized magnons, which could be treated as a system of non-interacting fermions. For k near π the energy is given by

$$E(k) = \sqrt{v^2(k-\pi)^2 + \Delta^2} \tag{2}$$

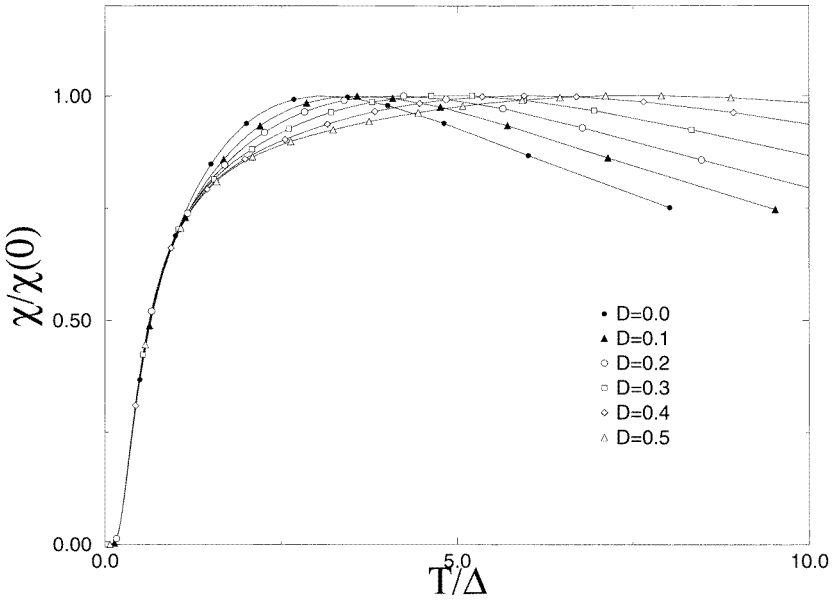

Figure 2. The normalized susceptibility χ/χ_0 as a function of T/Δ.

where v is the spin-wave velocity. This produces a density of states given by

$$g(E) = \frac{1}{\pi v}\frac{E}{\sqrt{E^2 - \Delta^2}}. \tag{3}$$

The zero-field susceptibility has the low-temperature form

$$\chi(T) = \frac{1}{v}\sqrt{\frac{2\Delta}{\pi T}}\exp\left(-\frac{\Delta}{T}\right).$$

Using the values of v and Δ given in reference [17], there is very good agreement with the results obtained with the TMRG. Fitting the susceptibility in the anisotropic case to this form gives an estimate of the gap Δ as a function of D. At the Haldane point ($D = 0$), Δ is estimated to be 0.415 which is within $\sim$1.5% of the zero-temperature DMRG result obtained by White and Huse [6]. As D is increased, the gap is reduced as is expected due to the splitting of the first excited state of the chain. To try and determine some sort of scaling for the low-temperature behaviour of $\chi(T)$, in figure 2 we plot $\chi(T)/\chi_{\max}$ versus T/Δ. For $D \leqslant 0.5$ the curves coincide at low temperature, thus demonstrating the dominance of $\Delta(D)$ in determining the susceptibility at low temperatures. In the region $0.8 \leqslant D \leqslant 1.2$, figure 3, the results that our method produces are unable to show conclusively whether the gap vanishes. At any given iteration, $T \sim 1/M$, where M is the size of the lattice in the Trotter direction; hence the algorithm tends to $T = 0$ asymptotically. As the number of iterations increases, so do the accumulated truncation and numerical errors. Hence, when the gap is reduced and the exponential behaviour of $\chi(T)$ is located in an ever-decreasing region close to $T = 0$, the results become less reliable.

Figure 4 shows $\chi(T)$ over the region $2 \leqslant D \leqslant 5$. The system again exhibits an energy gap which increases with D. Figure 5 shows the size of the gap as a function of D in the low- and high-D regimes.

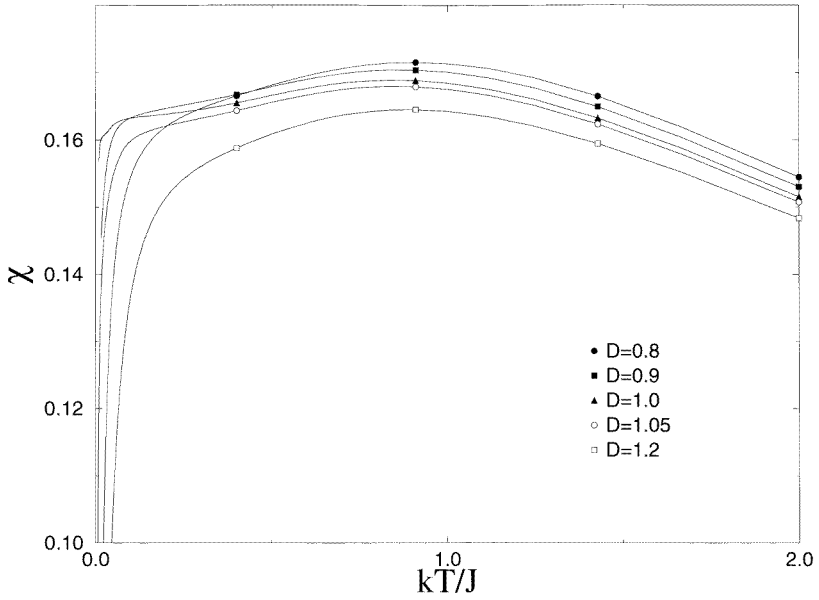

Figure 3. The magnetic susceptibility $\chi(T)$ for $0.8 \leqslant D \leqslant 1.2$.

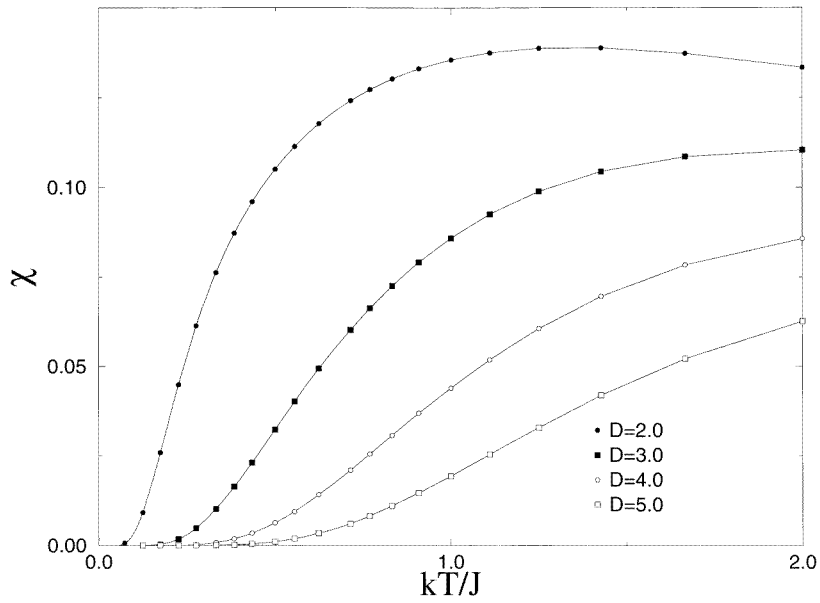

Figure 4. The magnetic susceptibility $\chi(T)$ for $2 \leqslant D \leqslant 5$.

In order to compare with experiment, we consider the compound NENP, for which susceptibility data from experiments on single-crystal samples are available. In this material the $S = 1$ Ni^{2+} ions form antiferromagnetic chains. The lack of any observed magnetic ordering down to very low temperatures confirms that the interchain interaction is very weak in comparison with the intrachain exchange energy J. The orthorhombic crystal structure

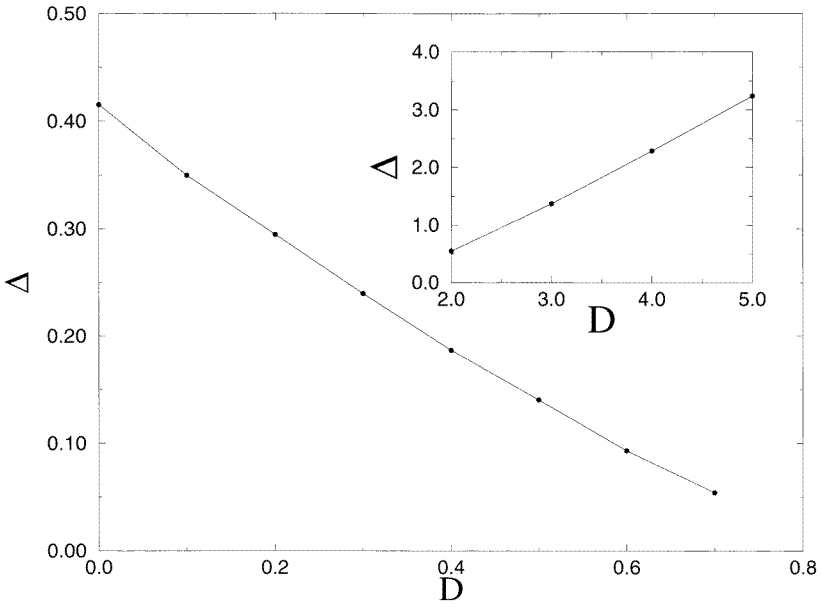

Figure 5. The energy gap Δ as a function of D in the region $0 \leqslant D \leqslant 0.7$. The inset shows Δ for $2 \leqslant D \leqslant 5$.

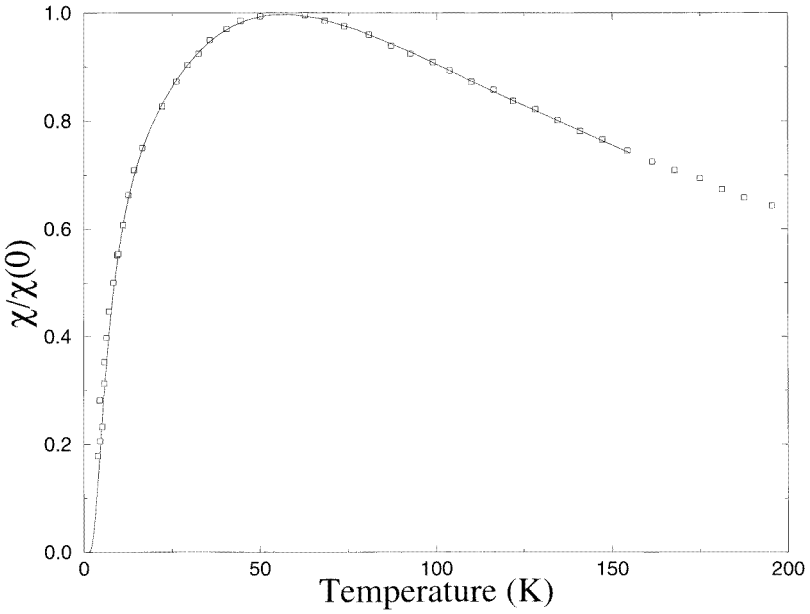

Figure 6. Comparison of the susceptibility calculated with the TMRG with the experimental data of reference [7].

leads to a single-ion anisotropy, D, along the chain direction. NENP has $D/J \approx 0.2$ with $J \approx 47$ K [18] and figure 6 shows the comparison of the zero-field susceptibility measured

along the chain direction calculated by the TMRG method using these parameters with the experimental data of Takeuchi *et al* [8]. The fit is good over the whole temperature range, being significantly better than that obtained by the QMC method at low temperatures and comparable to that obtained by series expansion at high temperatures. The TMRG method would appear to offer an accurate and computationally economical way of modelling the thermodynamics of real quasi-one-dimensional systems.

In conclusion, we have studied the effect of anisotropy on a one-dimensional spin chain at finite temperature. The TMRG method is seen to be a competitive one, accurately reproducing experimental results as well as giving approximate ground-state properties.

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