

# Optimized perturbation theory for molecular antiferromagnets

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The energy spectra of mesoscopic, i.e. few-body quantum systems are of great interest in several areas of physics such as nuclear physics, cluster physics or magnetism. One way to obtain an approximate spectrum is to diagonalize with reduced but carefully chosen basis sets. In this Letter we propose for the case of mesoscopic antiferromagnets to use the eigenstates of the rotational band Hamiltonian for this purpose. These states are not only well adapted, they can also be easily constructed.

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*Introduction*—The spectrum of many interesting molecular antiferromagnets is theoretically often inaccessible due to the prohibitive size of the underlying Hilbert space. Experimentally the system of interest might very well be accessible for instance by neutron scattering, EPR, specific heat or magnetization measurements. The interpretation of the experimental data thus suffers from numerical restrictions. A prominent example for this problem is given by the giant Keplerate molecules  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  [1],  $\{\text{Mo}_{72}\text{Cr}_{30}\}$  [2], and  $\{\text{Mo}_{72}\text{V}_{30}\}$  [3], in which 30 paramagnetic ions occupy the vertices of an icosidodecahedron and interact by nearest-neighbor antiferromagnetic exchange. These molecules are rather similar to the Kagome lattice antiferromagnet. Thus by studying them one can also gain further insight into the properties of the Kagome lattice antiferromagnet.

In this Letter we propose to apply an approximate diagonalization that is guided by perturbation theory arguments. It rests on the observation that the low-lying spectrum of many finite size, for instance molecular, antiferromagnets can be rather successfully approximated by so-called rotational bands (or towers of states) [4, 5, 6, 7, 8], which are the eigenstates of the rotational band Hamiltonian. We suggest to use these basis states for an approximate diagonalization of the full Heisenberg Hamiltonian. We argue that such a procedure should be rather good since in a perturbation theory picture the rotational band Hamiltonian plays the role of the unperturbed Hamiltonian which constitutes already the major part of the Hamiltonian. Thus one can consider the eigenstates of the rotational-band Hamiltonian as prediagonalized basis states for which the full Hamiltonian should have not too big off-diagonal matrix elements anymore. Similar ideas are currently applied in nuclear physics, see for instance Ref. [9]. The aim of our attempt is to obtain sufficiently many approximate eigenstates in order to accurately estimate thermodynamic functions depending on temperature and applied magnetic field.

This constitutes a major difference to other approximate methods such as Density Matrix Renormalization Group techniques (DMRG) [10, 11], that yield only a few states and practically are restricted to one-dimensional systems, and to Lanczos [12] or finite temperature Lanczos [13] methods, that currently cannot be applied in Hilbert spaces with dimensions bigger than approximately  $10^9$ . Our proposed method is also not restricted by the negative sign problem in contrast to Quantum Monte Carlo methods [14].

As further advantages of the proposed method we would like to mention that the approximate basis states can be constructed according to spin coupling schemes and that the matrix elements of the Hamiltonian matrix can then be evaluated using Irreducible Tensor Operator (ITO) techniques [15, 16, 17]. In addition point group symmetries can be applied, which altogether provides a much better characterization of the approximated spectrum than other approximate methods can deliver. We demonstrate the applicability of our approximate diagonalization as well as limitations by several examples.

*Theoretical Method*—It turns out that many magnetic molecules can be well described within the Heisenberg model,

$$\tilde{H} = - \sum_{u,v} J_{uv} \tilde{\vec{s}}(u) \cdot \tilde{\vec{s}}(v) . \quad (1)$$

Here the sum reflects the exchange interaction between spins given by spin operators  $\tilde{\vec{s}}(u)$  at sites  $u$ . A negative value of  $J_{uv}$  corresponds to antiferromagnetic coupling. For the following discussions an antiferromagnetic nearest-neighbor exchange of constant size  $J$  is assumed.

Since the Hamiltonian commutes with the total spin, we can find a common eigenbasis  $\{|\nu\rangle\}$  of  $\tilde{H}$ ,  $\tilde{S}^2$ , and  $\tilde{S}_z$  and denote the related eigenvalues by  $E_\nu$ ,  $S_\nu$ , and  $M_\nu$ , respectively. For not too large spin systems all eigenvalues can be obtained numerically, but with growing system size this method becomes impossible since the re-

lated Hilbert space grows as  $(2s+1)^N$  for  $N$  spins of spin quantum number  $s$ .

Nevertheless, it has been realized that the low-energy spectrum of many antiferromagnetically coupled spin systems can be rather well approximated by so-called rotational bands, which resemble the spectrum of a quantum rotor [32]. This is especially true for antiferromagnets that consist of sublattices, i.e. where spins on one sublattice interact only with those of other sublattices. Prominent examples are given by ring molecules with an even number of spins that are bipartite (two sublattices) or by clusters of cuboctahedral or icosidodecahedral structure that possess three sublattices. In such cases the Heisenberg Hamiltonian can be approximated by

$$\tilde{H}^{\text{rb}} = -\frac{DJ}{N} \left[ \tilde{S}^2 - \sum_{n=1}^{N_s} \tilde{S}_n^2 \right], \quad (2)$$

where the operators  $\tilde{S}_n$  are the total spins of the sublattices of the spin system. The prefactor  $DJ/N$  is the effective coupling strength of the sublattice spins [4]. The eigenvalues of this Hamiltonian are easily evaluated since total spin and sublattice spins mutually commute. The multiplicity of the energy levels is given by the various ways to couple the individual spins to the sublattice spins and the sublattice spins to the total spin. It has been shown that such a rotational band Hamiltonian describes the low-lying levels of bipartite systems with very high accuracy [4, 5, 6], even neutron scattering data can be analyzed without diagonalizing the full Hamiltonian [18]. In the case of frustrated three- and four-sublattice [19, 20] systems such an assumption – although less accurate – can still explain gross properties like the magnetization [5] or the position of resonances in inelastic neutron scattering [21]. Also in the context of finite square and triangular lattices of spin-1/2 Heisenberg antiferromagnets such an approximation has been verified [7, 8]. Figure 1 shows as an example the low-lying exact spectrum as well as the rotational band energies for an antiferromagnetic ring with  $N = 6$  and  $s = 5/2$ .

The idea we propose in this Letter is to use the eigenstates of the rotational band Hamiltonian (2) for a diagonalization of the full Hamiltonian (1). Technically this is done with Irreducible Tensor Operator (ITO) techniques [15, 16]. If one could take all eigenstates this would of course correspond to an exact diagonalization. But in cases where this is not possible, a subset of low-lying eigenstates of  $\tilde{H}^{\text{rb}}$  can still be used for an approximate diagonalization. The expectation is that such a procedure yields a largely improved energy spectrum compared to the plain rotational band spectrum or to spectra obtained by DMRG or Lanczos. The reason for that is that from a perturbation theory point of view

$$\tilde{H} = \tilde{H}^{\text{rb}} + \tilde{H}', \quad (3)$$

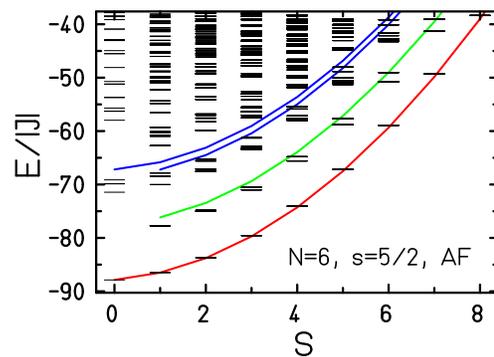


FIG. 1: (Color online) Low-lying spectrum of an antiferromagnetic ring with  $N = 6$  and  $s = 5/2$ : The exact energy eigenvalues of (1) are depicted by dashes. The rotational band energies according to (2) are given by curves in order to highlight their parabolic shape which is typical for a rotor.

and  $\tilde{H}'$  is relatively small compared to  $\tilde{H}^{\text{rb}}$ . Therefore, the rotational band model works as a guide to select a finite set of basis states for an approximate diagonalization. The fact that the eigenstates of  $\tilde{H}^{\text{rb}}$  do already possess spin rotational symmetry further improves the approximation.

With the help of examples we will demonstrate in the next part how good such an approximate diagonalization is, but some general remarks can be made already at this point. It was already observed that the rotational band approximation is much better for bipartite antiferromagnets, since they are not frustrated, as for systems with three or more sublattices. One can expect that also the approximate diagonalization using rotational band states will follow the same trend. The approximate diagonalization yields the new eigenstates as linear superposition of rotational band states. The influence of higher-lying rotational band levels on low-lying eigenstates should decrease with their energy difference as in perturbation theory where the energy difference appears in the denominator. Unfortunately, this can in principle be (over-)compensated if the density of states grows strongly with increasing energy and if the Hamiltonian still connects states even if they are far apart in energy. In the positive spirit of perturbation theory we hope that not both "ifs" have to be answered with yes. But even if in certain cases the absolute energy eigenvalue is only poorly met it could nevertheless be that the relative energies of the approximate levels are much better, which would be sufficient for a thermodynamic discussion.

*Numerical examples*—As a first example we discuss antiferromagnetic spin rings. For an even number of sites one expects rather good results since these systems do not suffer from frustration. In order to quantify the quality of the method we investigate the convergence of the energy levels as a function of the number of used rotational band states. For this purpose we group these states according

to their energy band, i.e. according to the quantum numbers of their total and sublattice spins.

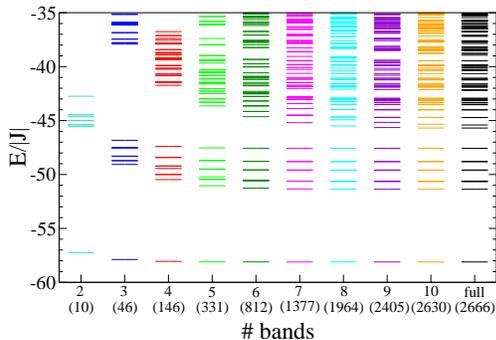


FIG. 2: (Color online) Convergence of the approximate energy levels as a function of the number of used rotational bands for a spin ring of  $N = 8$  spins  $s = 5/2$ .

Figure 2 shows how the levels of the subspace  $S = 0$  converge against the complete exact spectrum for a spin ring of  $N = 8$  spins  $s = 5/2$ . The numbers given at the  $x$ -axis denote the number of rotational bands used for the approximate diagonalization as well as in parenthesis the number of states contained in these bands. One realizes that the convergence is fast, and that the exact energy spectrum is rather well approximated using only 4 to 5 rotational bands for the diagonalization.

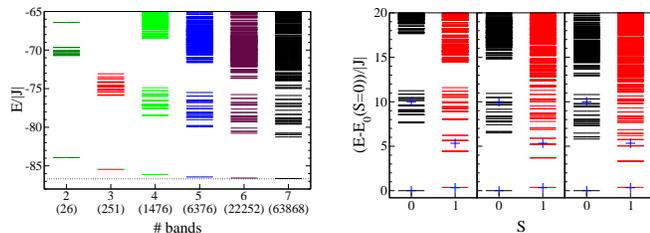


FIG. 3: (Color online) L.h.s.: Convergence of the approximate energy levels as a function of the number of used rotational bands for a spin ring of  $N = 12$  spins  $s = 5/2$ . R.h.s.: Approximate energy levels in subspaces  $S = 0$  and  $S = 1$  for 4, 5, and 6 used rotational bands. The crosses denote the positions of the two lowest rotational band energies for  $S = 0$  and  $S = 1$  ( $D = 4$  in (2)).

As an example for a large system we show the approximate spectrum for a ring of  $N = 12$  spins  $s = 5/2$  in Fig. 3. Such a system was synthesized on the basis of  $\text{Fe}^{\text{III}}$  ions [22]. Its parameters were determined using the rotational band approximation [23, 24] and later improved by means of QMC [25]. On the l.h.s. of Fig. 3 we show how the approximate energies converge in the subspace of  $S = 0$  which has a dimension of 1,949,156. The r.h.s. of Fig. 3 displays the subspaces of  $S = 0$  and  $S = 1$  together in order to demonstrate how the low-lying gap structure develops with the size of the truncated basis. We find that using about six bands, i.e. about 60,000

basis states provides a reasonable low-energy spectrum.

The understanding of the low-lying spectrum of the giant Keplerate molecules  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  [1],  $\{\text{Mo}_{72}\text{Cr}_{30}\}$  [2], and  $\{\text{Mo}_{72}\text{V}_{30}\}$  [3], in which 30 paramagnetic ions with spins  $s = 5/2, 3/2, 1/2$ , respectively, occupy the vertices of an icosidodecahedron, is of great importance due to its similarity with the kagome lattice antiferromagnet, see [26] for a recent review. For example, an interpretation of low-energy inelastic neutron scattering (INS) data in terms of rotational bands [21] or spinwave theory [27] has been only partially successful. A first improvement could be obtained in [28] where an approximate diagonalization using the states of just the two lowest rotational bands was performed. Nevertheless, the large low-lying density of states visible in the INS data was not reflected by any of the approximate spectra. Also for the interpretation of  $\mu\text{SR}$  data for  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  the rotational band model provides a first but not yet satisfactory approximation [29].

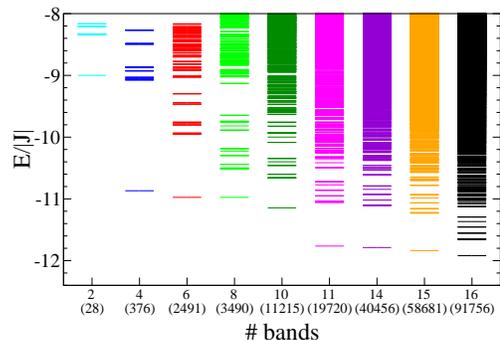


FIG. 4: (Color online) Convergence of the approximate energy levels as a function of the number of used rotational bands for an icosidodecahedron ( $N = 30$ ) of spins  $s = 1/2$ .

Figure 4 demonstrates that in this respect the proposed approximate diagonalization can yield a substantial improvement. The figure shows how the energy spectrum in the sector of total spin  $S = 0$  converges with the number of used rotational band states. Since this structure belongs to the geometrically most frustrated ones – Icosidodecahedron, Kagome, Pyrochlore – it is no surprise that the convergence is much slower than in the case of bipartite spin systems. In addition the convergence is also rather irregular, especially for the gap between the ground state and the first excited one in this subspace. But with nowadays numerical diagonalization capabilities one is able to arrive at a level of approximation that explains the high density of low-lying states, that is believed to be present in such highly frustrated antiferromagnets [30].

Finally we like to discuss our approximation for an icosidodecahedron ( $N = 30$ ) of spins  $s = 5/2$  as for example provided by  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  [1]. The total Hilbert space has the dimension of  $6^{30} \approx 10^{23}$ , therefore exact methods are nowadays (and in the foreseeable future) not appli-

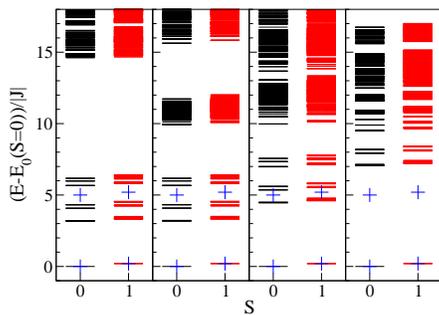


FIG. 5: (Color online) Approximate energy levels in subspaces  $S = 0$  and  $S = 1$  for 8, 9, 10, and 11 used rotational bands for an icosidodecahedron ( $N = 30$ ) of spins  $s = 5/2$ . The crosses denote the positions of the two lowest rotational band energies for  $S = 0$  and  $S = 1$  ( $D = 6$  in (2)).

cable. Figure 5 displays the approximate energy levels in subspaces  $S = 0$  and  $S = 1$  for 8, 9, 10, and 11 used rotational bands. Again the convergence is slow. Nevertheless, using only a tiny fraction of all basis states –  $\sim 10^5$  out of  $\sim 10^{23}$  – for the diagonalization provides a much richer spectrum than any of the methods used so far [21, 27, 28]. It is also interesting to note, that the rotational band model seems to provide an accurate estimate for the relative ground state energies in each sector of total spin  $S$  (crosses in Fig. 5), a fact that has already been noted in [31]. Figure 5 shows as well that the approximate spectrum is not yet converged. This explains, why linear and even non-linear spin wave theory for such frustrated systems yield poor results, since these methods correspond to an approximate diagonalization with two or a few more rotational bands.

*Summary & Outlook*—The approximate diagonalization in terms of low-lying rotational band states provides a promising description of the exact energy spectrum of mesoscopic antiferromagnets. This method can be further improved by employing point group symmetries, i.e. by diagonalizing in even smaller and better adapted subspaces. To this end the ITO technique has to be combined with point group symmetries, which in general is rather demanding [17]. Another route to improvements is given by an approximate diagonalization in terms of *important* states as suggested by the authors of Ref. [9]. This improvement aims at more accurately approximating some target states in order to obtain reliable energy gaps at the costs of less accurate higher-lying excited states. Both improvements will be tested in future investigations.

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physics where such bands are termed Yrast bands.