

ROTATIONAL BAND STRUCTURE OF LOW-LYING EXCITATIONS IN SMALL HEISENBERG SYSTEMS

JÜRGEN SCHNACK

Dept. of Physics, University of Osnabrück, Germany

MARSHALL LUBAN AND ROBERT MODLER

Ames Laboratory, Iowa State University, Ames, USA

We derive the low-temperature properties of the giant **molecular magnet** $\{\text{Mo}_{72}\text{Fe}_{30}\}$, where 30 Fe^{3+} paramagnetic ions occupy the sites of an icosidodecahedron and interact via isotropic nearest-neighbour antiferromagnetic **Heisenberg** exchange. The key idea of our model is that the low-lying excitations form a sequence of “**rotational bands**”, i.e., for each such band the excitation energies depend quadratically on the total spin quantum number. As **rotational bands** characterize the spectra of many magnetic molecules our method opens a new road towards a description of their low-temperature behaviour which is not otherwise accessible.

A new class of magnetic compounds known as **molecular magnets**¹ is attracting much attention. These compounds can be synthesized as single crystals of identical molecular units, each containing several paramagnetic ions that mutually interact via **Heisenberg** exchange. The intermolecular magnetic interactions are in the great majority of cases utterly negligible as compared to intramolecular interactions. Measurements of the magnetic properties therefore reflect those of the common, individual molecular unit. **Molecular magnets** such as $\{\text{Mn}_{12}\}$ and $\{\text{Fe}_8\}$ have been the focal point for intense study of subjects of broad scientific importance, such as quantum tunneling of magnetization and quantum coherence.² Very recently the first examples of a new paradigm of **molecular magnets**, based on so-called Keplerate structures, have been synthesized,³ and these offer numerous avenues for obtaining truly giant, highly symmetric arrays of paramagnetic ions. The archetype of this new class is referred to as $\{\text{Mo}_{72}\text{Fe}_{30}\}$.³ Embedded within a (diamagnetic) host molecule (mol. wt. 18,649), 30 Fe^{3+} paramagnetic ions (individual spins $s = 5/2$) occupy the sites of an icosidodecahedron and interact via isotropic, nearest-neighbor antiferromagnetic exchange. This Keplerate poses a major theoretical challenge. The dimension of the Hilbert space for $\{\text{Mo}_{72}\text{Fe}_{30}\}$ is a staggering 6^{30} , precluding the calculation of the energy eigenvalues on any computer. In this contribution we show that the major low-temperature properties of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ can be calculated using the result that the low-lying magnetic energy levels are governed by parallel **rotational bands**.⁴

The Hamiltonian including the interaction with a magnetic field B reads

$$\tilde{H} = -2J \sum_{(u<v)} \tilde{\mathfrak{z}}(u) \cdot \tilde{\mathfrak{z}}(v) + g\mu_B B \tilde{S}_z, \quad (1)$$

where J is the exchange constant with units of energy, and $J < 0$ corresponds to antiferromagnetic coupling, g is the spectroscopic splitting factor, and μ_B is the Bohr magneton. The vector operators $\tilde{\mathfrak{z}}(u)$ are the spin operators (in units of \hbar) of the individual paramagnetic ions.

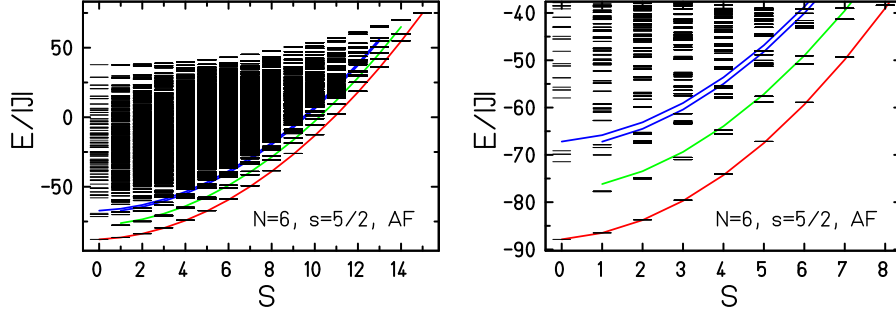


Figure 1. Spectrum of a ring of $N = 6$ spins with $s = 5/2$ interacting with next-neighbour antiferromagnetic **Heisenberg** exchange. The solid curves are the parabolic approximations to the **rotational bands**. The l.h.s. shows the full spectrum, the r.h.s. the low-energy part.

We exploit the fact that the set of minimal energies for each S forms a **rotational band**,

$$E_{S,min} \approx -J [D(N, s)/N] S(S+1) + E_a . \quad (2)$$

This has been noted on several occasions for ring structures with an even number N of sites,^{5,6} see also Fig. 1, as well as for many finite **Heisenberg** systems.^{7,8} For high-symmetry systems we provided an expression for the classical limit $D(N, \infty)$, henceforth denoted by D , which yields $D = 4$ for rings with even N and $D = 6$ for the icosidodecahedron, cube, and octahedron. Our investigations⁷ have shown that the numerical value of $D(N, s)$ for any finite s is always a little larger than D . The constant offset E_a in (2) is to be selected so that the highest level of the **rotational band**, which occurs for $S = Ns$, agrees with the largest energy eigenvalue of (1).

The **rotational band** (2) by itself is insufficient for calculating observables at low temperatures; it is essential to include the other low-lying excitation energies. This can be achieved via the introduction of an effective Hamilton operator whose form is set by incorporating the known symmetry of the ground state of the classical **Heisenberg** model. It has recently been established⁹ that the exact classical ground state of the icosidodecahedron for for $J < 0$ is describable in terms of three sublattice spin vectors $\vec{S}_A, \vec{S}_B,$ and \vec{S}_C with $|\vec{S}_A| = |\vec{S}_B| = |\vec{S}_C| = 25$, and with relative angles of 120° . We thus adopt as an effective Hamilton operator,^{7,10,11} replacing the field-free term of (1),

$$\tilde{H}^{\text{eff}} = -\frac{D J}{30} [\tilde{S}^2 - (\tilde{S}_A^2 + \tilde{S}_B^2 + \tilde{S}_C^2)] . \quad (3)$$

The three sublattice spin quantum numbers, S_A, S_B, S_C , can assume values $0, 1, \dots, 25$. The sublattice spin operators mutually commute and they also commute with \tilde{H}^{eff} . Thus the eigenvalues of \tilde{H}^{eff} are given in terms of the quantum numbers $S, S_A, S_B,$ and S_C . The lowest **rotational band**, Eq. 2, arises upon choosing $S_A = S_B = S_C = 25$ and allowing S to extend from 0 to 75. The next higher **rotational band** is obtained for the choice $S_A = S_B = 25, S_C = 24$ and its permutations. Note that these two bands are separated by an energy gap $\Delta = 10J$.

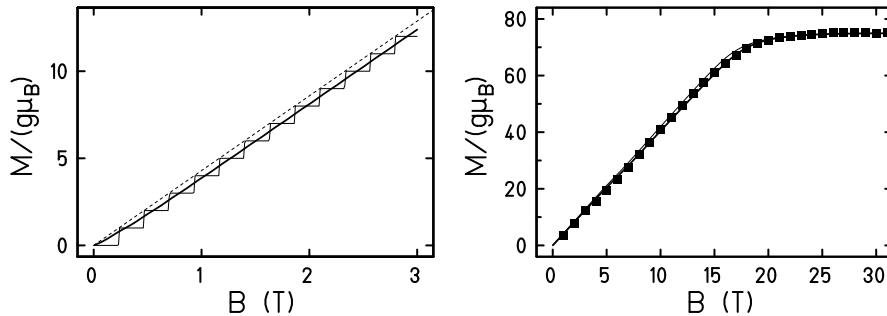


Figure 2. L.h.s.: The magnetisation according to (3) is shown for $T = 1$ mK (staircase) and 100 mK (thick solid curve) as well as for the corresponding classical **Heisenberg** model at $T = 0$ (dashed curve). R.h.s.: The thin curve displays the magnetisation following from (3) for $T = 4$ K. Experimental data using a pulsed field are given by solid squares; their size reflects an uncertainty of ± 0.5 T for the data. The thick curve shows the result of the improved approximation, taking $D(N, s) = 6.23$, and it closely reproduces the measured values.

Continuing this process leads to a sequence of parabolic bands. This is rather realistic for the second band, and indeed observed in many finite **Heisenberg** systems.⁷

The theoretical result for $\mathcal{M}/(g\mu_B)$ versus B at $T = 0$ K, as obtained using (3) and a Zeeman term, is a staircase with 75 steps of unit height which terminates at the critical field $B_c = 30|J|/(g\mu_B) = 17.7$ T. The values of J and g have been determined by high-temperature, low-field magnetic susceptibility measurements:¹² $J/k_B = -0.783$ K, and $g = 1.974$. For $B > B_c$ all spins are aligned parallel and the total moment is given by $\mathcal{M} = 75g\mu_B$. However, thermal broadening effects for $T \gtrsim 50$ mK reduce the staircase to a virtually linear ramp for $B < B_c$, and the result for 4 K is shown by the thin line in Fig. 2. The solid squares in Fig. 2 (r.h.s.) give the experimental data obtained using a pulsed field that led to an estimated effective spin temperature of approximately 4 K. The excellent agreement between theory and experiment confirms the underlying picture of **rotational bands** on which the model is based.

We attribute the very small discrepancy in the slope of the magnetization curve below the critical field to the fact that the classical coefficient $D = D(N, \infty)$ always underestimates the true coefficient $D(N, s)$ by a few percent.⁷ In order to improve approximation (3) we adjust $D(N, s)$ so that the resulting magnetization curve (thick curve in Fig. 2, r.h.s.) provides an optimal fit to the measured data. This is achieved by taking $D(N, s) = 6.23$, which is very close to $D = 6$. Finally, the resulting ground state energy of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ is $E_0/k_B \approx -364$ K. We are currently attempting to calculate $D(30, 5/2)$ from first principles using DMRG techniques.¹³

We now compare our theoretical results using (3) and a Zeeman term to our magnetization measurements at fixed magnetic fields. For both measured field strengths $B = 5.5$ T (not shown) and $B = 7.0$ T (Fig. 3, l.h.s.) we find good agreement to the experimental data. The rather flat behavior of the magnetization \mathcal{M} over a wide temperature range is a direct consequence of a sequence of **rotational bands**; it can be well understood with the help of the spectrum shown on the r.h.s.

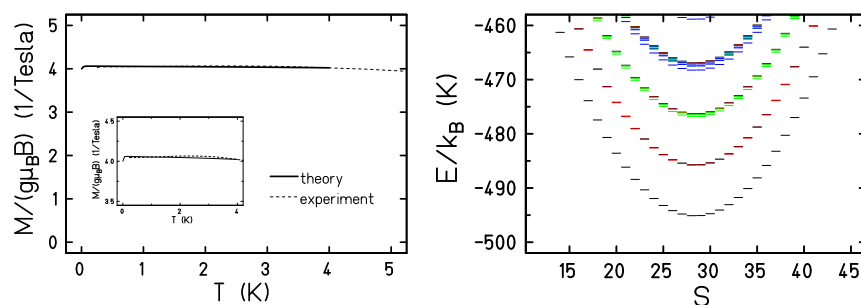


Figure 3. L.h.s.: Magnetisation vs. temperature using the four lowest bands of the improved approximate Hamiltonian with $B = 7.0$ T (solid line); experimental data (dashed line). The near constancy of M with T provides strong evidence that the lowest **rotational bands** are indeed parabolic. R.h.s.: Low-lying energy eigenvalues for $B = 7$ T.

of Fig. 3 for a finite magnetic field.⁴

The existence of **rotational bands** also implies the occurrence of resonances of the spin-lattice relaxation rate at low temperatures,¹⁴ which can be probed by proton NMR. In addition inelastic neutron scattering and EPR techniques should provide useful tests of the predicted spectrum. Anticipating that the Debye temperature of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ is of order 200–300 K, we believe that also specific heat measurements in the temperature range below 0.75 K can serve as a useful probe of the levels of the lowest **rotational band**.

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