8 Quantum Theory of Molecular Magnetism

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1 Introduction

In this chapter I would like to present a short introduction into the field of molecular magnetism and some of the theoretical techniques as well as results. Some parts of the presentation overlap with earlier presentations in Refs. [1,2].

The synthesis of magnetic molecules shows continuous progress for the past 20 years [3–13]. Each of the identical molecular units can contain as few as two and up to several dozens of paramagnetic ions ("spins"). One of the largest paramagnetic molecules synthesized to date, the polyoxometalate { $Mo_{72}Fe_{30}$ } [14] contains 30 iron ions of spin s = 5/2. Although these materials appear as macroscopic samples, i. e. crystals or powders, the intermolecular magnetic interactions are utterly negligible as compared to the intra-molecular interactions. Therefore, measurements of their magnetic properties reflect mainly ensemble properties of single molecules. Their magnetic features promise a variety of applications in physics, magneto-chemistry, biology, biomedicine and material sciences [3,5,15] as well as in quantum computing [16–19]. The most promising progress so far is being made in the field of spin crossover substances using effects like "Light Induced Excited Spin State Trapping (LIESST)" [20] as well as in the field of magnetic molecules on surfaces and investigating their static and transport properties [23–26].

It appears that in many of these molecules – especially those which contain iron-group elements or gadolinium – the localized single-particle magnetic moments couple in most cases antiferromagnetically (and much rarer ferromagnetically), and the spectrum is rather well described by the Heisenberg model [27] with isotropic nearest neighbor interaction sometimes augmented by terms which describe various anisotropies [28, 29]. Studying such spin arrays focuses on qualitatively new physics caused by the finite (mesoscopic) size of the system.

The determination of the energy spectra of magnetic molecules is a demanding numerical problem. The attempt to diagonalize the Hamilton matrix numerically is very often severely restricted due to the huge dimension of the underlying Hilbert space. For a magnetic system of N spins of spin quantum number s the dimension is $(2s + 1)^N$ which grows exponentially with N. Group theoretical methods can help to ease this numerical problem [29–37]. With such methods one is able to block-diagonalize the Hamiltonian and thus to treat spin systems of unprecedented size. Thermodynamic observables such as the magnetization are then easily evaluated. In addition it provides a spectroscopic labeling by irreducible representations that can be related to selection rules which can be helpful when interpreting transitions induced by Electron Paramagnetic Resonance (EPR), Nuclear Magnetic Resonance (NMR) or Inelastic Neutron Scattering (INS). Besides numerically exact methods, approximations such as the Density Matrix Renormalization Group (DMRG) [38–41] and the Finite-Temperature Lanczos-Method (FTLM) [42–45] are employed for magnetic molecules.

2 Substances

From the viewpoint of theoretical magnetism it is not so important which chemical structures magnetic molecules actually have. Nevertheless, it is very interesting to note that they appear in almost all branches of chemistry. There are inorganic magnetic molecules like polyoxometalates, metal-organic molecules, and purely organic magnetic molecules in which radicals carry the magnetic moments. It is also fascinating that such molecules can be synthesized in a huge variety of structures extending from rather asymmetric structures to highly symmetric rings.



Fig. 1: *Structure of Mn-12-acetate: On the l.h.s. the Mn ions are depicted by large bullets, on the r.h.s. the dominant couplings are given.*

One of the first magnetic molecules to be synthesized was Mn-12-acetate [46] (Mn₁₂) – $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ – which by now serves as the "drosophila" of molecular magnetism, see e. g. [3, 15, 47–49]. As shown in Fig. 1 the molecules contains four Mn(IV) ions (s = 3/2) and eight Mn(III) ions (s = 2) which are magnetically coupled to give an S = 10 ground state. The molecules possesses a magnetic anisotropy, which determines the observed relaxation of the magnetization and quantum tunneling at low temperatures [47, 50].

Although the investigation of magnetic molecules in general – and of Mn-12-acetate in particular – has made great advances over the past two decades, it is still a challenge to deduce the underlying microscopic Hamiltonian, even if the Hamiltonian is of Heisenberg type. Mn-12acetate is known for more than 20 years now and investigated like no other magnetic molecule,



Fig. 2: Structure of a chromium-4 and a chromium-8 ring. The Cr ions are depicted in red.

but only recently its model parameters could be estimated with satisfying accuracy [51,52]. Another very well investigated class of molecules is given by spin rings among which iron rings ("ferric wheels") are most popular [8,41,53–60]. Iron-6 rings for instance can host alkali ions such as lithium or sodium which allows to modify the parameters of the spin Hamiltonian within some range [61,62]. Another realization of rings is possible using chromium ions as paramagnetic centers [63,64]. Figure 2 shows the structure of two rings, one with four chromium ions the other one with eight chromium ions.



Fig. 3: Structure of $\{Mo_{72}Fe_{30}\}\)$, a giant Keplerate molecule where 30 iron ions are placed at the vertices of an icosidodecahedron. a) sketch of the chemical structure, b) magnetic structure showing the iron ions (spheres), the nearest neighbor interactions (edges) as well as the spin directions in the classical ground state. The dashed triangle on the left corresponds to the respective triangle on the right [66].

Another route to molecular magnetism is based on so-called Keplerate structures which allow the synthesis of truly giant and highly symmetric spin arrays [65]. The molecule $\{Mo_{72}Fe_{30}\}$ [14, 66] containing 30 iron ions of spin s = 5/2 may be regarded as the archetype of such structures. Figure 3 shows on the left the inner skeleton of this molecule – Fe and O-Mo-O bridges – as well as the classical ground state [67] depicted by arrows on the right [66].



Fig. 4: Structure of a spin tube that consists of stacked Cu₃ units (black spheres) [68–70].

One of the obvious advantages of magnetic molecules is that the magnetic centers of different molecules are well separated by the ligands of the molecules. Therefore, the intermolecular interactions are utterly negligible and magnetic molecules can be considered as being independent. Nevertheless, it is also desirable to build up nanostructured materials consisting of magnetic molecules in a controlled way. Figure 4 gives an example of a linear structure consisting of stacked Cu_3 units [68, 69]. These systems show new combinations of physical properties that stem from both molecular and bulk effects, the latter in the example consisting in Luttinger liquid behavior [70].



Fig. 5: Design principle of Mn_6Cr and related molecules: Two C_3 -symmetric ligands (shown on the left) enclose a central unit and thus preserve total C_3 symmetry [12, 71].

Many more structures than those sketched above can be synthesized nowadays and with the increasing success of coordination chemistry more are yet to come. The final hope of course is that magnetic structures can be designed according to the desired magnetic properties. One major step along this line is performed by the group of Thorsten Glaser in Bielefeld who synthesizes Single Molecule Magnets according to a rational design as illustrated in Fig. 5 [12,71]. Another example is given by the search for new sub-Kelvin refrigerant materials such as gadolinium containing compounds as shown in Fig. 6 [13,72].



Fig. 6: Examples of Gd-containing molecules for magnetic refrigeration [13, 72].

3 Theoretical techniques and results

3.1 Hamiltonian

It appears that in the majority of these molecules the interaction between the localized singleparticle magnetic moments can be rather well described by the Heisenberg model with isotropic (nearest neighbor) interaction and an additional anisotropy term [29, 30, 61, 73, 74]. Dipolar interactions are usually of minor importance. It is also found that antiferromagnetic interactions are favored in most molecules leading to nontrivial ground states.

Heisenberg Hamiltonian

For many magnetic molecules the dominant parts of the total Hamiltonian can be written as

$$H_{\sim} = H_{\text{Heisenberg}} + H_{\text{anisotropy}} + H_{\text{Zeeman}}$$
(1)

$$H_{\text{Heisenberg}} = -\sum_{i,j} J_{ij} \vec{s}_i \cdot \vec{s}_j$$
(2)

$$H_{\text{anisotropy}} = \sum_{i=1}^{N} \left[D_{i} \vec{e}_{i,3} \otimes \vec{e}_{i,3} + E_{i} \left\{ \vec{e}_{i,1} \otimes \vec{e}_{i,1} - \vec{e}_{i,2} \otimes \vec{e}_{i,2} \right\} \right]$$
(3)

$$H_{\sim} \text{Zeeman} = \mu_B \vec{B} \cdot \sum_i \mathbf{g}_i \cdot \vec{s}_i .$$
(4)

The Heisenberg Hamilton operator¹ in the form given in Eq. (2) is isotropic, J_{ij} is a symmetric matrix containing the exchange parameters between spins at sites *i* and *j*. The exchange parameters are usually given in units of energy, and $J_{ij} < 0$ corresponds to antiferromagnetic, $J_{ij} > 0$ to ferromagnetic coupling.² The sum in (2) runs over all possible tuples (i, j). The vector operators \vec{s}_i are the single-particle spin operators.

The single-ion anisotropy terms (3) usually simplify to a large extend in symmetric systems, for instance for symmetric spin rings, where the site-dependent unit vectors $\vec{e}_{i,3}$ often are all equal, and the strength as well is the same for all sites $D_i = d$ and $E_i \approx 0$.

The third part (Zeeman term) in the full Hamiltonian describes the interaction with the external magnetic field. With an isotropic and identical g-matrix the direction of the field can be assumed to be along the z-axis which simplifies the Hamiltonian very much.

Although the Hamiltonian looks rather simple, the eigenvalue problem is very often not solvable due to the huge dimension of the Hilbert space or because the number of exchange constants is too big to allow an accurate determination from experimental data. Therefore, one falls back to effective single-spin Hamiltonians for molecules with non-zero ground state spin and a large enough gap to higher-lying multiplets.

¹Operators are denoted by a tilde.

²One has to be careful with this definition since it varies from author to author

Single-spin Hamiltonian

For molecules like Mn_{12} and Fe_8 which possess a high ground state spin and well separated higher lying levels the following single-spin Hamiltonian

$$H_{\sim} = D_2 S_z^2 + D_4 S_z^4 + H'$$
(5)

$$H'_{\Sigma} = g\mu_B B_x S_x \tag{6}$$

is appropriate, see e. g. Ref. [49]. The first two terms of the Hamilton operator \underline{H} represent the anisotropy whereas \underline{H}' is the Zeeman term for a magnetic field along the x-axis. The total spin is fixed, i. e. S = 10 for Mn₁₂ and Fe₈, thus the dimension of the Hilbert space is dim $(\mathcal{H}) = 2S + 1$.

The effective Hamiltonian (5) is sufficient to describe the low-lying spectrum and phenomena like magnetization tunneling. Since H' does not commute with the z-component of the total spin S_{z} , every eigenstate $|M\rangle$ of S_{z} , i. e. the states with good magnetic quantum number M, is not stationary but will tunnel through the barrier and after half the period be transformed into $|-M\rangle$.

3.2 Evaluating the spectrum

The ultimate goal is to evaluate the complete eigenvalue spectrum of the full Hamilton operator (1) as well as all eigenvectors. Since the total dimension of the Hilbert space is usually very large, e. g. $\dim(\mathcal{H}) = (2s + 1)^N$ for a system of N spins of equal spin quantum number s, a straightforward diagonalization of the full Hamilton matrix is not feasible. Nevertheless, very often the Hamilton matrix can be decomposed into a block structure because of spin symmetries or space symmetries. Accordingly the Hilbert space can be decomposed into mutually orthogonal subspaces. Then for a practical evaluation only the size of the largest matrix to be diagonalized is of importance (relevant dimension).

Product basis

The starting point for any diagonalization is the product basis $|\vec{m}\rangle = |m_1, \dots, m_j, \dots, m_N\rangle$ of the single-particle eigenstates of all s_j^z

$$s_{\sim j}^{z} \mid m_{1}, \dots, m_{j}, \dots, m_{N} \rangle = m_{j} \mid m_{1}, \dots, m_{j}, \dots, m_{N} \rangle .$$

$$(7)$$

These states are sometimes called Ising states. They span the full Hilbert space and are used to construct symmetry-related basis states.

Symmetries of the problem

Since the isotropic Heisenberg Hamiltonian includes only a scalar product between spins, this operator is rotationally invariant in spin space, i. e. it commutes with \vec{S} and thus also with

$$\begin{bmatrix} H_{\text{Heisenberg}}, \vec{S}^2 \end{bmatrix} = 0 \quad , \qquad \begin{bmatrix} H_{\text{Heisenberg}}, S_z \end{bmatrix} = 0 \; . \tag{8}$$

In a case where anisotropy is negligible a well-adapted basis is thus given by the simultaneous eigenstates $|S, M, \alpha\rangle$ of \vec{S}^2 and S_z , where α enumerates those states belonging to the same S and M [33,36,37,75]. Since the applied magnetic field can be assumed to point into z-direction for vanishing anisotropy the Zeeman term automatically also commutes with $H_{\text{Heisenberg}}$, \vec{S}^2 , and S_z . Since M is a good quantum number the Zeeman term does not need to be included in the diagonalization but can be added later.

Besides spin symmetries many molecules possess spatial symmetries. One example is given by spin rings which have a translational symmetry. In general the symmetries depend on the point group of the molecule; for the evaluation of the eigenvalue spectrum its irreducible representations have to be used [30,33,36,37,61]. Thus, in a case with anisotropy one loses spin rotational symmetries but one can still use space symmetries. Without anisotropy one even gains a further reduction of the relevant dimension.

Dimension of the problem

The following section illuminates the relevant dimensions assuming certain symmetries [75]. If no symmetry is present the total dimension is just

$$\dim\left(\mathcal{H}\right) = \prod_{j=1}^{N} \left(2s_j + 1\right) \tag{9}$$

for a spin array of N spins with various spin quantum numbers. In many cases the spin quantum numbers are equal resulting in a dimension of the total Hilbert space of $\dim(\mathcal{H}) = (2s+1)^N$. If the Hamiltonian commutes with S_z then M is a good quantum number and the Hilbert space \mathcal{H} can be divided into mutually orthogonal subspaces $\mathcal{H}(M)$

$$\mathcal{H} = \bigoplus_{M=-S_{\text{max}}}^{+S_{\text{max}}} \mathcal{H}(M) , \quad S_{\text{max}} = \sum_{j=1}^{N} s_j .$$
(10)

For given values of M, N and of all s_j the dimension dim $(\mathcal{H}(M))$ can be determined as the number of product states (7), which constitute a basis in $\mathcal{H}(M)$, with $\sum_j m_j = M$. The solution of this combinatorial problem can be given in closed form [75]

$$\dim\left(\mathcal{H}(M)\right) = \frac{1}{(S_{\max} - M)!} \left[\left(\frac{d}{dz}\right)^{S_{\max} - M} \prod_{j=1}^{N} \frac{1 - z^{2s_j + 1}}{1 - z} \right]_{z=0}.$$
 (11)

For equal single-spin quantum numbers s, and thus a maximum total spin quantum number of $S_{\text{max}} = Ns$, (11) simplifies to

$$\dim (\mathcal{H}(M)) = f(N, 2s+1, S_{\max} - M) \quad \text{with}$$

$$f(N, \mu, \nu) = \sum_{n=0}^{\lfloor \nu/\mu \rfloor} (-1)^n \binom{N}{n} \binom{N-1+\nu-n\mu}{N-1}.$$
(12)

In both formulae (11) and (12), M may be replaced by |M| since the dimension of $\mathcal{H}(M)$ equals those of $\mathcal{H}(-M)$. $\lfloor \nu/\mu \rfloor$ in the sum symbolizes the greatest integer less or equal to ν/μ . Eq. (12) is known as a result of de Moivre [76].

If the Hamiltonian commutes with \vec{S}^2 and all individual spins are identical the dimensions of the orthogonal eigenspaces $\mathcal{H}(S, M)$ can also be determined. The simultaneous eigenspaces $\mathcal{H}(S, M)$ of \vec{S}^2 and \vec{S}_z are spanned by eigenvectors of \vec{H} . The one-dimensional subspace $\mathcal{H}(M = S_{\max}) = \mathcal{H}(S_{\max}, S_{\max})$, especially, is spanned by $|\Omega\rangle$, a state called magnon vacuum. The total ladder operators (spin rising and lowering operators) are

$$S_{z}^{\pm} = S_{x} \pm i S_{y} \,. \tag{13}$$

For S > M, \underline{S}^- maps any normalized \underline{H} -eigenstate $\in \mathcal{H}(S, M + 1)$ onto an \underline{H} -eigenstate $\in \mathcal{H}(S, M)$ with norm $\sqrt{S(S+1) - M(M+1)}$.

For $0 \leq M < S_{\max}$, $\mathcal{H}(M)$ can be decomposed into orthogonal subspaces

$$\mathcal{H}(M) = \mathcal{H}(M, M) \oplus S^{-}\mathcal{H}(M+1)$$
(14)

with

$$\sum_{n=1}^{\infty} \mathcal{H}(M+1) = \bigoplus_{S \ge M+1} \mathcal{H}(S, M) .$$
(15)

In consequence, the diagonalization of H in \mathcal{H} has now been traced back to diagonalization in the subspaces $\mathcal{H}(S, S)$, the dimension of which are for $S < S_{\text{max}}$

$$\dim\left(\mathcal{H}(S,S)\right) = \dim\left(\mathcal{H}(M=S)\right) - \dim\left(\mathcal{H}(M=S+1)\right) \tag{16}$$

and can be calculated according to (12).

The use of combined spin, i.e. SU(2), and point group symmetries is rather involved, compare [36, 37, 77]. I would therefore like to demonstrate the use of symmetries for the combined use of the S_z -symmetry and the translational symmetry which is a cyclic group.

As a special example I focus on the translational symmetry found in spin rings. The discussed formalism can as well be applied to other cyclic symmetries. Any such translation is represented by the cyclic shift operator \underline{T} or a multiple repetition. \underline{T} is defined by its action on the product basis (7)

$$T_{\sim} | m_1, \dots, m_{N-1}, m_N \rangle = | m_N, m_1, \dots, m_{N-1} \rangle.$$

$$(17)$$

The eigenvalues of T are the N-th roots of unity

$$z_k = \exp\left\{-i\frac{2\pi k}{N}\right\}, \qquad k = 0, \dots, N-1, \qquad p_k = 2\pi k/N,$$
 (18)

where k will be called translational (or shift) quantum number and p_k momentum quantum number or crystal momentum. The numbers z_k are called characters of the point group C_N .

The shift operator \underline{T} commutes not only with the Hamiltonian but also with total spin. Any $\mathcal{H}(S, M)$ can therefore be decomposed into simultaneous eigenspaces $\mathcal{H}(S, M, k)$ of $\underline{\vec{S}}^2$, \underline{S}_z and \underline{T} .

In the following we demonstrate how an eigenbasis of both S_z and T can be constructed, this basis spans the orthogonal Hilbert spaces $\mathcal{H}(M, k)$. A special decomposition of \mathcal{H} into orthogonal subspaces can be achieved by starting with the product basis and considering the equivalence relation

$$|\psi\rangle \cong |\phi\rangle \Leftrightarrow |\psi\rangle = T^n_{\sim} |\phi\rangle, \ n \in \{1, 2, \dots, N\}$$
(19)

for any pair of states belonging to the product basis. The equivalence relation then induces a complete decomposition of the basis into disjoint subsets, i.e. the equivalence classes. A "cycle" is defined as the linear span of such an equivalence class of basis vectors. The obviously orthogonal decomposition of \mathcal{H} into cycles is compatible with the decomposition of \mathcal{H} into the various $\mathcal{H}(M)$. Evidently, the dimension of a cycle can never exceed N. Cycles are called "proper cycles" if their dimension equals N, they are termed "epicycles" else. One of the N primary basis states of a proper cycle may arbitrarily be denoted as

$$|\psi_1\rangle = |m_1, \dots, m_N\rangle \tag{20}$$

and the remaining ones may be enumerated as

$$|\psi_{n+1}\rangle = T^n |\psi_1\rangle, \ n = 1, 2, \dots, N-1.$$
 (21)

The cycle under consideration is likewise spanned by the states

$$|\chi_k\rangle = \frac{1}{\sqrt{N}} \sum_{\nu=0}^{N-1} \left(e^{i\frac{2\pi k}{N}} T \right)^{\nu} |\psi_1\rangle$$
(22)

which are eigenstates of \underline{T} with the respective shift quantum number k. Consequently, every k occurs once in a proper cycle. An epicycle of dimension D is spanned by D eigenstates of \underline{T} with each of the translational quantum numbers $k = 0, N/D, \ldots, (D-1)N/D$ occurring exactly once. As a rule of thumb one can say that the dimension of each $\mathcal{H}(M, k)$ is approximately $\dim(\mathcal{H}(M, k)) \approx \dim(\mathcal{H}(M))/N$. An exact evaluation of the relevant dimensions for spin rings can be obtained from Ref. [75].

Exact diagonalization

If the relevant dimension is small enough, the respective Hamilton matrices can be diagonalized, either analytically [75, 78, 79] or numerically, see e.g. [30, 33, 80–85].

Again, how such a project is carried out, will be explained with the help of an example, a simple spin ring with N = 6 and s = 1/2. The total dimension is $\dim(\mathcal{H}) = (2s + 1)^N = 64$. The Hamilton operator (2) simplifies to

$$H_{\sim}_{\text{Heisenberg}} = -2J \sum_{j=1}^{N} \vec{s_j} \cdot \vec{s_{j+1}}, \quad N+1 \equiv 1.$$
(23)

We start with the magnon vacuum $|\Omega\rangle = |+++++\rangle$ which spans the Hilbert space $\mathcal{H}(M)$ with M = Ns = 3. " \pm " are shorthand notations for $m = \pm 1/2$. The dimension of the subspace dim $(\mathcal{H}(M = Ns))$ is one and the energy eigenvalue is $E_{\Omega} = -2JNs^2 = -3J$. $|\Omega\rangle$ is an eigenstate of the shift operator with k = 0. Since S is also a good quantum number in this example $|\Omega\rangle$ has to be an eigenstate of \tilde{S}^2 , too, the quantum number is S = Ns.

The next subspace $\mathcal{H}(M)$ with M = Ns - 1 = 2 is spanned by $|-++++\rangle$ and the five other vectors which are obtained by repetitive application of \underline{T} . This subspace obviously has the dimension N, and the cycle spanned by $\underline{T}^n | -+++++\rangle$, $n = 0, \ldots, N-1$ is a proper one. Therefore, each k quantum number arises once. The respective eigenstates of \underline{T} can be constructed according to Eq. (22) as

$$|M = 2, k\rangle = \frac{1}{\sqrt{N}} \sum_{\nu=0}^{N-1} \left(e^{i\frac{2\pi k}{N}} T \right)^{\nu} |-++++\rangle.$$
(24)

All subspaces $\mathcal{H}(M, k)$ have dimension one. Since $\sum_{k=1}^{n} |\Omega\rangle$ is a state belonging to $\mathcal{H}(M = Ns - 1)$ with the same k-quantum number as $|\Omega\rangle$ it is clear that $|M = 2, k = 0\rangle$ is a already an eigenstate of \vec{S}^2 with S = Ns. The other five $|M = 2, k \neq 0\rangle$ must have S = Ns - 1. The next subspace $\mathcal{H}(M)$ with M = Ns - 2 = 1 is spanned by three basic vectors, i.e. $|--++++\rangle$, $|-++++\rangle$, $|-++++\rangle$ and the repetitive applications of T onto them. The first two result in proper cycles, the third vector $|-++-++\rangle$ results in an epicycle of dimension three, thus for the epicycle we find only k quantum numbers k = 0, 2, 4. The energy eigenvalues found in the subspace $\mathcal{H}(M = Ns - 1)$ ("above") must reappear here which again allows to address an S quantum number to these eigenvalues. The dimension of the subspace $\mathcal{H}(M = 1)$ is 15, the dimensions of the subspaces $\mathcal{H}(M, k)$ are 3 (k = 0), 2 (k = 1), 3 (k = 2), 2 (k = 3), 3 (k = 4), and 2 (k = 5).

The last subspace to be considered belongs to M = 0 and is spanned by $|--++\rangle$, $|-+-+\rangle$, $|-+-+\rangle$, $|-+-+\rangle$ and repetitive applications of T. Its dimension is 20. Here $|-+-+-+\rangle$ leads to an epicycle of dimension two.

The Hamilton matrices in subspaces with M < 0 need not be diagonalized due to the S_{z} -symmetry, i.e. eigenstates with negative M can be obtained by transforming all individual $m_j \rightarrow -m_j$. Summing up the dimensions of all $\mathcal{H}(M)$ yields $1+6+15+20+15+6+1 = 64 \sqrt{}$. Figure 7 shows the resulting energy spectrum both as a function of total spin S and as a function of translational quantum number k.

Lanczos method

Complex hermitian matrices can be completely diagonalized numerically on a normal PC up to a size of about 10,000 by 10,000 which corresponds to about 1.5 Gigabyte of necessary RAM. Nevertheless, for larger systems one can still use numerical methods to evaluate low-lying energy levels and the respective eigenstates with high accuracy. Very accurate methods rest on the construction of a so-called Krylov space. One of these methods to partially diagonalize a huge matrix was proposed by Cornelius Lanczos in 1950 [86,87]. This method uses a (random)



Fig. 7: Energy eigenvalues as a function of total spin quantum number S (l.h.s.) and k (r.h.s.).

initial vector. It then generates an orthonormal system in such a way that the representation of the operator of interest is tridiagonal. Every iteration adds one row and one column to the tridiagonal matrix. With growing size of the matrix its eigenvalues converge against the true ones until, in the case of finite dimensional Hilbert spaces, the eigenvalues reach their true values. The key point is that the extremal eigenvalues converge rather quickly compared to the other ones [88]. Thus, after about 100 Lanczos steps the ground state energy is already approximated to 10 figures although the dimension of the underlying Hilbert space is 10^8 .

A simple Lanczos algorithm looks like the following. One starts with an arbitrary vector $|\psi_0\rangle$, which has to have an overlap with the (unknown) ground state. The next orthogonal vector is constructed by application of H and projecting out the original vector $|\psi_0\rangle$

$$|\psi_{1}^{\prime}\rangle = (1 - |\psi_{0}\rangle\langle\psi_{0}|) \underbrace{H}_{\approx} |\psi_{0}\rangle = \underbrace{H}_{\approx} |\psi_{0}\rangle - \langle\psi_{0}|\underbrace{H}_{\approx} |\psi_{0}\rangle |\psi_{0}\rangle, \qquad (25)$$

which yields the normalized vector

$$|\psi_1\rangle = \frac{|\psi_1'\rangle}{\sqrt{\langle\psi_1'|\psi_1'\rangle}} \,. \tag{26}$$

Similarly all further basis vectors are generated

$$|\psi_{k+1}'\rangle = (1 - |\psi_k\rangle\langle\psi_k| - |\psi_{k-1}\rangle\langle\psi_{k-1}|) H |\psi_k\rangle$$

$$= H |\psi_k\rangle - \langle\psi_k|H|\psi_k\rangle|\psi_k\rangle - \langle\psi_{k-1}|H|\psi_k\rangle|\psi_{k-1}\rangle$$

$$(27)$$

and

$$|\psi_{k+1}\rangle = \frac{|\psi'_{k+1}\rangle}{\sqrt{\langle\psi'_{k+1}|\psi'_{k+1}\rangle}}.$$
 (28)

The new Lanczos vector is by construction orthogonal to the two previous ones. Without proof we repeat that it is then also orthogonal to all other previous Lanczos vectors. This constitutes the tridiagonal form of the resulting Hamilton matrix

$$T_{i,j} = \langle \psi_i | \underset{\sim}{H} | \psi_j \rangle \quad \text{with} \quad T_{i,j} = 0 \quad \text{if} \quad |i-j| > 1 .$$
(29)

The Lanczos matrix T can be diagonalized at any step. Usually one iterates the method until a certain convergence criterion is fulfilled.

The eigenvectors of H can be approximated using the eigenvectors ϕ_{μ} of T

$$|\chi_{\mu}\rangle \approx \sum_{i=0}^{n} \phi_{\mu,i} |\psi_{i}\rangle, \qquad (30)$$

where μ labels the desired energy eigenvalue, e.g. the ground state energy. *n* denotes the number of iterations, and $\phi_{\mu,i}$ is the *i*-th component of the n-dimensional eigenvector ϕ_{μ} of *T*. The simple Lanczos algorithm has some problems due to limited accuracy. One problem is that eigenvalues may collapse. Such problems can be solved with more refined formulations of the method [87].

Density Matrix Renormalization Group Method

The DMRG technique [38] has become one of the standard numerical methods for quantum lattice calculations in recent years [40]. Its basic idea is the reduction of Hilbert space while focusing on the accuracy of a target state. For this purpose the system is divided into subunits – blocks – which are represented by reduced sets of basis states. The dimension m of the truncated block Hilbert space is a major input parameter of the method and to a large extent determines its accuracy. For further details please see the lecture of Ulrich Schollwöck.

DMRG is best suited for chain-like structures. Many accurate results have been achieved by applying DMRG to various (quasi-)one-dimensional systems [84,89,90]. The best results were found for the limit of infinite chains with open boundary conditions. It is commonly accepted that DMRG reaches maximum accuracy when it is applied to systems with a small number of interactions between the blocks, e.g. systems with only nearest-neighbor interaction [91].

It is not *a priori* clear how good results for finite systems like magnetic molecules are. Such systems are usually not chain-like, so in order to carry out DMRG calculations a mapping onto a one-dimensional structure has to be performed [91]. Since the spin array consists of a count-able number of spins, any arbitrary numbering is already a mapping onto a one-dimensional structure. However, even if the original system had only nearest-neighbor exchange, the new one-dimensional system has many long-range interactions depending on the way the spins are enumerated. Therefore, a numbering which minimizes long range interactions is preferable.



Fig. 8: *Two-dimensional and one-dimensional projection of the icosidodecahedron, the site numbers are those used in [39], the lines represent interactions.*

Fig. 8 shows the graph of interactions for the molecule $\{Mo_{72}Fe_{30}\}$ which was used in Ref. [39]. For finite systems a block algorithm including sweeps, which is similar to the setup in White's original article [38], has turned out to be most efficient.

For illustrative purposes we use a simple Heisenberg Hamiltonian, compare (2). The Hamiltonian is invariant under rotations in spin space. Therefore, the total magnetic quantum number M is a good quantum number and we can perform our calculation in each orthogonal subspace $\mathcal{H}(M)$ separately [41,92].

When DMRG is applied to spin systems that are not one-dimensional, the usual way is to map the system on a one-dimensional chain with long-range interactions, i.e., to number the spins of the lattice [93]. However, if not very simple systems such as, e.g., ladders are investigated, it is not clear, which numbering is best suited. Such a problem also occurs, when DMRG is applied in the context of quantum chemistry, where models similar to the Hubbard model with long-range interactions appear and the ordering, i.e., the numbering of the orbitals is relevant. Since long-range interactions diminish the accuracy of DMRG (cf. Ref. [94]) it is clear that a good ordering needs to minimize such long-range interactions.

We have tested several numberings for the icosidodecahedron. The resulting coupling matrices J_{ij} are shown in Fig. 9. The numbering used by Exler and Schnack in an earlier investigation [39] (see top left of Fig. 9) gives a very regular "interaction pattern" with rather-short-ranged interactions, but the "periodic boundaries", i.e., interactions between the first and the last spins, are clearly not optimal for the DMRG algorithm with two center sites. As proposed in Ref. [95],



Fig. 9: Depiction of the coupling matrix (J_{ij}) for four different numberings of the vertices of the icosidodecahedron. Nonzero entries are denoted by the orange squares. Top left: numbering according to Exler and Schnack (see Ref. [39]); top right: result of the RCMD algorithm; bottom left: result of the Sloan algorithm; bottom right: unoptimized numbering.



Fig. 10: *DMRG* results for different numberings (see Fig. 9) of the spins sitting on the vertices of the icosidodecahedron. The plot shows the error in the ground state energy as a function of the number of DMRG sweeps. The numbers above the symbols denote the number of kept density matrix eigenstates for the sweep [92].

we have used a variant of the reverse Cuthill-McKee algorithm [96, 97], the RCMD algorithm, which aims to number the vertices such that the bandwidth of the matrix is minimized. We have also used the Sloan algorithm [98] which minimizes the "envelope size", i.e., the sum of the "row bandwidths". (The bandwidth is the maximum of the row bandwidths.) The figure also shows an unoptimized numbering for comparison.

The results of DMRG calculations (using the ALPS DMRG code [99]) for the different spin numberings are shown in Fig. 10. We have calculated the ground state energy of the s = 1/2icosidodecahedron with an increasing number of kept density matrix eigenstates (*m*) so that the convergence can be investigated and a comparison with the exact ground state energy (see Ref. [100]) is possible. One can see that the different optimized numberings (Exler/Schnack, RCMD, and Sloan) give almost identical results whereas the unoptimized numbering gives much worse results. These results show that a "good" numbering of the spins is absolutely essential if the DMRG method is applied to a spin system with a complicated structure. For the following results we have always used the numbering as proposed by Exler and Schnack.

As a next step we have calculated the lowest energies in the M subspaces for the icosidodecahedron with s > 1/2 using DMRG. The results for the s = 1/2 system already showed that DMRG is able to produce very accurate results for this system with relative errors smaller than 10^{-3} [39,92].

Figure 11 shows the lowest energy eigenvalues in the subspaces of total magnetic quantum number M for the icosidodecahedron with s = 1 and s = 3/2 as obtained by DMRG and – for the large-M subspaces (M > 18 for s = 1 and M > 33 for s = 3/2) – Lanczos calculations. We have used up to m = 2500 density matrix eigenstates for the s = 1 case and up to m = 2000 for the s = 3/2 case. The largest truncated weight within a sweep is of the order of $7 \cdot 10^{-4}$ for the M = 0 subspace of the s = 1 icosidodecahedron and of the order of $4 \cdot 10^{-4}$ for the



Fig. 11: Lowest energy eigenvalues in the subspaces of total magnetic quantum number M as obtained by DMRG calculations [92]. The eigenvalues for the smallest subspaces, i.e., for large M, were calculated using the Lanczos algorithm. For the DMRG calculations, the ALPS DMRG code was employed [99]. For the s = 1 system we have kept m = 2500 density matrix eigenstates in all DMRG calculations. For the s = 3/2 system we have kept m = 2000 states for the subspaces up to M = 4, m = 1500 states for the subspaces $5 \le M \le 23$, and 1000 states for the subspaces M > 23.

s = 3/2 case. That the truncated weight for the s = 1 icosidodecahedron is larger than for s = 3/2 although more states have been used for s = 1 indicates that it cannot be reliably used for a quantitative estimate of the error. The reason for this behavior might be that the results are not yet fully converged for the value of m that we have used, although we have carried out up to 60 sweeps for the calculations.

The rotational band model, compare next section, predicts a behavior of the form $E_{\min}(M) = aM(M+1) + b$, i.e., a parabolic dependence [101]. The insets of Fig. 11 show that this is an overall good approximation for the energy eigenvalues of the full Heisenberg model. The simple rotational band approximation predicts a proportionality constant of a = 0.1. The linear fits as shown in the insets give the results a = 0.111 for s = 1 and a = 0.108 for s = 3/2, very close to the simple rotational band approximation. However, if one uses these (DMRG) data to



Fig. 12: Zero-temperature magnetization curves of the icosidodecahedron as obtained by DMRG calculations (cf. Fig. 11). The data for s = 1/2 is taken from Ref. [100], the classical result from [67]. The data is normalized to the saturation field and magnetization. L.h.s.: s = 1/2, 1, 3/2 and classical result. R.h.s.: s = 3/2, 2, 5/2 and classical result [92].



Fig. 13: Ground state energy of the s = 5/2 icosidodecahedron as a function of the DMRG sweep. The numbers show the retained density matrix eigenstates for the current sweep [92].

calculate the zero-temperature magnetization curve, it becomes clear that there are some crucial deviations from the ideal parabolic dependence. If there was an ideal parabolic dependence, the resulting magnetization curve would consist of steps with constant widths. Fig. 12 shows the resulting zero-temperature magnetization curves as calculated using the DMRG data.

One can see, that the magnetization curves do not consist of steps with constant widths. There are some anomalies as expected for frustrated systems. The plateaus at $\mathcal{M}/\mathcal{M}_{sat} = 1/3$ are clearly visible. The magnetization jumps due to the independent magnons [102] are also visible. Since the jump has a height of $\Delta M = 3$, it is clear that this effect vanishes for $s \to \infty$ in the plot because the magnetization is normalized by the saturation magnetization $\mathcal{M}_{sat} = 30g\mu_B s$. For $s \to \infty$, the classical result, i.e., a strictly linear magnetization curve [67], will be reached. On the contrary, the plateau seems to be very stable when increasing s. A similar behavior has already been found for the cuboctahedron, compare Ref. [100]. For the cases s = 2 and s = 5/2 we have calculated the lowest energy eigenvalues only in some M subspaces, including those subspaces that are relevant for the calculation of the plateau width. We have kept m = 2000 density matrix eigenstates for these calculations. The plateau is clearly visible.

In the following we focus on the s = 5/2 case and the comparison to previous results on this system. Fig. 13 shows the ground state energy as a function of the DMRG sweep and as a function of the kept density matrix eigenstates. One can see that even for 2000 kept states and more than 30 sweeps the result is not yet converged. A much larger number of states is needed to get convergence. Also, an extrapolation to $m \to \infty$ is not reliably possible because for that many more sweeps would have to be performed.

For m = 2000 we obtain the value $E_0^{\text{DMRG}} \approx -216.5 J$. This value can be compared with previous results. The DMRG result of Exler and Schnack for the ground state energy (with m = 120) is approximately -211.1 J [39], a value that is much higher and thus much more imprecise than our result. The very recent result of Neuscamman and Chan using correlator product states in combination with variational Monte Carlo is -216.3 J [103]. This demonstrates that modern DMRG is able to accurately estimate relative ground state energies, at least much more accurate than determined by other methods.

3.3 Evaluation of thermodynamic observables

Exact evaluation

For the sake of completeness we want to outline how basic observables can be evaluated both as function of temperature T and magnetic field B. We will assume that $\left[\frac{H}{2}, \frac{S_z}{2}\right] = 0$ for this part, so that the energy eigenvectors $|\nu\rangle$ can be chosen as simultaneous eigenvectors of S_z with eigenvalues $E_{\nu}(B)$ and M_{ν} . The dependence of $E_{\nu}(B)$ on B is simply given by the Zeeman term. If H_{2} and S_z do not commute the respective traces for the partition function and thermodynamic means have to be evaluated starting from their general definitions. The partition function is defined as

$$Z(T,B) = \operatorname{Tr}\left\{ e^{-\beta \frac{H}{\widetilde{\omega}}} \right\} = \sum_{\nu} e^{-\beta E_{\nu}(B)} .$$
(31)

Then the magnetization and the susceptibility per molecule can be evaluated from the first and the second moment of S_z

$$\mathcal{M}(T,B) = -\frac{1}{Z} \operatorname{Tr} \left\{ g\mu_B \sum_{z} e^{-\beta H} \right\} = -\frac{g\mu_B}{Z(T,B)} \sum_{\nu} M_{\nu} e^{-\beta E_{\nu}(B)}$$
(32)

$$\chi(T,B) = \frac{\partial \mathcal{M}(T,B)}{\partial B} = \frac{(g\mu_B)^2}{k_B T} \left\{ \frac{1}{Z} \sum_{\nu} M_{\nu}^2 \, \mathrm{e}^{-\beta E_{\nu}(B)} - \left(\frac{1}{Z} \sum_{\nu} M_{\nu} \, \mathrm{e}^{-\beta E_{\nu}(B)} \right)^2 \right\}$$
(33)

In a similar way the internal energy and the specific heat are evaluated from first and second moment of the Hamiltonian

$$U(T,B) = -\frac{1}{Z} \operatorname{Tr} \left\{ \underset{\sim}{H} e^{-\beta \underset{\sim}{H}} \right\} = -\frac{1}{Z} \sum_{\nu} E_{\nu}(B) e^{-\beta E_{\nu}(B)}$$
(34)

$$C(T,B) = \frac{\partial U(T,B)}{\partial T}$$

$$= \frac{1}{k_B T^2} \left\{ \frac{1}{Z} \sum_{\nu} (E_{\nu}(B))^2 e^{-\beta E_{\nu}(B)} - \left(\frac{1}{Z} \sum_{\nu} E_{\nu}(B) e^{-\beta E_{\nu}(B)} \right)^2 \right\}.$$
(35)

Approximate evaluation by means of the Finite-Temperature Lanczosmethod

For the evaluation of thermodynamic properties in the canonical ensemble the exact partition function Z depending on temperature T and magnetic field B is given by

$$Z(T,B) = \sum_{\nu} \langle \nu | e^{-\beta H} | \nu \rangle.$$
(36)

Here $\{ |\nu\rangle \}$ denotes an arbitrary orthonormal basis of the respective Hilbert space. Following the ideas of Refs. [42, 43] the unknown matrix elements are approximated as

$$\langle \nu | e^{-\beta H} \rangle \approx \sum_{n=1}^{N_L} \langle \nu | n(\nu) \rangle e^{-\beta \epsilon_n^{(\nu)}} \langle n(\nu) | \nu \rangle.$$
 (37)

For the evaluation of the right hand side of Eq. (37) $|\nu\rangle$ is taken as the initial vector of a Lanczos iteration. This iteration consists of N_L Lanczos steps, which span a respective Krylov space. As common for the Lanczos method the Hamiltonian is diagonalized in this Krylov space. This yields the N_L Lanczos eigenvectors $|n(\nu)\rangle$ as well as the associated Lanczos energy eigenvalues $\epsilon_n^{(\nu)}$. They are enumerated by $n = 1, \ldots, N_L$. The notation $n(\nu)$ is chosen to remind one that the Lanczos eigenvectors $|n(\nu)\rangle$ belong to the Krylov space derived from the original state $|\nu\rangle$.

The number of Lanczos steps N_L is a parameter of the approximation that needs to be large enough to reach the extremal energy eigenvalues but should not be too large in order not to run into problems of numerical accuracy. $N_L \approx 100$ is a typical and good value.

In addition, the complete and thus very large sum over all $\nu = 1, \ldots, \dim(\mathcal{H})$ states $|\nu\rangle$ is replaced by a summation over a subset of R random vectors. These vectors are truly random, they do not need to belong to any special basis set. Altogether this yields for the partition function

$$Z(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(\nu)}} |\langle n(\nu) | \nu \rangle|^2.$$
(38)

Although this already sketches the general idea, it will always improve the accuracy if symmetries are taken into account as in the following formulation

$$Z(T,B) \approx \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_{\Gamma}} \sum_{\nu=1}^{R_{\Gamma}} \sum_{n=1}^{N_{L}} e^{-\beta \epsilon_{n}^{(\nu,\Gamma)}} |\langle n(\nu,\Gamma) | \nu,\Gamma \rangle|^{2}.$$
(39)

Here Γ labels the irreducible representations of the employed symmetry group. The full Hilbert space is decomposed into mutually orthogonal subspaces $\mathcal{H}(\Gamma)$. An observable would then be calculated as

$$O(T,B) \approx \frac{1}{Z(T,B)} \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_{\Gamma}} \sum_{\nu=1}^{R_{\Gamma}} \sum_{n=1}^{N_{L}} e^{-\beta \epsilon_{n}^{(\nu,\Gamma)}} \langle n(\nu,\Gamma) | \mathcal{Q} | \nu,\Gamma \rangle \langle \nu,\Gamma | n(\nu,\Gamma) \rangle .$$

$$(40)$$

It was noted in Ref. [104] that this approximation of the observable O(T, B) may contain large statistical fluctuations at low temperatures due to the randomness of the set of states $\{ | \nu, \Gamma \rangle \}$. It was shown that this can largely be cured by assuming a symmetrized version of Eq. (40). For our investigations this is irrelevant.

Our very positive experience is that even for large problems the number of random starting vectors as well as the number of Lanczos steps can be chosen rather small, e.g. $R \approx 20$, $N_L \approx 100$ [44,45,72]. Figure 14 displays the zero-field differential susceptibility of the cuboctahedron with s = 3/2 as an example. One notices that the approximate result, that anyway deviates from the exact one only for $0.5 \le k_B T/|J| \le 3$, quickly approaches the exact curve with increasing number R of initial states. Already for R = 20 the approximation is practically indistinguishable from the exact one; an increase to R = 100 does not further improve this observable [44].



Fig. 14: Zero-field differential susceptibility of the cuboctahedron with s = 3/2. The various curves depict the investigated scenarios $R_1 = 1$, $R_2 = 5$, $R_3 = 20$, and $R_4 = 100$; $N_L = 100$. The exact dependence is given by the dots [44].

It is foreseeable that the method does not work optimally in very small subspaces or subspaces with large degeneracies of energy levels especially if the symmetry is not broken up into irreducible representations Γ . The underlying reason is given by the properties of the Lanczos method itself that fails to dissolve such degeneracies. The other case of small subspaces can be solved by including their energy eigenvalues and eigenstates exactly.

Another technical issue is given by the fact that the chosen random vectors $|\nu, \Gamma\rangle$ should be mutually orthogonal. Although one could orthonormalize the respective vectors, this is for practical purposes not really necessary. The reason is, that two vectors with random components are practically always orthogonal, because their scalar product is a sum over fluctuating terms that nearly vanishes especially in very large Hilbert spaces.

Since Lanczos iterations consist of matrix vector multiplications they can be parallelized by openMP directives. In our programs this is further accelerated by an analytical state coding and an evaluation of matrix elements of the Heisenberg Hamiltonian "on the fly" [105].

4 General properties of spectra

In the following I discuss some properties of the spectra of magnetic molecules with isotropic and antiferromagnetic interaction.

Non-bipartite spin rings

With the advent of magnetic molecules it appears to be possible to synthesize spin rings with an odd number of spins [106]. Although related to infinite spin rings and chains such systems have not been considered mainly since it does not really matter whether an infinite ring has an odd or an even number of spins. In addition the sign rule of Marshall and Peierls [107] and the famous theorems of Lieb, Schultz, and Mattis [108, 109] provided valuable tools for the understanding of even rings which have the property to be bipartite and are thus non-frustrated. These theorems explain the degeneracy of the ground states in subspaces $\mathcal{H}(M)$ as well as their shift quantum number k or equivalently crystal momentum quantum number $p_k = 2\pi k/N$. Nowadays exact diagonalization methods allow to evaluate eigenvalues and eigenvectors of \mathcal{H} for small even and odd spin rings of various numbers N of spin sites and spin quantum numbers s where the interaction is given by antiferromagnetic nearest neighbor exchange [80–82, 110– 112]. Although Marshall-Peierls sign rule and the theorems of Lieb, Schultz, and Mattis do not apply to non-bipartite rings, i.e. frustrated rings with odd N, it turns out that such rings nevertheless show astonishing regularities. Unifying the picture for even and odd N, we find for the ground state without exception [111–113]:

- 1. The ground state belongs to the subspace $\mathcal{H}(S)$ with the smallest possible total spin quantum number S; this is either S = 0 for $N \cdot s$ integer, then the total magnetic quantum number M is also zero, or S = 1/2 for $N \cdot s$ half integer, then $M = \pm 1/2$.
- 2. If $N \cdot s$ is integer, then the ground state is non-degenerate.
- 3. If $N \cdot s$ is half integer, then the ground state is fourfold degenerate.
- 4. If s is integer or $N \cdot s$ even, then the shift quantum number is k = 0.
- 5. If s is half integer and $N \cdot s$ odd, then the shift quantum number turns out to be k = N/2.
- 6. If $N \cdot s$ is half integer, then $k = \lfloor (N+1)/4 \rfloor$ and $k = N \lfloor (N+1)/4 \rfloor$ is found. $\lfloor (N+1)/4 \rfloor$ symbolizes the greatest integer less or equal to (N+1)/4.

In the case of s = 1/2 one knows the k-quantum numbers for all N via the Bethe ansatz [82, 110], and for spin s = 1 and even N the k quantum numbers are consistent with Ref. [81]. It appears that for the properties of the first excited state such rules do not hold in general, but only for "high enough" N > 5 [112]. Then, as can be anticipated from table 1, we can conjecture that

- if N is even, then the first excited state has S = 1 and is threefold degenerate, and
- if N is odd and the single particle spin is half-integer, then the first excited state has S = 3/2 and is eightfold degenerate, whereas
- if N is odd and the single particle spin is integer, then the first excited state has S = 1 and is sixfold degenerate.

Considering relative ground states in subspaces $\mathcal{H}(M)$ one also finds – for even as well as for odd N – that the shift quantum numbers k show a strikingly simple regularity for $N \neq 3$

$$k \equiv \pm (Ns - M) \left\lceil \frac{N}{2} \right\rceil \mod N , \qquad (41)$$

s		N								
	2	3	4	5	6	7	8	9	10	
	1.5	0.5	1	0.747	0.934	0.816	0.913	0.844	0.903	$E_0/(NJ)$
$\frac{1}{2}$	1	4	1	4	1	4	1	4	1	deg
2	0	1/2	0	1/2	0	1/2	0	1/2	0	S
	1	1, 2	0	1, 4	3	2, 5	0	2, 7	5	k
	4.0	3.0	2.0	2.236	1.369	2.098	1.045	1.722	0.846	$\Delta E/ J $
$\frac{1}{2}$	3	4	3	2	3	8	3	8	3	deg
2	1	3/2	1	1/2	1	3/2	1	3/2	1	S
	0	0	2	0	0	1,6	4	3, 6	0	k
	4	2	3	2.612	2.872	2.735	2.834	2.773	2.819	$E_0/(NJ)$
1	1	1	1	1	1	1	1	1	1	deg
	0	0	0	0	0	0	0	0	0	S
	0	0	0	0	0	0	0	0	0	k
	4.0	2.0	2.0	1.929	1.441	1.714	1.187	1.540	1.050	$\Delta E/ J $
1	3	9	3	6	3	6	3	6	3	deg
	1	1	1	1	1	1	1	1	1	S
	1	0, 1, 2	2	2, 3	3	3, 4	4	4, 5	5	k
	7.5	3.5	6	4.973	5.798	5.338	5.732	5.477	5.704	$E_0/(NJ)$
$\frac{3}{2}$	1	4	1	4	1	4	1	4	1	deg
-	0	1/2	0	1/2	0	1/2	0	1/2	0	S
	1	1, 2	0	1,4	3	2, 5	0	2, 7	5	k
	4.0	3.0	2.0	2.629	1.411	2.171	1.117	1.838	0.938	$\Delta E/ J $
$\frac{3}{2}$	3	16	3	8	3	8	3	8	3	deg
2	1	3/2	1	3/2	1	3/2	1	3/2	1	S
	0	0, 1, 2	2	2, 3	0	1,6	4	3, 6	0	k
	12	6	10	8.456	9.722	9.045	9.630	9.263	9.590	$E_0/(NJ)$
2	1	1	1	1	1	1	1	1	1	deg
	0	0	0	0	0	0	0	0	0	S
	0	0	0	0	0	0	0	0	0	k
	4.0	2.0	2.0	1.922	1.394	1.652	1.091	1.431	0.906	$\Delta E/ J $
2	3	9	3	6	3	6	3	6	3	deg
	1	1	1	1	1	1	1	1	1	S
	1	0, 1, 2	2	2, 3	3	3, 4	4	4, 5	5	k
	17.5	8.5	15	12.434	14.645	13.451	14.528	13.848	14.475	$\overline{E_0/(NJ)}$
$\frac{5}{2}$	1	4	1	4	1	4	1	4	1	deg
	0	1/2	0	1/2	0	1/2	0	1/2	0	S
	1	1, 2	0	1,4	3	2, 5	0	2, 7	5	k

Table 1: Properties of ground and first excited state of AF Heisenberg rings for various N and s: ground state energy E_0 , gap ΔE , degeneracy deg, total spin S and shift quantum number k.

where $\lceil N/2 \rceil$ denotes the smallest integer greater than or equal to N/2 [113]. For N = 3 and $3s - 2 \ge |M| \ge 1$ one finds besides the ordinary k-quantum numbers given by (41) extraordinary k-quantum numbers, which supplement the ordinary ones to the complete set $\{k\} = \{0, 1, 2\}$.

For even N the k values form an alternating sequence 0, N/2, 0, N/2, ... on descending from the magnon vacuum with M = Ns as known from the sign-rule of Marshall and Peierls [107]. For odd N it happens that the ordinary k-numbers are repeated on descending from $M \le Ns-1$ to M - 1 iff N divides [2(Ns - M) + 1].

Using the k-rule one can as well derive a rule for the relative ground state energies and for the respective S quantum numbers:

- For the relative ground state energies one finds that if the k-number is different in adjacent subspaces, $E_{\min}(S) < E_{\min}(S+1)$ holds. If the k-number is the same, the energies could as well be the same.
- Therefore, if N (even or odd) does not divide $(2(Ns M) + 1)\lceil N/2 \rceil$, then any relative ground state in $\mathcal{H}(M)$ has the total spin quantum number S = |M|.
- This is always true for the absolute ground state which therefore has S = 0 for Ns integer and S = 1/2 for Ns half integer.

The k-rule (41) is founded in a mathematically rigorous way for N even [107–109], N = 3, M = Ns, M = Ns - 1, and M = Ns - 2 [113]. An asymptotic proof for large enough N can be provided for systems with an asymptotically finite excitation gap, i.e. systems with integer spin s for which the Haldane conjecture applies [114, 115]. In all other cases numerical evidence was collected and the k-rule as a conjecture still remains a challenge [113].

Rotational bands

For many spin systems with constant isotropic antiferromagnetic nearest neighbor Heisenberg exchange the minimal energies $E_{min}(S)$ form a rotational band, i.e. depend approximately quadratically on the total spin quantum number S [101, 116, 117]

$$E_{min}(S) \approx E_a - J \frac{D(N,s)}{N} S(S+1) .$$
(42)

The occurrence of a rotational band has been noted on several occasions for an even number of spins defining a ring structure, see, e.g., Ref. [117]. The minimal energies have been described as "following the Landé interval rule" [54–56, 58]. However, one finds that the same property also occurs for rings with an odd number of spins as well as for the various polytope configurations we have investigated, in particular for quantum spins positioned on the vertices of a tetrahedron, cube, octahedron, icosahedron, triangular prism, and an axially truncated icosahedron. Rotational modes have also been found in the context of finite square and triangular lattices of spin-1/2 Heisenberg antiferromagnets [118, 119].

There are several systems, like spin dimers, trimers, squares, tetrahedra, and octahedra which possess a strict rotational band since their Hamiltonian can be simplified by quadrature. As an example the Heisenberg square, i.e., a ring with N = 4 is presented. Because the Hamilton



Fig. 15: Energy spectra of antiferromagnetically coupled Heisenberg spin rings (horizontal dashes). The crosses connected by the dashed line represent the fit to the rotational band according to (46), which matches both the lowest and the highest energies exactly. On the left the dashed line reproduces the exact rotational band, whereas on the right it only approximates it, but to high accuracy. The solid line on the right corresponds to the approximation Eq. (47).

operator (23) can be rewritten as

$$H_{\sim} = -J \left(\vec{S}^2 - \vec{S}^2_{13} - \vec{S}^2_{24} \right) , \qquad (43)$$

$$\vec{S}_{13} = \vec{s}(1) + \vec{s}(3)$$
 (44)

$$\vec{S}_{24} = \vec{s}(2) + \vec{s}(4) , \qquad (45)$$

with all spin operators \vec{S}^2 , \vec{S}^2_{13} and \vec{S}^2_{24} commuting with each other and with H, one can directly obtain the complete set of eigenenergies, and these are characterized by the quantum numbers S, S_{13} and S_{24} . In particular, the lowest energy for a given total spin quantum number S occurs for the choice $S_{13} = S_{24} = 2s$

$$E_{min}(S) = -J \left[S \left(S+1 \right) - 2 \cdot 2s \left(2s+1 \right) \right] = E_0 - J S \left(S+1 \right), \tag{46}$$

where $E_0 = 4s(2s + 1)J$ is the exact ground state energy. The various energies $E_{min}(S)$ form a rigorous parabolic rotational band of excitation energies. Therefore, these energies coincide with a parabolic fit (crosses connected by the dashed line on the left of Fig. 15) passing through the antiferromagnetic ground state energy and the highest energy level, i.e., the ground state energy of the corresponding ferromagnetically coupled system.

It turns out that an accurate formula for the coefficient D(N, s) of (46) can be developed using the sublattice structure of the spin array [116]. As an example we repeat the basic ideas for Heisenberg rings with an even number of spin sites [58]. Such rings are bipartite and can be decomposed into two sublattices, labeled A and B, with every second spin belonging to the same sublattice. The classical ground state (Néel state) is given by an alternating sequence of opposite spin directions. On each sublattice the spins are mutually parallel. Therefore, a quantum trial state, where the individual spins on each sublattice are coupled to their maximum values, $S_A = S_B = Ns/2$, could be expected to provide a reasonable approximation to the true



Fig. 16: The low-lying levels of a spin ring, N = 6 and s = 5/2 in this example, can be grouped into the lowest (Landé) band, the first excited (Excitation) band and the quasi-continuum (QC). For the spin levels of the L- and E-band k is given in brackets followed by the energy. Arrows indicate strong transitions from the L-band. Associated numbers give the total oscillator strength f_0 for these transitions [117].

ground state, especially if s assumes large values. For rings with even N the approximation to the respective minimal energies for each value of the total spin $\vec{S} = \vec{S}_A + \vec{S}_B$ is then [58]

$$E_{min}^{\text{approx}}(S) = -\frac{4J}{N} \left[S(S+1) - 2\frac{Ns}{2} \left(\frac{Ns}{2} + 1\right) \right] \,. \tag{47}$$

This approximation exactly reproduces the energy of the highest energy eigenvalue, i.e., the ground state energy of the corresponding ferromagnetically coupled system (S = Ns). For all smaller S the approximate minimal energy $E_{min}^{approx}(S)$ is bounded from below by the true one (Rayleigh-Ritz variational principle). The solid curve displays this behavior for the example of N = 6, s = 3/2 on the right of Fig. 15. The coefficient "4" in Eq. (47) is the classical value, i.e. for each fixed even N the coefficient D(N, s) approaches 4 with increasing s [116, 120].

The approximate spectrum, (47), is similar to that of two spins, \vec{S}_A and \vec{S}_B , each of spin quantum number Ns/2, that are coupled by an effective interaction of strength 4J/N. Therefore, one can equally well say that the approximate rotational band considered in (47) is associated with an effective Hamilton operator

$$H_{\sim}^{\text{approx}} = -\frac{4J}{N} \left[\vec{S}^{2} - \vec{S}^{2}_{A} - \vec{S}^{2}_{B} \right] , \qquad (48)$$

where the two sublattice spins, \vec{S}_A , \vec{S}_B , assume their maximal value $S_A = S_B = Ns/2$. Hamiltonian (48) is also known as Hamiltonian of the Lieb-Mattis model which describes a system



Fig. 17: Structure of the icosidodecahedron (left) and the cuboctahedron (right).

where each spin of one sublattice interacts with every spin of the other sublattice with equal strength [109, 121].

It is worth noting that this Hamiltonian reproduces more than the lowest levels in each subspace $\mathcal{H}(S)$. At least for bipartite systems also a second band is accurately reproduced as well as the gap to the quasi-continuum above, compare Fig. 16. This property is very useful since the approximate Hamiltonian allows the computation of several observables without diagonalizing the full Hamiltonian.

Magnetization jumps

Although the spectra of many magnetic molecules possess an approximate rotational band of minimal energies $E_{min}(S)$ and although in the classical limit, where the single-spin quantum number s goes to infinity, the function $E_{min}(S)$ is even an exact parabola if the system has coplanar ground states [122], one finds that for certain coupling topologies, including the cuboctahedron and the icosidodecahedron (see Fig. 17), that this rule is violated, e.g. for high total spins [102, 123, 124]. More precisely, for the icosidodecahedron the last four points of the graph of E_{min} versus S, i. e. the points with $S = S_{max}$ to $S = S_{max} - 3$, lie on a straight line

$$E_{min}(S) = 60Js^2 - 6Js(30s - S).$$
⁽⁴⁹⁾

An analogous statement holds for the last three points of the corresponding graph for the cuboctahedron. These findings are based on numerical calculations of the minimal energies for several *s* both for the icosidodecahedron as well as for the cuboctahedron. For both these and other systems a rigorous proof of the high spin anomaly can be given [102, 125].

The idea of the proof can be summarized as follows: A necessary condition for the anomaly is certainly that the minimal energy in the one-magnon space is degenerate. Therefore, localized one-magnon states can be constructed which are also of minimal energy. When placing a second localized magnon on the spin array, there will be a chance that it does not interact with the first one if a large enough separation can be achieved. This new two-magnon state is likely the state of minimal energy in the two-magnon Hilbert space because for antiferromagnetic interaction two-magnon bound states do not exist. This procedure can be continued until no further independent magnon can be placed on the spin array. In a sense the system behaves as if it consists of non-interacting bosons which, up to a limiting number, can condense into



Fig. 18: *Icosidodecahedron: Left: minimal energy levels* $E_{min}(S)$ *as a function of total spin* S. *Right: magnetization curve at* T = 0 [102].

a single-particle ground state. In more mathematical terms: To prove the high-spin anomaly one first shows an inequality which says that all points $(S, E_{min}(S))$ lie above or on the line connecting the last two points. For specific systems as those mentioned above what remains to be done is to construct particular states that exactly assume the values of E_{min} corresponding to the points on the bounding line, then these states are automatically of minimal energy.

The observed anomaly (linear instead of parabolic dependence) results in a corresponding jump of the magnetization curve \mathcal{M} vs. B, see Fig. 18. In contrast, for systems which obey the Landé interval rule the magnetization curve at very low temperatures is a staircase with equal steps up to the highest magnetization. The anomaly could indeed be observed in magnetization measurements of the Keplerate {Mo₇₂Fe₃₀}. Unfortunately, the magnetization measurements [66, 101] performed so far suffer from too high temperatures which smear out the anomaly.

Nevertheless, it may be possible to observe truly giant magnetization jumps in certain twodimensional spin systems which possess a suitable coupling (e.g. Kagomé) [123, 126]. In such systems the magnetization jump can be of the same order as the number of spins, i.e. the jump remains finite – or in other words is macroscopic – in the thermodynamic limit $N \rightarrow \infty$. Thus, this effect is a true macroscopic quantum effect. It is also related to so-called flat bands of energy eigenvalues [124, 127–131].

5 Magnetocalorics

The use of magnetic molecules for sub-Kelvin cooling is one of the later ideas in the field of molecular magnetism. The mean (internal) energy, the magnetization and the magnetic field are thermodynamic observables just as pressure and volume. Therefore, we can design thermodynamic processes which work with magnetic materials as a medium. This has of course already been done for a long time. The most prominent application is magnetization cooling which is mainly used to reach sub-Kelvin temperatures [132]. The first observation of sub-Kelvin temperatures is a nice example of how short an article can be to win the Nobel prize (Giauque, Chemistry, 1949). Nowadays magnetization cooling is used in ordinary refrigerators.

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LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of Gd₂(SO₄)₃·8H₂O

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3$ $\cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to $1.5^{\circ}K$.

On March 19, starting at a temperature of about 3.4° K, the material cooled to 0.53° K. On April 8, starting at about 2° , a temperature of 0.34° K was reached. On April 9, starting at about 1.5° , a temperature of 0.25° K was attained.

It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

> W. F. GIAUQUE D. P. MACDOUGALL

Department of Chemistry, University of California, Berkeley, California, April 12, 1933.

Fig. 19: The first observation of sub-Kelvin temperatures [132] is a nice example of how short an article can be to win the Nobel prize (Giauque, Chemistry, 1949).

In early magnetocaloric experiments simple refrigerants like paramagnetic salts have been used. We will therefore consider such examples first. For a paramagnet the Hamiltonian consists of the Zeeman term only. We then obtain for the partition function

$$Z(T, B, N) = \left(\frac{\sinh[\beta g\mu_B B(s+1/2)]}{\sinh[\beta g\mu_B B/2]}\right)^N.$$
(50)

Then the magnetization is

$$\mathcal{M}(T,B,N) = Ng\mu_B\left((s+1/2)\mathrm{coth}[\beta g\mu_B B(s+1/2)] - 1/2\mathrm{sinh}[\beta g\mu_B B/2]\right), (51)$$

and the entropy reads

$$S(T, B, N) = Nk_B \ln\left(\frac{\sinh[\beta g\mu_B B(s+1/2)]}{\sinh[\beta g\mu_B B/2]}\right) - k_B \beta B \mathcal{M}(T, B, N) .$$
(52)

Besides their statistical definition both quantities follow from the general thermodynamic relationship

$$dF = \left(\frac{\partial F}{\partial T}\right)_B dT + \left(\frac{\partial F}{\partial B}\right)_T dB = -SdT - \mathcal{M}dB, \qquad (53)$$

where $F(T, B, N) = -k_BT \ln[Z(T, B, N)]$.

Looking at Eq. (50) it is obvious that all thermodynamic observables for a paramagnet depend on temperature and field via the combination B/T, and so does the entropy. Therefore, an adiabatic demagnetization (S = const) means that the ratio B/T has to remain constant, and thus temperature shrinks linearly with field, i.e.

$$\left(\frac{\partial T}{\partial B}\right)_{S}^{\text{para}} = \frac{T}{B}.$$
(54)



Fig. 20: Left: Sketch of an antiferromagnetically coupled spin dimer. Right: Dependence of the energy levels on magnetic field for an antiferromagnetically coupled spin-1/2 dimer. At the critical field B_c the lowest triplet level crosses the ground state level with S = 0.

This situation changes completely for an interacting spin system. Depending on the interactions the adiabatic cooling rate $\frac{\partial T}{\partial B}$ can be smaller or bigger than the paramagnetic one (54) and even change sign, i.e. one would observe heating during demagnetization. It is nowadays understood that the cooling rate acquires extreme values close to phase transitions due to the excess entropy associated with such processes [133–136].

In the following this statement will be made clear by discussing the example of a simple antiferromagnetically coupled spin-1/2 dimer, shown on the left of Fig. 20. In a magnetic field such a system experiences a "quantum phase transition" if the lowest triplet level crosses the original ground state with S = 0, see Fig. 20 on the right. Although one would hesitate to call such an ordinary ground state level crossing quantum phase transition it nevertheless is one. At T = 0 the magnetization $\mathcal{M}(T = 0, B)$ is a non-analytic function of the magnetic field B. At the critical field B_c where the levels cross the magnetization exhibits a step.

In addition the entropy, which at T = 0 is zero for the non-degenerate ground state acquires a finite value at the critical field B_c due to the degeneracy of the crossing levels. This enhancement remains present even at temperatures T > 0, it is shown on the left of Fig. 21. In addition the heat capacity varies strongly around the critical field as is shown on the right of Fig. 21.



Fig. 21: Left: Entropy of the dimer (Fig. 20) as function of B and T. Right: Heat capacity of the dimer as function of B and T.



Fig. 22: *Isentropes of the spin dimer. The straight lines show the behavior of a paramagnet for comparison. B is along the x-axis, T along the y-axis.*

The behavior of the entropy as well as the heat capacity explains how the adiabatic cooling rate

$$\left(\frac{\partial T}{\partial B}\right)_{S} = -T \frac{\left(\frac{\partial S}{\partial B}\right)_{T}}{C}$$
(55)

depends on field and temperature. Figure 22 shows the isentropes of the antiferromagnetically coupled dimer both as function of field B and temperature T. The straight lines show the behavior of a paramagnet for comparison. Three regions are highlighted.

- a: For low fields and high temperatures $\frac{\partial T}{\partial B}$ is smaller than for the paramagnet.
- b: For high fields and high temperatures the interacting system assumes the paramagnetic limit, i.e.
 <u>\[\frac{\partername{D}}{\partial B} \]
 is the same in both systems.

 </u>
- c: For low temperatures and fields just above the critical field $\frac{\partial T}{\partial B}$ is much bigger than the cooling rate of the paramagnet.
- Not highlighted but nevertheless very exciting is the region at low temperature just below the critical field where the "cooling" rate $\frac{\partial T}{\partial B}$ has the opposite sign, i.e. upon demagnetizing the system heats up and upon magnetizing the system cools down.

The rate $\frac{\partial T}{\partial B}$, Eq. (55), depends directly on the derivative of the entropy with respect to the magnetic field. Therefore, it is clear that the effect will be enhanced if a high degeneracy can be obtained at some critical field. This is indeed possible in several frustrated materials where giant magnetization jumps to saturation are observed [123, 124, 135–137].

As a final example I would like to discuss the M=Cu and M=Ni members of the family of Gd_4M_8 molecules which were synthesized quite recently [13]. The eigenvalues of the respective spin Hamiltonians could be determined numerically exactly for the case of Gd_4Cu_8 and by means of the Finite-Temperature Lanczos Method for Gd_4Ni_8 [45].



Fig. 23: Theoretical heat capacity per molecule for Gd_4Cu_8 (left) and Gd_4Ni_8 (right) at various magnetic fields.

For Gd₄Cu₈ the model Hamiltonian (2) includes the following parameters: $J_{GdGd} = -0.1 \text{ cm}^{-1}$, $J_{GdCu} = +0.9 \text{ cm}^{-1}$, $J_{CuCu} = -8.0 \text{ cm}^{-1}$. The spectroscopic splitting factor was taken as g = 2.0. For Gd₄Ni₈ the model parameters were chosen as: $J_{GdGd} = -0.1 \text{ cm}^{-1}$, $J_{GdNi} = +0.17 \text{ cm}^{-1}$, $J_{NiNi} = +12.0 \text{ cm}^{-1}$. Again we took g = 2.0. In order to provide a feeling for the energy scale of inverse centimeters we would like to mention that one inverse centimeter (wave number) corresponds to about 1.44 K in thermal energy. A coupling of about a tenth of an inverse centimeter or Kelvin is typical for interactions between gadolinium ions. In the following all other interactions or corrections such as temperature independent paramagnetism, different g factors for different ions or a possible single-ion anisotropy in the case of nickel have been neglected. Despite these approximations all theoretical curves agree nicely with the experimental ones published in Ref. [13].

Figure 23 displays the theoretical heat capacity per molecule for Gd_4Cu_8 (left) and Gd_4Ni_8 (right) at various magnetic fields. The behavior is for both compounds qualitatively similar.

The isothermal magnetic entropy change, shown in 24, turns out to be very different; it is much



Fig. 24: Theoretical isothermal entropy change per molecule for Gd_4Cu_8 (left) and Gd_4Ni_8 (right) for various field differences: $-\Delta S(T, B) = -[S(T, B) - S(T, 0)].$



Fig. 25: Theoretical isentropes for Gd_4Cu_8 (left) and for Gd_4Ni_8 (right) [13, 45].

larger for Gd_4Ni_8 . The reason is that for Gd_4Ni_8 the low-lying multiplets belong to large total spin quantum numbers which leads to larger entropies at low temperatures. This is made even clearer by Fig. 25 displaying the isentropes as function of both temperature and magnetic field: Gd_4Cu_8 (left) possesses a non-degenerate $S_t = 0$ ground state that is separated from a triplet and a quintet, whereas Gd_4Ni_8 (right) has a ground state with $S_t = 22$. In the latter case all isentropes with $S \le k_B \log(45)$ run into absolute zero, which is clearly visible in Fig. 25. On the contrary, since Gd_4Cu_8 possesses a non-degenerate $S_t = 0$ ground state all isentropes approach temperatures T > 0 when B goes to zero.

Although this behavior suggests that Gd_4Ni_8 should be a very good refrigerant, this does not need to be the case. At sub-Kelvin temperatures dipolar interactions become very important. They prevent a closer approach of T = 0 [138]. Dipolar interactions could be tamed by molecules that possess an $S_t = 0$ ground state, but a non-degenerate ground state would not be helpful due to its vanishing entropy. Therefore, we suggest to investigate molecules which have a degenerate – the more the better – ground state with $S_t = 0$. A ground state degeneracy can be induced by frustration, thus a tetrahedron with antiferromagnetic coupling would be a first candidate [45].

Summarizing, one can say that low-dimensional frustrated spin systems and especially magnetic molecules are substances with an interesting magnetocaloric behavior and may turn out to be useful new refrigerants for special applications.

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