Properties of Small Magnetic Molecules

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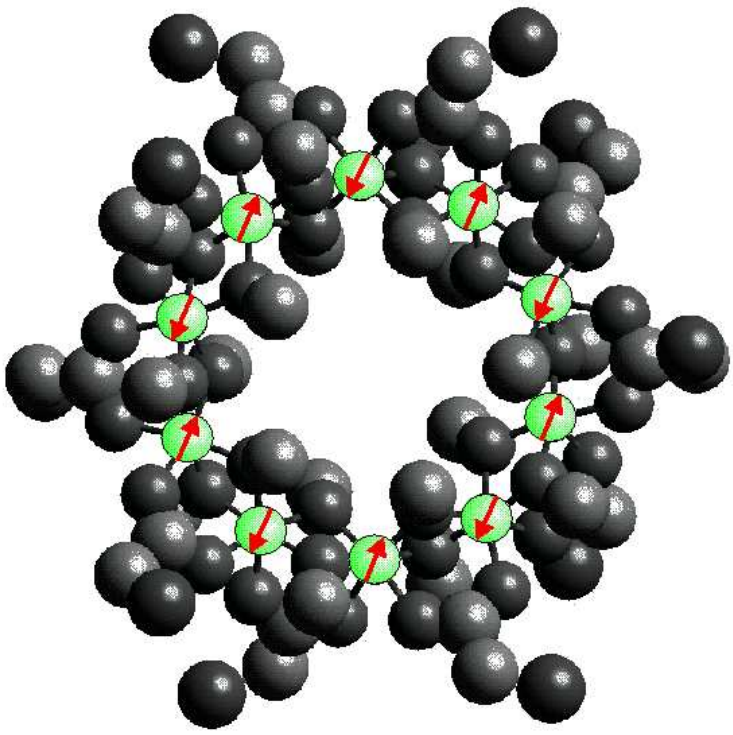

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I am a bloody beginner in spin dynamics

Origin and other interests

- nuclear physics (Gesellschaft für Schwerionenforschung, Darmstadt)
- molecular dynamics for fermions (FMD), dynamics at intermediate energies - fragmentation reactions
- thermostated molecular dynamics (Nosé-Hoover)
- ideal Fermi and Bose gases

Motivated for spins by Chr. Schröder[a]

- thermostated classical spin dynamics (Nosé-Hoover thermostat modified by Bulgac and Kusnezov)
- classical equations of motion

$$\frac{d}{dt}\,\vec{S}^{\alpha} = \frac{\partial\, H}{\partial\, \vec{S}^{\alpha}} \times \vec{S}^{\alpha}\ ,\ H = -J_c \sum_{\alpha=1}^{N} \vec{S}^{\alpha} \cdot \vec{S}^{\alpha+1} - \mu_c \vec{B} \cdot \sum_{\alpha=1}^{N} \vec{S}^{\alpha}$$

- coupling of a deterministic or a stochastic thermostat
- time averaging to determine thermodynamic properties like susceptibility, spin-spin-correlation functions etc.
- classical treatment works astonishingly well
- WHY? WHAT ABOUT QUANTUM MECHANICS?

[a] university of Osnabrück, now Philips research

Small Magnetic Molecules

Properties

- new class of nanometer-size magnetic materials;
- molecules host from two up to thirty interacting paramagnetic ions;
- large number of nonmagnetic organic ligands;
- weak intermolecular interactions;
- measurements on a bulk sample reflect intramolecular interactions only;
- well described by the Heisenberg model, additional terms like single side anisotropy rather small;
- speculations about applications range from mesoscopic magnets in biological systems, computer displays, quantum computer, 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

Research

Interesting obeservables

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

Some groups in the field

- Prof. Dr. Dante Gatteschi, university of Florence
- Dr. Bernd Pilawa, Universität Karlsruhe
- Dr. Oliver Waldmann, Universität Erlangen-Nürnberg
- Prof. Dr. Achim Müller, Universität Bielefeld
- Prof. Dr. Johannes Richter, Universität Magdeburg
- Prof. Dr. Fabricius, Dr. Löw, Dr. Karbach, Prof. Dr. Stolze, Universität Wuppertal
- Ames Lab, Iowa: Prof. Dr. Marshall Luban, ...
- Gruppe Makroskopische Systeme und Quantentheorie, Universität Osnabrück

Contents

1. Relevant dimensions in the Heisenberg model
2. General properties of the antiferromagnetic ground state of small Heisenberg rings
3. Classical limit for spin dimers and trimers

Heisenberg Model

Hamilton operator (AF: $J < 0$)

$$\underset{\sim}{H} = \underset{\sim}{H}_0 + \underset{\sim}{H}_F = -\sum_{x,y}^{N} J(x,y)\, \underset{\sim}{\vec{s}}(x) \cdot \underset{\sim}{\vec{s}}(y) + g\,\mu_B\, B \sum_{x}^{N} \underset{\sim}{s}^3(x)$$

$$\underset{\sim}{H}_0 = -\sum_{x,y} J(x,y) \left\{ \underset{\sim}{s}^3(x) \underset{\sim}{s}^3(y) + \frac{1}{2}\left[\underset{\sim}{s}^+(x) \underset{\sim}{s}^-(y) + \underset{\sim}{s}^-(x) \underset{\sim}{s}^+(y) \right] \right\}$$

spin operators

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

product basis

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

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

Relevant Dimension I

Symmetry about the 3-axis

$$\left[\underset{\sim}{H}, \underset{\sim}{S}^3\right] = 0 \quad , \quad \underset{\sim}{S}^3 = \sum_x \underset{\sim}{s}^3(x)$$

Eigenvalues M

$$M = -S_{\max}, -S_{\max}+1, \ldots, S_{\max} \quad \text{with} \quad S_{\max} = \sum_{x=1}^{N} s(x)$$

Subspaces $\mathcal{H}(M)$

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

Subspaces $\mathcal{H}(M)$ for equal $s(x) = s$

$$\dim\left(\mathcal{H}(M)\right) = \sum_{n=0}^{[(S_{\max}-M)/(2s+1)]} (-1)^n \binom{N}{n} \times \binom{N-1+(S_{\max}-M)-n(2s+1)}{N-1}$$

Problem equivalent to that of scoring sum M in a throw with N dice of $(2s+1)$ faces.

Relevant Dimension II

Rotational symmetry

e.g. for $s(x) = s, \forall x$

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

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

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

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

consider decrement in M

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

The orthogonal subspace belongs to $S = S_{\max} - 1$. 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 $\mathcal{H}(S, S)$

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

Relevant Dimension III

Cyclic shift symmetry

all $s(x) = s$ and $J(x,y) = J(|x-y|)$; cyclic shift operator

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

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

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

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

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]

[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. (to be published 1999)

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

Relevant Dimension IV

Relevant dimensions

		N							
		2	3	4	5	6	7	8	9
s	$\frac{1}{2}$	1	2	3	5	9	14	28	48
	$\frac{1}{2}$	**1**	**1**	**1**	**1**	**2**	**2**	**4**	6
	1	1	3	6	15	40	105	280	750
	1	**1**	**1**	**2**	**3**	8	15	37	84
	$\frac{3}{2}$	1	4	11	36	120	426	1505	5300
	$\frac{3}{2}$	**1**	**2**	**4**	8	23	61	192	590
	2	1	5	17	70	295	1260	5620	25200
	2	**1**	**2**	5	14	53	180	712	2800
	$\frac{5}{2}$	1	6	24	120	609	3150	16576	88900
	$\frac{5}{2}$	**1**	**2**	7	24	105	450	2085	9884

Table 1: Relevant dimension assuming only invariance with respect to rotations (upper rows) and assuming also invariance with respect to cyclic shifts (lower rows). The highlighted cases can be solved analytically.

Ground State Properties of AF Heisenberg Rings

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

Next neighbour interaction with constant J.

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 cyclic 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

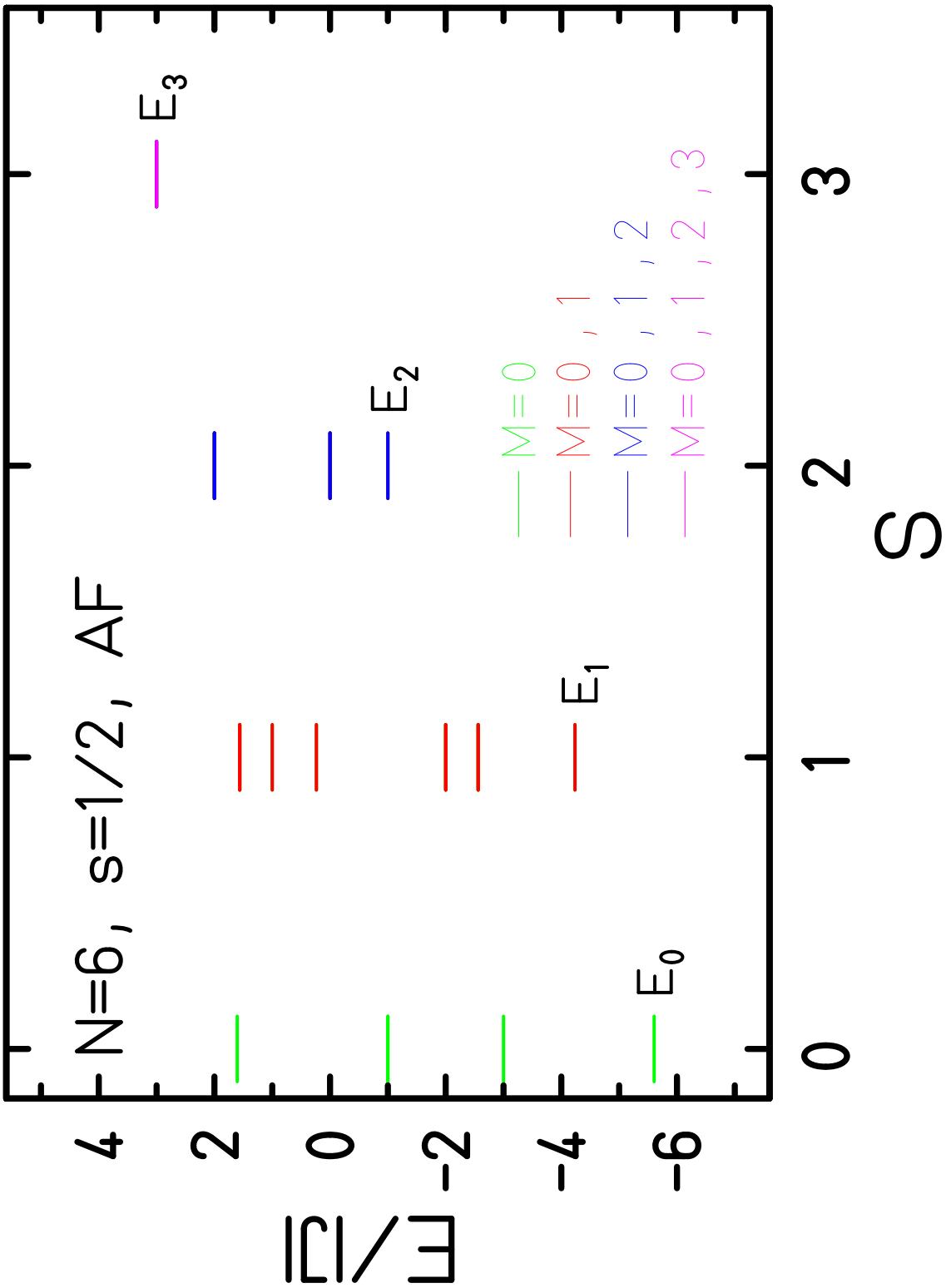
$$|\,\Psi_0\,\rangle = \sum_{\mathbf{m}} c(\mathbf{m})\,|\,\mathbf{m}\,\rangle \text{ with } \sum_{i=1}^{N} m_i = M$$

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

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

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

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 $S = 1/2$;
- degeneracy explained by angular momentum coupling;
- $N = 2$: the two spins couple to a total spin running from $S = 0$ to $= 2s$;
- $N = 3$: the first two spins couple 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

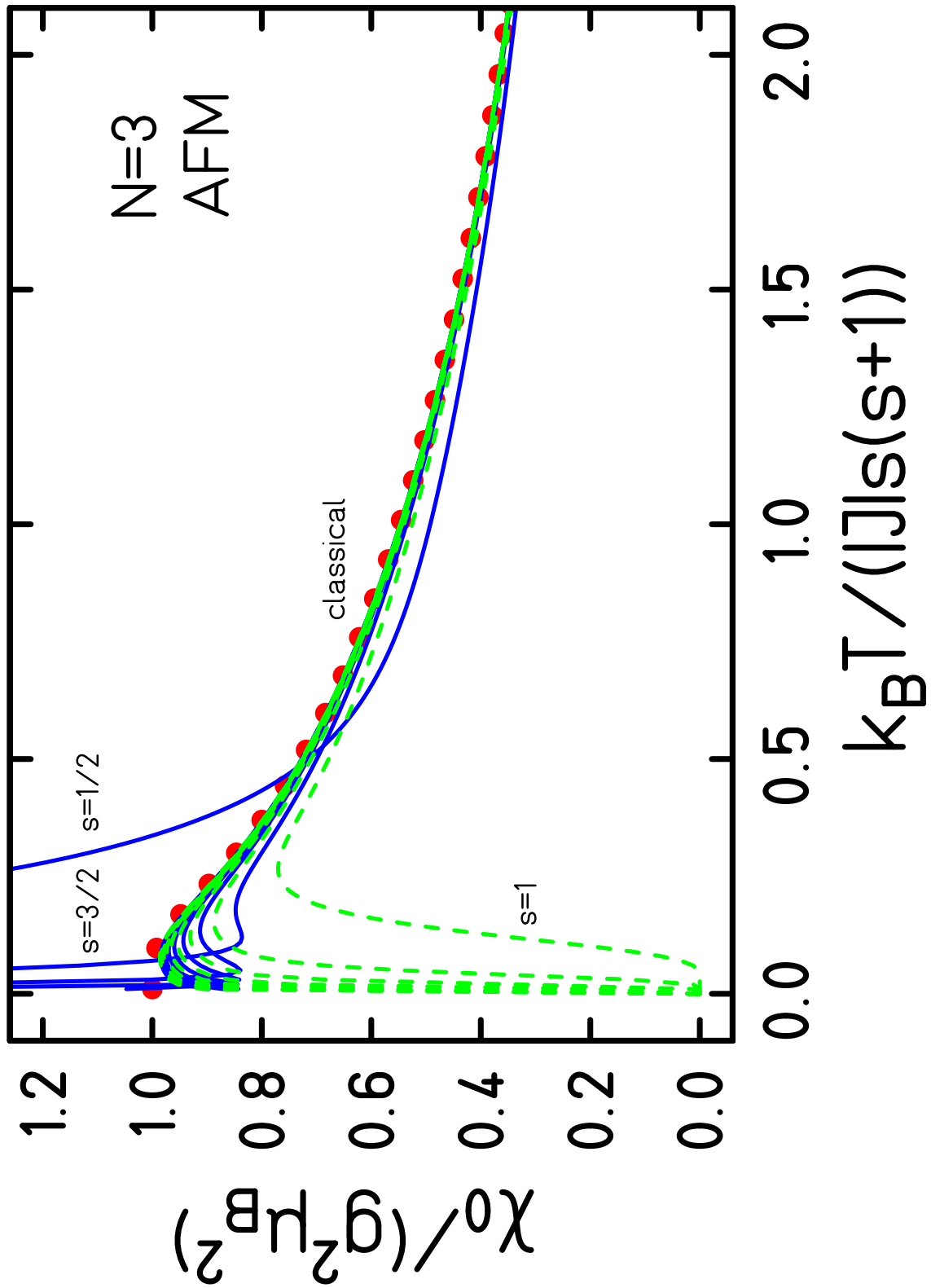
$$|\, \mathbf{m}_0 \,\rangle := |\, \frac{1}{2}\,, \frac{1}{2}\,, -\frac{1}{2}\,, \frac{1}{2}\,, -\frac{1}{2}\,, \frac{1}{2}\,, -\frac{1}{2} \cdots \rangle$$

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

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

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 $N - \lfloor (N+1)/4 \rfloor$.

Zero Field Suszeptibility



Classical limit

Aim

- understand limits and applicability of classical spin dynamics
- here: limit of high spin quantum number s

Idea (shown for the dimer)

$$\underset{\sim}{H} = \frac{J}{\hbar^2}\, \underset{\sim}{\vec{s}}_1 \cdot \underset{\sim}{\vec{s}}_2 = \frac{J}{2\hbar^2}\, \left(\underset{\sim}{\vec{S}}^2 - \underset{\sim}{\vec{s}}_1^{\,2} - \underset{\sim}{\vec{s}}_2^{\,2} \right) \quad ; \quad \underset{\sim}{\vec{S}} = \underset{\sim}{\vec{s}}_1 + \underset{\sim}{\vec{s}}_2$$

$$\underset{\sim}{\vec{\epsilon}}_n = \frac{\underset{\sim}{\vec{s}}_n}{\sqrt{\hbar^2\, s(s+1)}} \quad , \quad \left[\underset{\sim}{\epsilon}_{n\,x}, \underset{\sim}{\epsilon}_{n\,y} \right] = \frac{i}{\sqrt{s(s+1)}}\, \underset{\sim}{\epsilon}_{n\,z} \overset{s\to\infty}{\longrightarrow} 0$$

$$H_c = J_c\, \vec{e}_1 \cdot \vec{e}_2 \quad , \quad J_c = J\, s(s+1)$$

Procedure

- in order to gain the high spin limit, spectra for different s have to be mapped onto the same energy interval;
- compared quantities: density of states, autocorrelation function

$$\begin{aligned} \langle\langle\, \underset{\sim}{\vec{s}}_1(t) \cdot \underset{\sim}{\vec{s}}_1(0)\, \rangle\rangle &= \frac{1}{Z} \mathrm{tr} \left\{ \underset{\sim}{\vec{s}}_1(t) \cdot \underset{\sim}{\vec{s}}_1(0)\, e^{-\beta \underset{\sim}{H}} \right\} \\ Z &= \mathrm{tr} \left\{ e^{-\beta \underset{\sim}{H}} \right\} \end{aligned}$$

Spin Dimer I

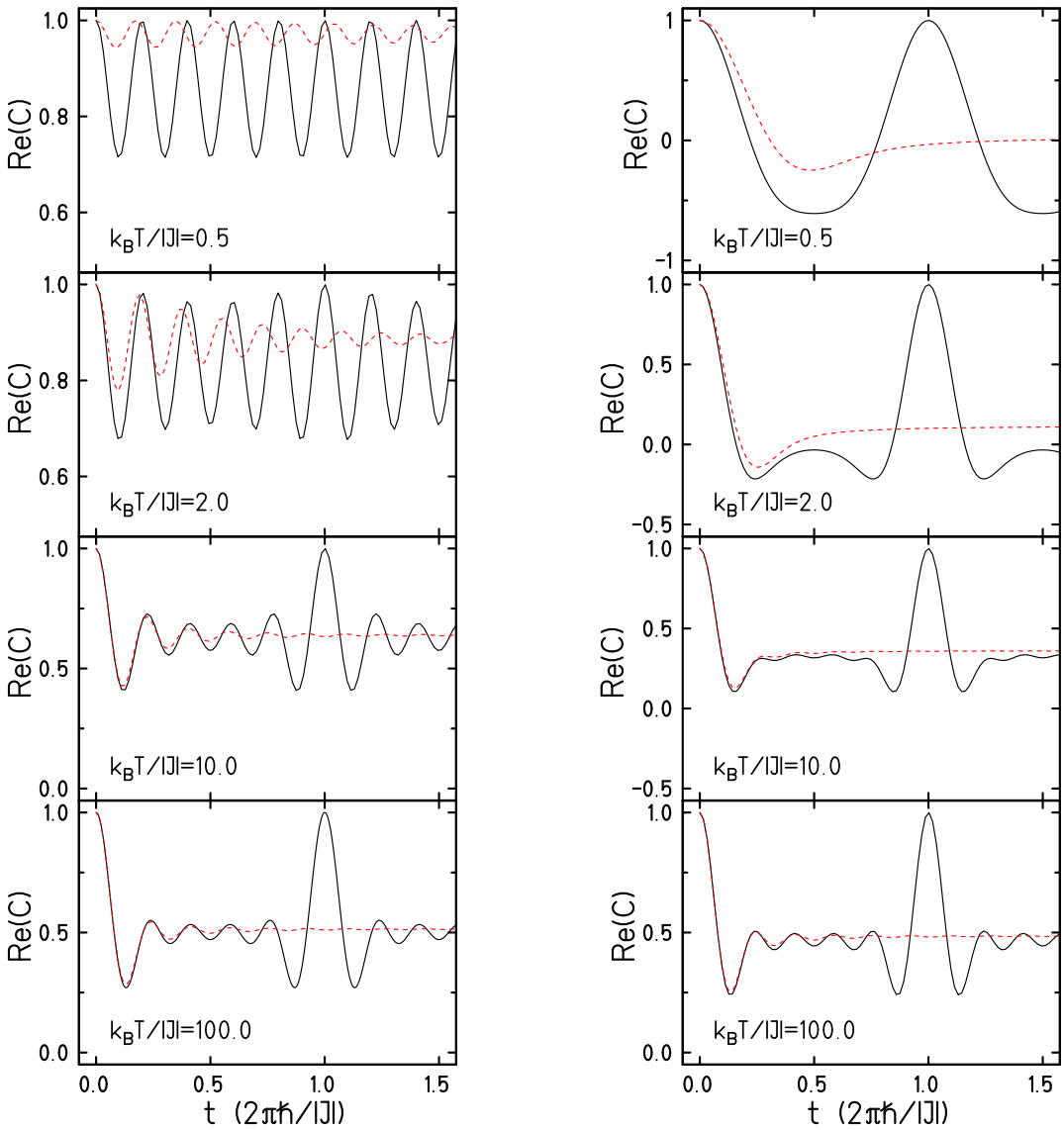


Figure 1: Normalized autocorrelation function Re $(C(t))$ for a spin-$\frac{5}{2}$-dimer for four different temperatures (solid lines). The left panels display our results for the ferromagnetic dimer, the right panels the antiferromagnetic case. The dashed lines show the classical result.

Spin Dimer II

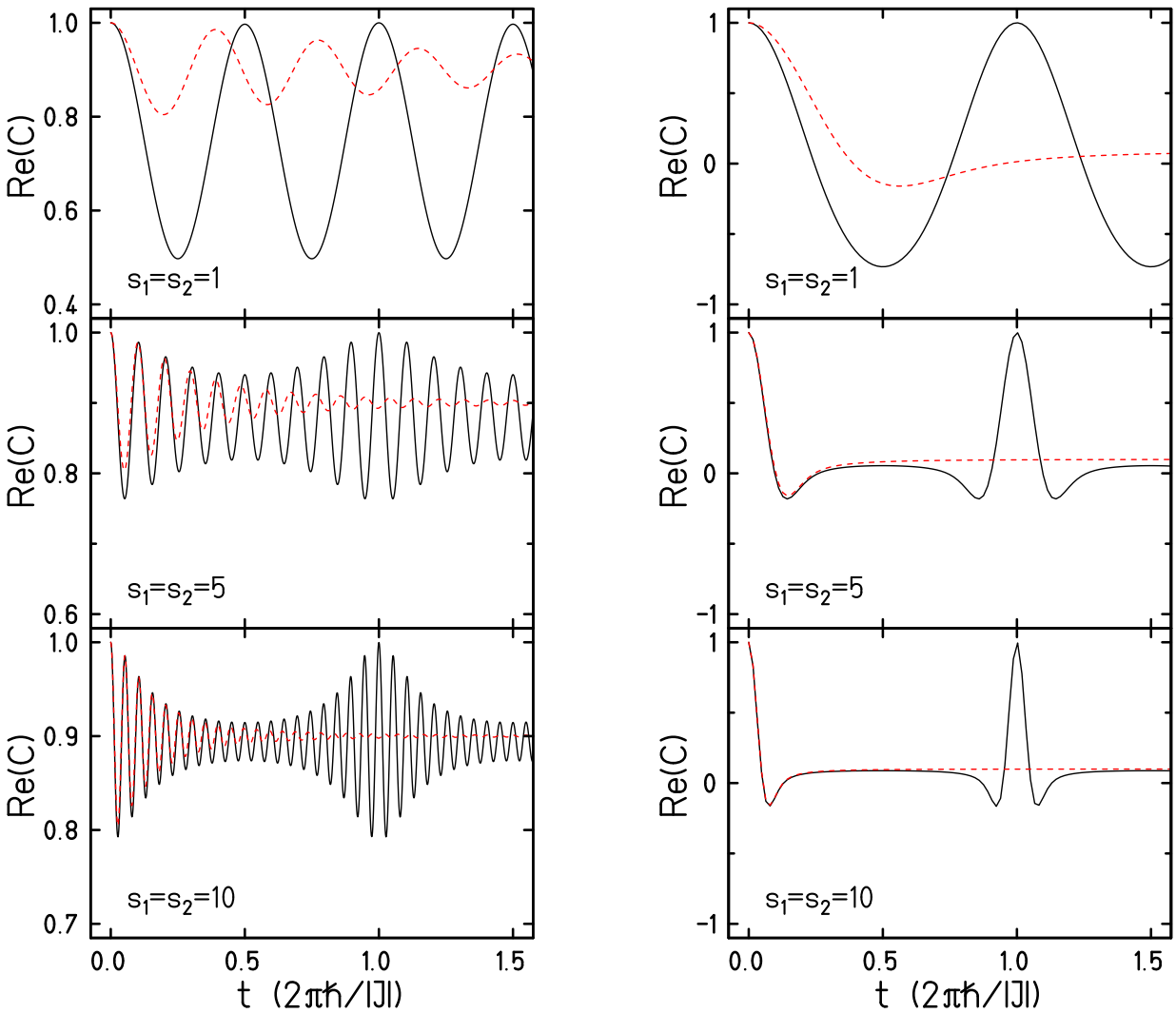


Figure 2: Normalized autocorrelation function for three different spins at the temperature $k_B\,T/(J\,s\,(s+1)) = 0.2$. The left panels displays the ferromagnetic dimer, the right panels the antiferromagnetic one. The solid lines show the quantum result, the dashed lines the classical.

Spin Trimer

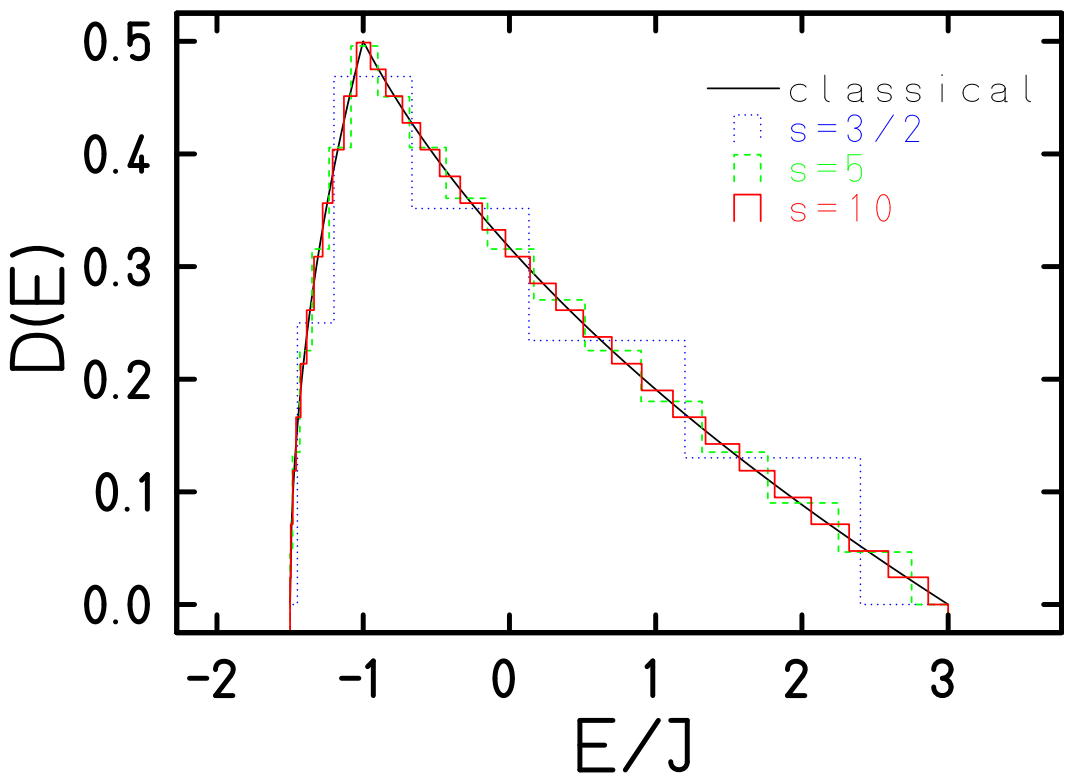


Figure 3: Normalized density of states for quantum Heisenberg trimers (dashed) and the classical counterpart (solid).

Classical density of states

$$D_c(E) = \begin{cases} \frac{1}{2J_c}\sqrt{\frac{2E}{J_c}+3} & : \quad -\frac{3}{2}\,J_c \leq E \leq -J_c \\ \frac{1}{4J_c}(3-\sqrt{\frac{2E}{J_c}+3}) & : \quad -J_c < E \leq 3J_c \\ 0 & : \quad \text{else} \end{cases}$$

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.
- Comparison of classical and quantum spin dynamics