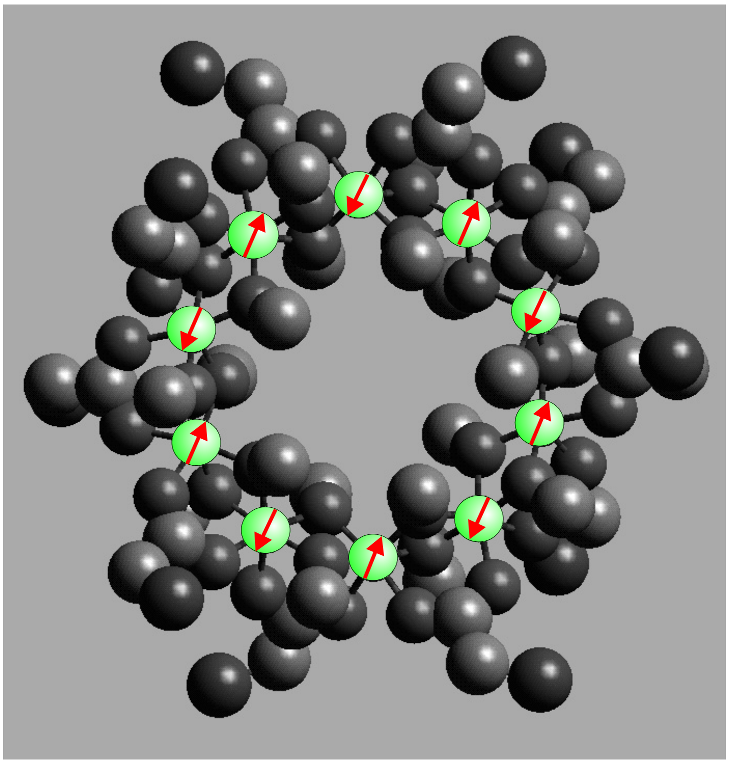
Ground state properties of antiferromagnetically coupled spin rings

Jürgen Schnack

K. Bärwinkel, H.-J. Schmidt

Universität Osnabrück



http://obelix.physik.uni-osnabrueck.de/∼schnack/

Small Magnetic Molecules

Properties

- new class of nanometer-size magnetic materials;
- molecules host from two up to thirty interacting paramagnetic ions; many nonmagnetic organic ligands;
- week intermolecular interactions; measurements on a bulk sample reflect intramolecular interactions only;
- well described in the Heisenberg model;
- speculations about applications range from mesoscopic magnets in biological systems, computer displays, photonic switches to catalysts (VDI report)

Structure

- simple clusters like a dimer (Fe_2) or a tetrahedron (Cr_4)
- magnetic rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, ...) and others (Cr_8, Cu_6, Cu_8)
- complex clusters (Mn_{12})
- spin quantum number: s(Cu)=1/2, s(Cr)=3/2, s(Fe)=5/2

Interesting obeservables

- molecular structure, Hamilton operator and its parameters
- magnetisation, susceptibility, specific heat
- NMR, neutron scattering $\Leftrightarrow$ spin-spin-correlation function
- ground state properties

Heisenberg Model

Hamilton operator: $J < 0$ AF

$$\underset{\sim}{H} = -J \sum_{x=1}^{N} \underset{\sim}{\vec{s}}(x) \cdot \underset{\sim}{\vec{s}}(x+1)$$

$$\underset{\sim}{H} = -J \sum_{x} \Big\{ \underset{\sim}{s}^3(x)\,\underset{\sim}{s}^3(x+1) + \frac{1}{2}\Big[\underset{\sim}{s}^+(x)\,\underset{\sim}{s}^-(x+1) + \underset{\sim}{s}^-(x)\,\underset{\sim}{s}^+(x+1)\Big]\Big\}$$

Spin operators

$$\Big[\underset{\sim}{s}^a(x), \underset{\sim}{s}^b(y)\Big] = i\,\epsilon_{abc}\,\underset{\sim}{s}^c(x)\,\delta_{xy} \quad , \quad \underset{\sim}{s}^\pm(x) = \underset{\sim}{s}^1(x) \pm i\,\underset{\sim}{s}^2(x)$$

Product basis

$$\underset{\sim}{s}^3(x)\,|\,m_1,\dots,m_x,\dots,m_N\,\rangle = m_x\,|\,m_1,\dots,m_x,\dots,m_N\,\rangle$$

Method: decompose the Hilbert space into mutually orthogonal subspaces invariant w.r.t. $\underset{\sim}{H}$!

Rotational Symmetry

Global and about the 3-axis

$$\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}\right] = \left[\underset{\sim}{H}, \underset{\sim}{S}^3\right] = 0 \quad \& \quad \left[\underset{\sim}{\vec{S}}^2, \underset{\sim}{S}^3\right] = 0$$

Construction of $\mathcal{H}(S, M)$

magnon vacuum state spans $\mathcal{H}(S = S_{\text{max}}, M = S_{\text{max}})$

$$|\, \Omega \,\rangle = |\, m_1 = s(1), m_2 = s(2), \dots, m_N = s(N) \,\rangle$$

consider decrement in M

$$\underset{\sim}{S}^- \,|\, \Omega \,\rangle \in \mathcal{H}(M = S_{\text{max}} - 1) \text{ with } S = S_{\text{max}}$$

The orthogonal subspace belongs to $S = S_{\text{max}} - 1$. Proceeding one finds that each $\mathcal{H}(M)$ can be decomposed into orthogonal subspaces

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

diagonalization necessary only in the subspaces $\mathcal{H}(S, S)$

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

Cyclic shift symmetry

Cyclic shift operator $\underset{\sim}{T}$

be all $s(x) = s$

$$\underset{\sim}{T} \mid m_1, \dots, m_{N-1}, m_N \,\rangle \quad = \quad \mid m_N, m_1, \dots, m_{N-1} \,\rangle$$

$$\left[\underset{\sim}{H}, \underset{\sim}{T}\right] = 0 \quad \& \quad \left[\underset{\sim}{T}, \underset{\sim}{\vec{S}}\right] = 0$$

Eigenvalues of $\underset{\sim}{T}$

$$z = \exp\left\{-i\,\frac{2\pi k}{N}\right\} \quad , \quad k = 0, 1, \dots, N-1$$

Construction of $\mathcal{H}(S, M, k)$

The subspaces $\mathcal{H}(S, M, k)$ are constructed using cycles and keeping track of proper cycles as well as epicycles.[a]

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[a] K. Bärwinkel, H.J. Schmidt, J. Schnack, *Structure and relevant dimension of the Heisenberg model and applications to spin rings*, J. Magn. Magn. Mater. (1999) in print

Example $N = 6$, $s = 1/2$

$M = 3$: **maximum dimension 1**

$$|\,\Omega\,\rangle = |+\,+\,+\,+\,++\rangle$$

$M = 2$: **maximum dimension 1**

$|-\,+\,+\,+\,++\rangle$ generates proper cycle of dimension 6

$M = 1$: **maximum dimension 2**

$|-\,-\,+\,+\,++\rangle$ generates proper cycle of dimension 6

$|-\,+\,-\,+\,++\rangle$ generates proper cycle of dimension 6

$|-\,+\,+\,-\,++\rangle$ generates epicycle of dimension 3

$M = 0$: **maximum dimension 2**

$|-\,-\,-\,+\,++\rangle$ generates proper cycle of dimension 6

$|-\,-\,+\,-\,++\rangle$ generates proper cycle of dimension 6

$|-\,+\,-\,-\,++\rangle$ generates proper cycle of dimension 6

$|-\,+\,-\,+\,-+\rangle$ generates epicycle of dimension 2

Ground State Properties I

s		N = 2	3	4	5	6	7	8	9	10	
$\frac{1}{2}$		1.5	0.5	1	0.747	0.934	0.816	0.913	0.844	0.903	$E/(NJ)$
		1	4	1	4	1	4	1	4	1	deg
		1	1, 2	0	1, 4	3	2, 5	0	2, 7	5	k
		$-$		$+$		$-$		$+$		$-$	π
1		4	2	3	2.612	2.872	2.735	2.834	2.773	2.819	$E/(NJ)$
		1	1	1	1	1	1	1	1	1	deg
		0	0	0	0	0	0	0	0	0	k
		$+$	$-$	$+$	$-$	$+$	$-$	$+$			π
$\frac{3}{2}$		7.5	3.5	6	4.973	5.798	5.338	5.732	5.477		$E/(NJ)$
		1	4	1	4	1	4	1	4		deg
		1	1, 2	0	1, 4	3	2, 5	0	2, 7		k
		$-$		$+$		$-$					π
2		12	6	10	8.456	9.722	9.045	9.630			$E/(NJ)$
		1	1	1	1	1	1	1			deg
		0	0	0	0	0	0	0			k
		$+$	$+$	$+$	$+$	$+$					π
$\frac{5}{2}$		17.5	8.5	15	12.434	14.645	13.451				$E/(NJ)$
		1	4	1	4	1	4				deg
		1	1, 2	0	1,4	3	2, 5				k
		$-$		$+$							π

Ground State Properties II

Ground state properties

1. ground state belongs to subspace $\mathcal{H}(S)$ with the smallest possible total spin quantum number S;
2. if Ns integer, then the ground state is non-degenerate,
3. if Ns half integer, then the ground state is fourfold degenerate,
4. if s integer or Ns even, then the translational shift quantum number is $k = 0$;
5. if s is half integer and Ns odd, then $k = N/2$;
6. if Ns is half integer, then $k = \lfloor (N+1)/4 \rfloor$ and $k = N - \lfloor (N+1)/4 \rfloor$; $\lfloor \cdot \rfloor$ greatest integer less or equal;
7. Non-degenerate ground states are also eigenstates of the spin flip operator $\underset{\sim}{C}$. For half integer s and necessarily even N we find that $\pi = -1$ if $N/2$ is odd and $\pi = +1$ if $N/2$ is even. The situation is more complicated for integer s. Here rows of alternating π for odd s change with rows of $\pi = +1$ for even s. This behaviour was also checked for $s = 3$ and $s = 4$, but not displayed in the table.
8. Non-degenerate ground states contain all product states of the Hilbert subspace with $M = 0$. Only for ground states with $k = 0$ and $\pi = -1$ those product states, which remain in the same cycle after application of the spin flip, have coefficients zero.

Lieb-Mattis-Theorem for spin rings[a]

Presupposition

Subdivide system into two sublattices A and B, such that the spins of each sublattice interact only with those of the other, i.e. valid for spin rings with an even number of spins.

Proposition

- each Hilbert subspace $\mathcal{H}(M)$ contains a non-degenerate ground state;
- this ground state has $S = |M|$ with ground state energy E_S;
- $E_S < E_{S+1}$;
- expanding the ground state in the product basis yields a sign rule for the coefficients

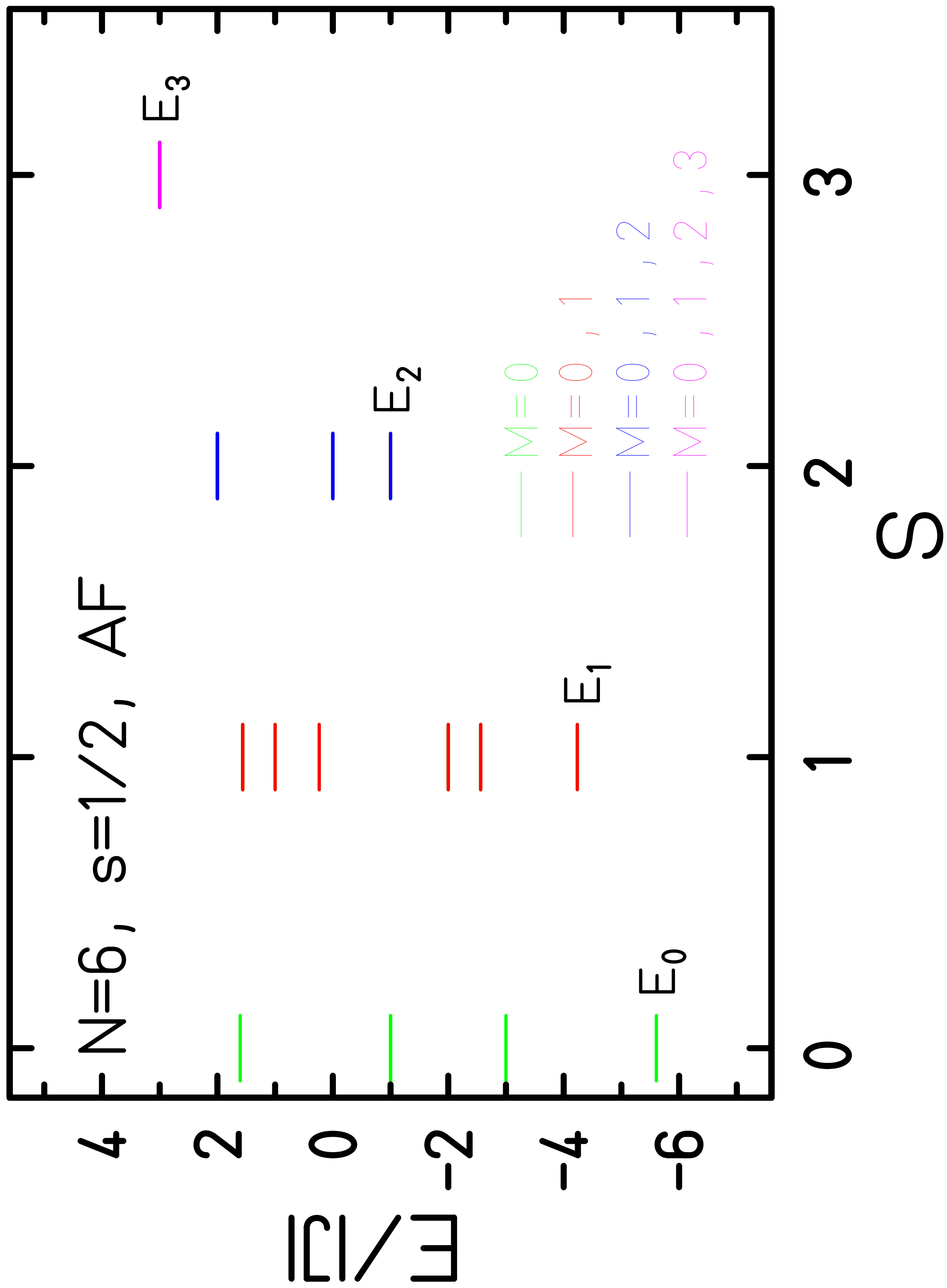
$$| \Psi_0 \rangle = \sum_{\mathbf{m}} c(\mathbf{m}) \, | \mathbf{m} \rangle \text{ with } \sum_{i=1}^{N} m_i = M$$

$$c(\mathbf{m}) = (-1)^{\left(\frac{N s}{2} - \sum_{i=1}^{N/2} m_{2i} \right)} a(\mathbf{m})$$

All $a(\mathbf{m})$ are non-zero, real and of equal sign.

[a]E.H. Lieb, T.D. Schultz, D.C. Mattis, Ann. Phys. (N.Y.) **16** (1961) 407; E.H. Lieb, D.C. Mattis, J. Math. Phys. **3** (1962) 749

Spectrum $N = 6,\ s = 1/2,\ M \geq 0$



k values for Lieb-Mattis rings

Lieb-Mattis explains k values for even rings

Consider the action of the cyclic shift operator on the product basis states. The change in sign of the coefficient, whose absolute value is not altered, then is

$$\frac{c(m_1,\dots,m_{N-1},m_N)}{c(m_N,m_1,\dots,m_{N-1})} = (-1)^{\left(\sum_{i=1}^{N/2} m_{2i}-\sum_{i=1}^{N/2} m_{2i-1}\right)} = (-1)^{(Ns)}$$

Since k can be only 0 or $N/2$ for non-degenerate eigenstates, for odd $N\cdot s$ we find $k = N/2$, whereas even $N\cdot s$ implies $k = 0$.

Properties for $N \leq 4$

$\underset{\sim}{H}$ can be simplified

$$N = 2 \quad : \quad \underset{\sim}{H} = -J \left(\underset{\sim}{\vec{S}}^2 - \underset{\sim}{\vec{s}}_1^2 - \underset{\sim}{\vec{s}}_2^2 \right) ,$$

$$N = 3 \quad : \quad \underset{\sim}{H} = -J \left(\underset{\sim}{\vec{S}}^2 - \underset{\sim}{\vec{s}}_1^2 - \underset{\sim}{\vec{s}}_2^2 - \underset{\sim}{\vec{s}}_3^2 \right) ,$$

$$N = 4 \quad : \quad \underset{\sim}{H} = -J \left(\underset{\sim}{\vec{S}}^2 - \underset{\sim}{\vec{S}}_{13}^2 - \underset{\sim}{\vec{S}}_{24}^2 \right)$$

$$\underset{\sim}{\vec{S}}_{13} = \underset{\sim}{\vec{s}}(1) + \underset{\sim}{\vec{s}}(3) \ , \ \underset{\sim}{\vec{S}}_{24} = \underset{\sim}{\vec{s}}(2) + \underset{\sim}{\vec{s}}(4)$$

- energy eigenvalues depend monotonically on $S \Rightarrow$ AF ground state belongs to the minimal total spin, either $S = 0$ or $S = 1/2$
- explain degeneracy by angular momentum coupling
- $N = 2$: couple the two spins to a total spin running from $S = 0$ to $= 2s$
- $N = 3$: couple the first two spins to integers $S = 0, \ldots 2s$, for half integer s two possibilities to couple to $S = 1/2$, for integer s one possibility to couple to zero;
- $N = 4$: $\underset{\sim}{\vec{S}}^2$, $\underset{\sim}{\vec{S}}_{13}^2$ and $\underset{\sim}{\vec{S}}_{24}^2$ commute, lowest energy if $S = 0$ and $S_{13} = S_{24} = 2s$, i.e. one possibility

Speculations about the k selection rule

Consider "MAMU state"

$N \cdot s$ half integer; $S = 1/2$; restrict to $\mathcal{H}(M = 1/2)$;
$|\,\mathbf{m}_0\,\rangle$ is maximally alternating but minimally undulating

$$|\,\mathbf{m}_0\,\rangle := |\,\frac{1}{2}\,,\frac{1}{2}\,,-\frac{1}{2}\,,\frac{1}{2}\,,-\frac{1}{2}\,,\frac{1}{2}\,,-\frac{1}{2}\cdots\rangle$$

It appears that the cycle generated by $|\,\mathbf{m}_0\,\rangle$ is always contained in the ground state, i.e. for arbitrary s! May $|\,\Psi_0; k\,\rangle$ be one ground state, then

$$\langle\,\Psi_0; k\,|\,\underset{\sim}{H}\,|\,\Psi_0; k\,\rangle = -4J\,\left(a(\mathbf{m}_0)\right)^2\,N\,\cos\left(\frac{4\pi k}{N}\right) + \text{remaining terms}\,.$$

It seems that the dependence of the remaining terms on k is rather unimportant, thus a lower energy eigenvalue may be obtained if k is as close as possible to $N/4$, i.e. $k = \lfloor (N+1)/4 \rfloor$ and $N - \lfloor (N+1)/4 \rfloor$.

Summary

Properties of Heisenberg spin rings

We found systematic properties of Heisenberg spin rings

- that relate $N \cdot s$ to the degeneracy of the ground state;
- that show a k value selection rule;
- that exceed the applicability of the Lieb-Mattis theorem.

Outlook

- Search for justifications for the odd N cases.
- Search for general relations between topology and ground state properties, e.g. for regular molecules like Keplerates.