

Bounding and approximating parabolas for the spectrum of Heisenberg spin systems

HEINZ-JÜRGEN SCHMIDT¹, JÜRGEN SCHNACK¹, and MARSHALL LUBAN²

¹ *Universität Osnabrück, Fachbereich Physik, D-49069 Osnabrück, Germany*

² *Ames Laboratory & Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

PACS. 75.10.Jm – Quantized spin models.

PACS. 75.10.Hk – Classical spin models.

PACS. 75.50.Xx – Molecular magnets.

Abstract. – We prove that for a wide class of quantum spin systems with isotropic Heisenberg coupling the energy eigenvalues which belong to a total spin quantum number S have upper and lower bounds depending at most quadratically on S . The only assumption adopted is that the mean coupling strength of any spin w. r. t. its neighbours is constant for all N spins. The coefficients of the bounding parabolas are given in terms of special eigenvalues of the $N \times N$ coupling matrix which are usually easily evaluated. In addition we show that the bounding parabolas, if properly shifted, provide very good approximations of the true boundaries of the spectrum. We present numerical examples of frustrated rings, a cube, and an icosahedron.

Introduction. – The study of finite spin systems is not only interesting in its own right but has also important applications for understanding so-called “molecular magnets”. The synthesis of these systems has undergone rapid progress in recent years building on successes in coordination and polyoxometalate chemistry [1–4]. Each of the identical molecular units can contain as few as two and up to several dozen paramagnetic ions. The largest paramagnetic molecule synthesized to date, the polyoxometalate $\{\text{Mo}_{72}\text{Fe}_{30}\}$, contains 30 iron ions of spin $s = 5/2$ [5]. It appears that in the majority of these molecules the localized single-particle magnetic moments (“spins”) couple antiferromagnetically and the spectrum is rather well described by the Heisenberg model [6–10].

Since the dimension of the Hilbert space for N spins of spin quantum number s , given by $(2s+1)^N$, grows rapidly with N and s , the numerical evaluation of all energy eigenvalues may be impossible even if the obvious symmetries of the Hamiltonian are exploited [11]. Hence it is indispensable to resort to approximation methods, either analytical or numerical. However, it appears also desirable to extend the body of rigorous results on spin systems, which could serve as a basis or source of inspiration for the development of approximate models. For example, the Berezin-Lieb inequalities [12, 13] relating spectral properties of the quantum systems to those of their classical counterparts provide a foundation for classical or semi-classical treatments of spin systems. Among the Berezin-Lieb inequalities are the following

rigorous estimates

$$(s+1)^2 E_{\min}^{\text{classic}} \leq E_{\min} \leq s^2 E_{\min}^{\text{classic}} \quad (1)$$

for the ground state energy $E_{\min} < 0$ of quite general Heisenberg model systems, where $E_{\min}^{\text{classic}}$ denotes the minimal energy of the corresponding classical spin system described with unit vectors.

In this article we extend the findings of Lieb and Berezin and prove similar inequalities for the extremal values $E_{\min}(S)$ and $E_{\max}(S)$ of the energy levels belonging to a given quantum number S of the total spin. It turns out that the S -resolved eigenvalue spectrum is bounded by two parabolas. The proof rests mainly on a linear transformation of the spin observables according to the eigenbasis of the coupling matrix \mathbb{J} . The bounding parabolas depend only on N, s and three special eigenvalues j, j_{\min}, j_{\max} of \mathbb{J} . If $E_{\min}^{\text{classic}} = Nj_{\min}$, which is satisfied for all systems where $E_{\min}^{\text{classic}}$ has been determined (see [14]), our estimate $s(s+1)E_{\min}^{\text{classic}}$ for $S=0$ improves the lower Berezin-Lieb estimate, eq. (1). Hence we conjecture that also for arbitrary S our bounds yield the correct s^2 -term of the asymptotic series of $E_{\min}(S)$ and $E_{\max}(S)$ for $s \rightarrow \infty$.

We compare the derived bounds with the actual numerically calculated eigenvalue spectrum for various systems. As expected, the bounds are rather close to the actual spectrum if s is large, but there is a considerable gap for small s . For special bipartite systems which we call ‘‘homogeneous Lieb-Mattis systems’’ we have derived a closer lower bound even for small s .

In addition, we provide numerical evidence that the bounding parabolas, if properly shifted, turn out to be very good approximations of the true boundaries of the spectrum, which is especially useful for the approximation of low-lying excitations.

Definitions and simple results. – We consider spin systems with N spin sites, spin quantum number s and isotropic Heisenberg coupling between all sites μ and ν with coupling constants $J_{\mu\nu}$. Let $\tilde{s}_{\mu}^{(i)}$ ($i=1,2,3$) denote the three components of the spin observable \tilde{s}_{μ} at site μ and, as usual,

$$\vec{\tilde{S}} \equiv \sum_{\mu} \vec{\tilde{s}}_{\mu}, \quad \tilde{S}^{(i)} \equiv \sum_{\mu} \tilde{s}_{\mu}^{(i)}, \quad (2)$$

denote the total spin vector and its various components. All linear operators occurring in this context operate on a $\dim = (2s+1)^N$ -dimensional Hilbert space \mathcal{H} . The eigenspace of $\vec{\tilde{S}}^2$ corresponding to the eigenvalue $S(S+1)$ will be denoted by \mathcal{H}_S .

The Heisenberg Hamilton operator can be written as

$$\tilde{H} \equiv \sum_{\mu\nu} J_{\mu\nu} \vec{\tilde{s}}_{\mu} \cdot \vec{\tilde{s}}_{\nu}. \quad (3)$$

Throughout this Letter the coupling constants $J_{\mu\nu}$ are assumed to satisfy

$$J_{\mu\nu} = J_{\nu\mu} \quad J_{\mu\mu} = 0, \quad j \equiv \sum_{\nu} J_{\mu\nu}, \quad (4)$$

with j being independent of μ . The latter may be viewed as a kind of weak homogeneity assumption. The matrix of coupling constants will be denoted by \mathbb{J} . Its trace vanishes due to $J_{\mu\mu} = 0$. Being symmetrical, it has a complete set of (ordered) eigenvalues j_1, \dots, j_N . One of them is the row sum j with $\mathbf{1} \equiv \frac{1}{\sqrt{N}}(1, 1, \dots, 1)$ as the corresponding eigenvector.

Let \mathbb{J}' denote the matrix \mathbb{J} restricted to the subspace orthogonal to $\mathbf{1}$, and j_{\max} (j_{\min}) the largest (smallest) eigenvalue of \mathbb{J}' . Since we made no assumptions on the signs of the $J_{\mu\nu}$, it may happen that some of the numbers j, j_{\min}, j_{\max} coincide. In most cases of interest, the $N \times N$ -matrix \mathbb{J} can be easily diagonalized, either analytically or numerically, in contrast to the $\dim \times \dim$ -dimensional Hamilton matrix. We will denote the α -th normalized eigenvector of \mathbb{J} by $(c_{1\alpha}, \dots, c_{N\alpha})$, i. e.

$$\sum_{\nu} J_{\mu\nu} c_{\nu\alpha} = j_{\alpha} c_{\mu\alpha}, \quad \mu, \alpha = 1, \dots, N, \quad (5)$$

and

$$\sum_{\mu} \overline{c_{\mu\alpha}} c_{\mu\beta} = \delta_{\alpha\beta}, \quad \alpha, \beta = 1, \dots, N, \quad (6)$$

where we also allow for the possibility to choose complex eigenvectors. Sums over $\alpha = 1, \dots, N$ excluding α_j will be denoted by \sum' , where α_j denotes the index (within the ordered set of all eigenvalues) of the eigenvalue j belonging to the eigenvector $\mathbf{1}$.

For later use we will consider a transformation of the spin observables analogous to the transformation onto the eigenbasis of \mathbb{J} and define

Definition 1 $\vec{\tau}_{\alpha} \equiv \sum_{\mu} \overline{c_{\mu\alpha}} \vec{s}_{\mu}$, and $Q_{\alpha} \equiv \vec{\tau}_{\alpha}^{\dagger} \cdot \vec{\tau}_{\alpha}$, $\alpha = 1, \dots, N$.

The inverse transformation then yields

$$\vec{s}_{\mu} = \sum_{\alpha} c_{\mu\alpha} \vec{\tau}_{\alpha}, \quad \mu = 1, \dots, N. \quad (7)$$

In particular, $\vec{\tau}_{\alpha_j} = \vec{S}/\sqrt{N}$. The following lemma follows directly from the definitions:

Lemma 1 $Ns(s+1) = \sum_{\mu} (\vec{s}_{\mu})^2 = \sum_{\alpha} Q_{\alpha} = \frac{1}{N} \vec{S}^2 + \sum'_{\alpha} Q_{\alpha}$.

Bounding parabolas. – Our main result is formulated in the following theorem:

Theorem 1 1. The following operator inequality holds:

$$\frac{j - j_{\min}}{N} \vec{S}^2 + j_{\min} Ns(s+1) \leq \underline{H} \leq \frac{j - j_{\max}}{N} \vec{S}^2 + j_{\max} Ns(s+1). \quad (8)$$

2. Consequently, if $|\varphi\rangle$ is an arbitrary normalized vector lying in the subspace \mathcal{H}_S , the following bounds hold for the expectation value of \underline{H} :

$$\frac{j - j_{\min}}{N} S(S+1) + j_{\min} Ns(s+1) \leq \langle \varphi | \underline{H} | \varphi \rangle \leq \frac{j - j_{\max}}{N} S(S+1) + j_{\max} Ns(s+1). \quad (9)$$

Proof: We rewrite the Hamiltonian in the following form and conclude

$$\begin{aligned} \underline{H} &= \sum_{\mu\nu\alpha\beta} J_{\mu\nu} \overline{c_{\mu\alpha}} c_{\nu\beta} \vec{\tau}_{\alpha}^{\dagger} \cdot \vec{\tau}_{\beta} = \sum_{\beta} j_{\beta} Q_{\beta} = \frac{j}{N} \vec{S}^2 + \sum'_{\beta} j_{\beta} Q_{\beta} \\ &\geq \frac{j}{N} \vec{S}^2 + j_{\min} \sum'_{\beta} Q_{\beta} \\ &= \frac{j}{N} \vec{S}^2 + j_{\min} \left(Ns(s+1) - \frac{1}{N} \vec{S}^2 \right) = \frac{j - j_{\min}}{N} \vec{S}^2 + j_{\min} Ns(s+1), \end{aligned} \quad (10)$$

using (6), the positivity of Q_β , and lemma 1. The other inequality follows analogously. ■

As a check of our theorem 1 we consider the mean energy $\overline{E}(S)$ within the subspace \mathcal{H}_S . Let P_S denote the projector onto \mathcal{H}_S and define $\overline{E}(S) \equiv \text{Tr} \{ \underline{H} P_S \} / \text{Tr} \{ P_S \}$. Then we obtain the following

Proposition 1

$$\begin{aligned} \frac{j - j_{\min}}{N} S(S+1) + j_{\min} N s(s+1) &\leq \overline{E}(S) = \frac{j}{N-1} (S(S+1) - N s(s+1)) \quad (11) \\ &\leq \frac{j - j_{\max}}{N} S(S+1) + j_{\max} N s(s+1) . \end{aligned}$$

Anticipating that formula (11) for $\overline{E}(S)$ is valid, which is proven in [15], this proposition of course follows from theorem 1, but we want to give an independent proof of the stated inequalities for the interested reader.

Proof: Since $S \leq Ns$ and $1 \leq N$ it follows that

$$S(S+1) \leq Ns(Ns+1) \leq N^2 s(s+1). \quad (12)$$

Moreover,

$$0 = \text{Tr} \{ \mathbb{J} \} = j + \sum_{\alpha} ' j_{\alpha} \leq j + (N-1)j_{\max}, \quad (13)$$

and, analogously,

$$0 \geq j + (N-1)j_{\min}. \quad (14)$$

The first inequality of the proposition is equivalent to

$$((N-1)(j - j_{\min}) - Nj) S(S+1) + N^2 s(s+1)(j + (N-1)j_{\min}) \leq 0 \quad (15)$$

or

$$-((N-1)j_{\min} + j) (S(S+1) - N^2 s(s+1)) \leq 0. \quad (16)$$

But (16) follows directly from (12) and (14). The second inequality of the proposition is proven in a completely analogous way. ■

In the classical limit $s \rightarrow \infty$ the bounds of theorem 1 assume the values

$$E_{\text{lower}}(S) \equiv \frac{j - j_{\min}}{N} S^2 + j_{\min} N s^2, \quad (17)$$

$$E_{\text{upper}}(S) \equiv \frac{j - j_{\max}}{N} S^2 + j_{\max} N s^2. \quad (18)$$

It is plausible and can be shown analogously to the proof of theorem 1 [14] that the corresponding classical Hamilton function assumes only values between these bounds. The classical parabolas (17), (18) intersect in the point $S = Ns, E = jNs^2$ which corresponds to the (quantum or classical) ferromagnetic ground state. For special systems with nearest neighbour coupling J , including the N -polygon (ring), the cube, and the octahedron, it can be shown that the bounds $E_{\text{lower}}(S)$ and $E_{\text{upper}}(S)$ are assumed for some classical states [14].

For a special class of bipartite spin systems we can extend theorem 1 and obtain an improved lower bounding parabola.

Definition 2 Let the set of spin sites be divided into two disjoint subsets \mathcal{A} and \mathcal{B} such that the coupling constants within \mathcal{A} or \mathcal{B} are ≤ 0 , but ≥ 0 between \mathcal{A} and \mathcal{B} . Moreover, we assume that the partial row sum j^+ of positive entries of \mathbb{J} will be constant for all rows. Hence the same holds for $j^- \equiv j - j^+$. Further we assume that \mathbb{J} is irreducible, i. e. that the spin system cannot be decomposed into unconnected parts.

Then the spin system will be called an HLM-system (“homogeneous Lieb-Mattis system”, see [16–18]). Further, we will denote by δ the (positive) difference between the second smallest eigenvalue of \mathbb{J}' and j_{\min} .

It follows that for HLM-systems $|\mathcal{A}| = |\mathcal{B}| = N/2$. Examples are even rings or cubes with suitable coupling.

Theorem 2 For HLM systems the following operator inequality holds:

$$\frac{j - j_{\min}}{N} \vec{\mathcal{S}}^2 + j_{\min} N s(s+1) + \delta(N-2)s \leq \underline{H}. \quad (19)$$

Proof: Due to the HLM-assumption, \mathbb{J} has an eigenvector $\frac{1}{\sqrt{N}}(1, \dots, 1, -1, \dots, -1)$ with eigenvalue $j^- - j^+$, if the spin sites are suitably permuted. By the theorem of Geršgorin (c.f. [19], 7.2), $j^- - j^+$ will be the smallest eigenvalue j_{\min} and non-degenerate (theorem of Perron-Frobenius, c.f. [19], 9.2). It follows that

$$Q_{\min} = \vec{T}_{\min}^\dagger \cdot \vec{T}_{\min} = \frac{1}{N} (\vec{\mathcal{S}}_{\mathcal{A}} - \vec{\mathcal{S}}_{\mathcal{B}})^2 = \frac{1}{N} (2(\vec{\mathcal{S}}_{\mathcal{A}}^2 + \vec{\mathcal{S}}_{\mathcal{B}}^2) - \vec{\mathcal{S}}^2), \quad (20)$$

where $\vec{\mathcal{S}}_{\mathcal{A}} \equiv \sum_{\mu \in \mathcal{A}} \vec{\mathcal{S}}_{\mu}$ and $\vec{\mathcal{S}}_{\mathcal{B}} \equiv \sum_{\mu \in \mathcal{B}} \vec{\mathcal{S}}_{\mu}$. The largest eigenvalue of Q_{\min} within the subspace \mathcal{H}_S is assumed for the maximal value of the spin quantum numbers $S_{\mathcal{A}} = S_{\mathcal{B}} = Ns/2$, hence

$$P_S Q_{\min} P_S \leq \frac{1}{N} \left(4 \frac{Ns}{2} \left(\frac{Ns}{2} + 1 \right) - S(S+1) \right) = Ns^2 + 2s - \frac{1}{N} S(S+1). \quad (21)$$

Thus we may improve the inequality (12) by inserting the following term (suppressing the P_S)

$$\sum_{\alpha}' (j_{\alpha} - j_{\min}) Q_{\alpha} \geq \delta \left(\sum_{\alpha}' Q_{\alpha} - Q_{\min} \right) \quad (22)$$

$$= \delta \left(Ns(s+1) - \frac{1}{N} S(S+1) - Q_{\min} \right) \quad (23)$$

$$\geq \delta(N-2)s. \quad (24)$$

The last inequality follows from (21). This completes the proof. \blacksquare

It may very well be that a derivation of an improved inequality along this line is also possible for other than bipartite systems. Note that we have not yet used symmetry assumptions up to weak homogeneity (4). The key point is to obtain better estimates for Q_{α} than those already following from (9).

Examples. – In the following figures 1, 2, and 3 we present examples for the bounding parabolas. The energy spectra of fig. 1 have been calculated for the Hamilton operator of spin rings with nearest neighbour and next-nearest neighbour interaction

$$H = 2J \left(\sum_{\mu=1}^N \vec{\mathcal{S}}_{\mu} \cdot \vec{\mathcal{S}}_{\mu+1} + \alpha \sum_{\mu=1}^N \vec{\mathcal{S}}_{\mu} \cdot \vec{\mathcal{S}}_{\mu+2} \right), \quad (25)$$

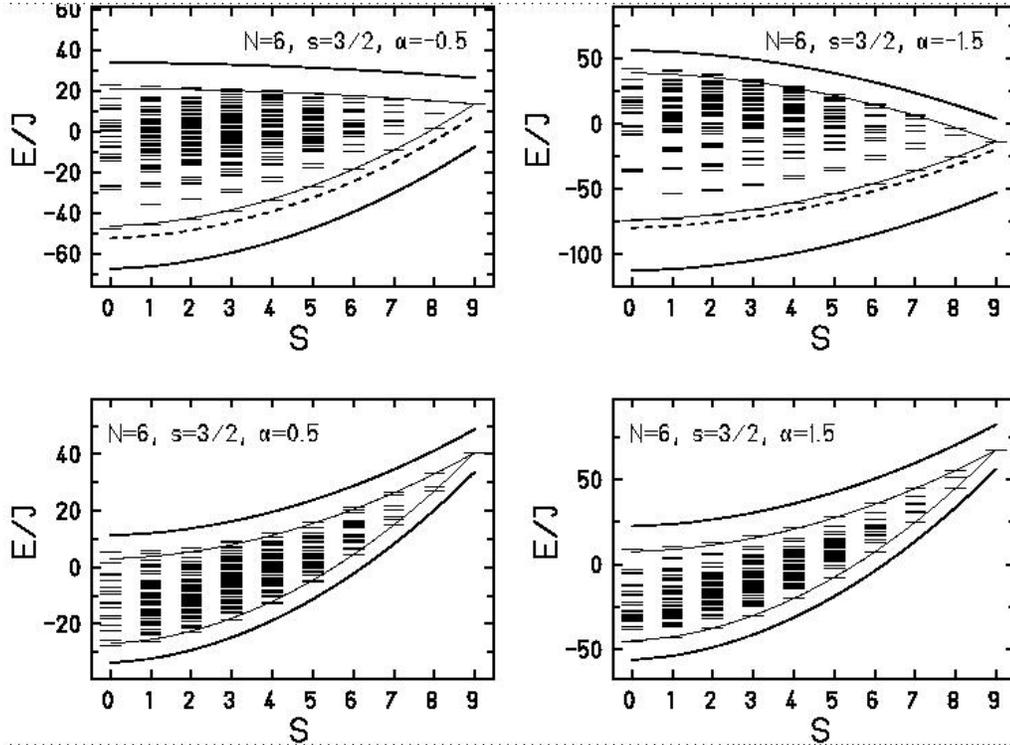


Fig. 1 – Energy spectrum of Heisenberg rings with antiferromagnetic exchange between nearest neighbours and a competing next-nearest-neighbour interaction. Bounding parabolas according to theorem 1 are always depicted by thick solid curves, those according to theorem 2 by dashed curves. The thin curves depict the approximating parabolas.

where the sum is understood mod N . In fig. 1 we display spectra for a ring with $N = 6$ and $s = 3/2$ for various ratios α of the two coupling constants.

We also consider the Hamiltonian of a system of spins occupying the vertices of a cube as well as of an icosahedron with nearest neighbours interaction of constant strength J , see fig. 2.

In all examples the bounding parabolas provide rigorous bounds, but unfortunately not very narrow ones, especially for small s . Only in the cases of bipartite systems the lower bound is impressively close to the boundary of the true spectrum, even if s is small.

Approximating parabolas. – From the figures it appears that the extremal values $E_{\min}(S)$ and $E_{\max}(S)$ of the exact energy spectrum also lie on approximate parabolas. This is not a novel observation. It has been noted on several occasions, that for Heisenberg rings with antiferromagnetic nearest-neighbour interaction and with an even number N of sites the set of minimal energies $E_{\min}(S)$ forms a rotational band [20, 21]. Further examples, including rings for both even and odd N , tetrahedra, cubes, octahedra, icosahedra, triangular prisms, and axially truncated icosahedra, suggest that this “rotational band structure hypothesis” holds for general Heisenberg spin systems [22]. The parabolas of our theorem 1 have a similar curvature but a different shift constant compared with the rotational bands. If they are

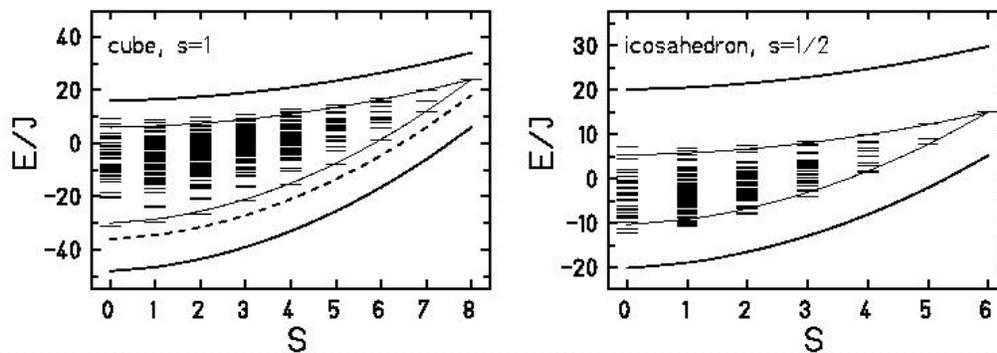


Fig. 2 – Energy spectrum of an antiferromagnetically coupled Heisenberg cube (l.h.s.; $j = 3, j_{\min} = -3, j_{\max} = 1$) and of an antiferromagnetically coupled icosahedron (r.h.s.; $j = 5, j_{\min} = -\sqrt{5}, j_{\max} = \sqrt{5}$).

shifted in such a way, that they meet the highest level of the rotational band, which occurs for $S = Ns, E = Njs^2$, the resulting approximation is very close to the true boundaries of the spectrum, compare the thin curves in figures 1, 2, and 3. Moreover, it turns out that the shifted parabolas exactly meet the minimal and maximal energies of $S = Ns - 1$

$$\begin{aligned} E_{\min}(Ns - 1) &= jNs^2 + 2(j_{\min} - j)s \\ E_{\max}(Ns - 1) &= jNs^2 + 2(j_{\max} - j)s . \end{aligned} \quad (26)$$

Identifying the curvature for the lower parabola with $(j - j_{\min})/N$ provides a very useful approximation for the curvature of the true low-lying rotational band, and thus complements the derivations of [22] which are based on the sublattice structure of the spin array. The classical counterparts $E_{\text{lower}}(S)$ and $E_{\text{upper}}(S)$ of the bounding parabolas are also rather close to the true boundaries of the spectrum.

By using these proposed methods one can predict the detailed shape of the spectrum and related properties of molecular magnets without diagonalizing a huge Hamilton matrix.

The overwhelming numerical evidence for the existence of a rotational band of minimal energies [22]

$$E_{\min}(S, s) \approx \frac{D(s)}{N} S(S + 1) + E_0(s) \quad (27)$$

for general Heisenberg spin systems cannot be mere coincidence. We believe that the derived bounding parabolas provide a first step towards proving this general behaviour.

We thank the National Science Foundation and the Deutscher Akademischer Austauschdienst for supporting a mutual exchange program. The Ames Laboratory is operated for the United States Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

REFERENCES

- [1] GATTESCHI D., *Adv. Mater.*, **6** (1994) 635.

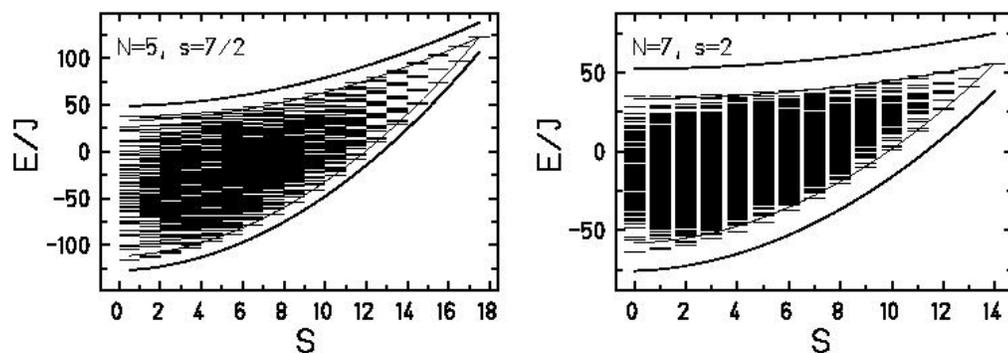


Fig. 3 – Energy spectrum of antiferromagnetically coupled Heisenberg rings with $N = 5$, $s = 7/2$ (l.h.s.; $j = 2$, $j_{\min} = -(1 + \sqrt{5})/2$, $j_{\max} = -(1 - \sqrt{5})/2$) and $N = 7$, $s = 2$ (r.h.s.; $j = 2$, $j_{\min} = -1/3 - \sqrt{7}/3 \cos(\phi) - \sqrt{7}/3 \sin(\phi) = -1.80194$, $j_{\max} = -1/3 + 2\sqrt{7}/3 \cos(\phi) = 1.24698$; $\phi = 1/3 \arctan(3\sqrt{3})$).

- [2] WINPENNY R.E.P., *Comment Inorg. Chem.*, **20** (1999) 233.
- [3] MÜLLER A. *et al.*, *Chem. Rev.*, **98** (1998) 239.
- [4] GATTESCHI D. *et al.*, *Chem. Commun.*, (2000) 725.
- [5] MÜLLER A. *et al.*, *Angew. Chem. Int. Ed. Engl.*, **38** (1999) 3238; the complete chemical formula of the compound is $[\text{Mo}_{72}\text{Fe}_{30}\text{O}_{252}(\text{Mo}_2\text{O}_7(\text{H}_2\text{O}))_2(\text{Mo}_2\text{O}_8\text{H}_2(\text{H}_2\text{O}))(\text{CH}_3\text{COO})_{12}(\text{H}_2\text{O})_{91}] \cdot 150\text{H}_2\text{O}$.
- [6] BENCINI A. and GATTESCHI D., *Electron parametric resonance of exchange coupled systems* (Springer, Berlin, Heidelberg) 1990.
- [7] CANESCHI A. *et al.*, *Inorg. Chem.*, **34** (1995) 4660.
- [8] DELFS C. *et al.*, *Inorg. Chem.*, **32** (1993) 3099.
- [9] PILAWA B. *et al.*, *J. Magn. Magn. Mater.*, **177** (1997) 748.
- [10] WALDMANN O. *et al.*, *Inorg. Chem.*, **38** (1999) 5879.
- [11] BÄRWINKEL K. and SCHMIDT H.-J. and SCHNACK J., *J. Magn. Magn. Mater.*, **212** (2000) 240.
- [12] LIEB E., *Commun. Math. Phys.*, **31** (1973) 327
- [13] BEREZIN F.A., *Commun. Math. Phys.*, **40** (1975) 153
- [14] SCHMIDT H.-J. and LUBAN M., in preparation
- [15] SCHMIDT H.-J. and LUBAN M., *cond-mat/0012225*, (submitted).
- [16] MARSHALL W., *Proc. Royal. Soc. A (London)*, **232** (1955) 48.
- [17] LIEB E.H. and SCHULTZ T. and MATTIS D.C., *Ann. Phys. (N.Y.)*, **16** (1961) 407.
- [18] LIEB E.H. and MATTIS D.C., *J. Math. Phys.*, **3** (1962) 749.
- [19] LANCASTER P., *Theory of Matrices* (Academic Press, New York and London) 1969.
- [20] CANESCHI A. *et al.*, *Chem. Eur. J.*, **2** (1996) 1379.
- [21] ABBATI G.L. *et al.*, *Inorg. Chim. Acta*, **297** (2000) 291.
- [22] SCHNACK J. and LUBAN M., *Phys. Rev. B*, **63** (2001) 014418.