Heisenberg model for magnetic molecules

Jürgen Schnack, Klaus Bärwinkel, Detlef Mentrup, Heinz-Jürgen Schmidt
Universität Osnabrück

Marshall Luban
Ames Laboratory & Department of Physics and Astronomy,
Iowa State University, Ames, Iowa 50011, USA

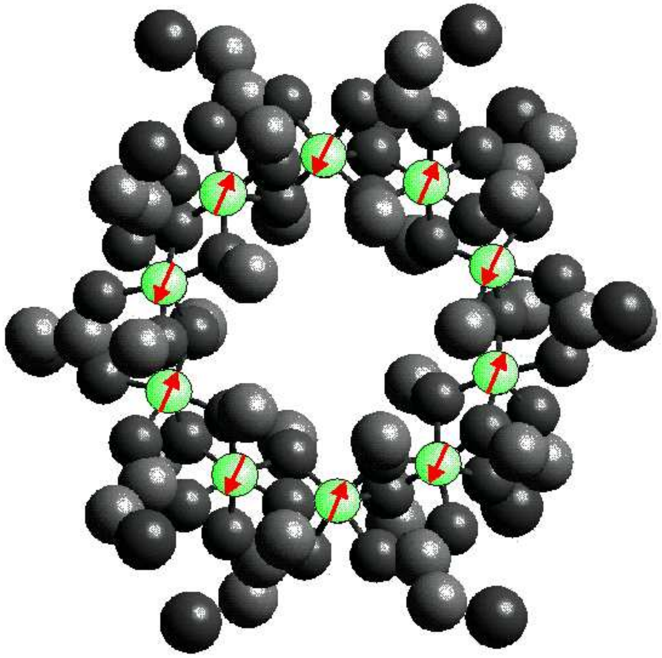
Magnetic molecules are an interesting new class of organo-metallic materials. A matrix of organic groups hosts paramagnetic ions. The interaction of these ions can be well described by the Heisenberg model.
The talk introduces some classes of molecules, their properties and modeling.

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

Properties of magnetic molecules

- 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; very often AF coupling
- speculations about applications range from mesoscopic magnets in biological systems, computer displays, quantum computer, photonic switches to catalysts (VDI report), very important are spin-crossover substances which show light induced excited spin state trapping (LIESST)

Structure of magnetic molecules



- 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 properties & observables

- molecular structure, properties of bonds, e.g. length & angle
- appropriate model Hamilton operator and its parameters, parameters often determined by susceptibility measurement
- magnetisation, susceptibility, specific heat
- properties of ground and first excited state, general statements like those of the Lieb-Schultz-Mattis theorem
- NMR – spin-lattice-relaxation rates, neutron scattering, torque magnetometry
- tunneling of the magnetization

Heisenberg model

Hamilton operator (AF: $J < 0$, F: $J > 0$)

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

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

Spin operators

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

Very often all individual spin quantum numbers are the same, like in the iron rings.

Typical observables in the canonical ensemble

Mean energy and specific heat

$$
\begin{aligned}
\langle\langle\, \underset{\sim}{H} \,\rangle\rangle &= \frac{1}{Z}\,\mathrm{tr}\left\{\underset{\sim}{H}\, e^{-\beta \underset{\sim}{H}}\right\} \quad , \quad Z = \mathrm{tr}\left\{e^{-\beta \underset{\sim}{H}}\right\} \quad , \quad \beta = \frac{1}{kT} \\
C &= \frac{d}{dT}\,\langle\langle\, \underset{\sim}{H} \,\rangle\rangle = -\frac{1}{kT^2}\left(\langle\langle\, \underset{\sim}{H}^2 \,\rangle\rangle - \langle\langle\, \underset{\sim}{H} \,\rangle\rangle^2\right)
\end{aligned}
$$

Zero-field magnetic susceptibility

$$
\chi_0 = \left(\frac{\partial\, \mathcal{M}}{\partial\, B}\right)_{B=0} = g^2 \mu_B^2 \beta \left(\frac{1}{Z}\,\mathrm{tr}\left\{\left(\underset{\sim}{S}^3\right)^2 \mathrm{e}^{-\beta \underset{\sim}{H}}\right\}\right)_{B=0}
$$

Problem

Dimension of the problem

- if the eigensystem of the Hamilton operator was known,
  the thermodynamic properties of all observable would be accessible;
- but the dimension of the Hilbert space grows fast with spin quantum number s and number of spins N
- total dimension $\dim(\mathcal{H}) = (2s+1)^N$, for Fe_{10}: 60466176
- even considering symmetries the largest dimension to deal with prevents an exact (numerical) treatment

Classical Heisenberg Model

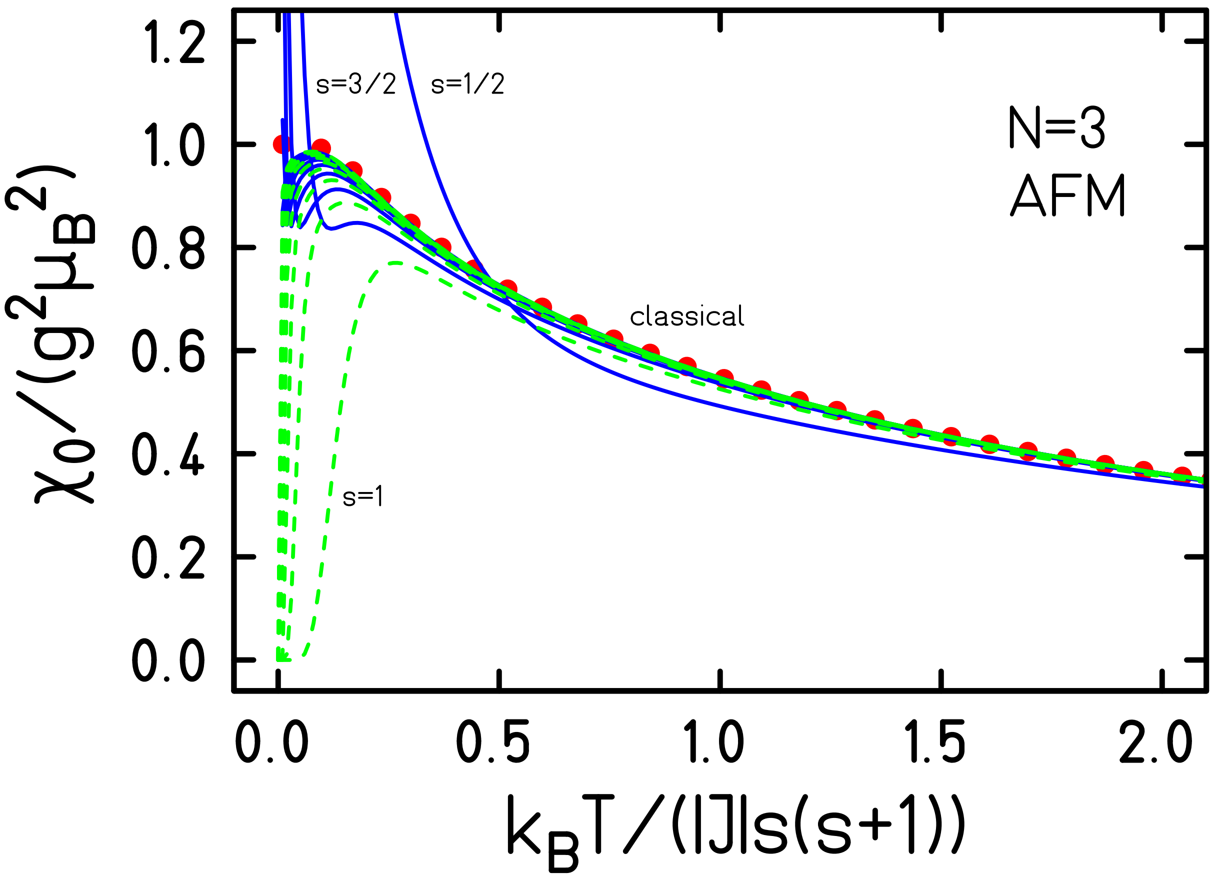
Hamilton function

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

- classical spin model works for rather large systems; not restricted to low dimensions, symmetric configurations or next-neighbour interactions
- works very well for many observables down to temperatures of the order of the coupling strength $|J|/k$ (Christian Schröder[a])
- but discrete spectrum (gaps) important at low temperatures
- odd-even effects in small molecules visible with quantum mechanical treatment
- for small spin systems time-dependent functions recurrent in quantum mechanical treatment, but damped in classical treatment, see e.g. $\langle\langle\, \underset{\sim}{\vec{s}}_1(t) \cdot \underset{\sim}{\vec{s}}_1(0)\, \rangle\rangle$

[a]C. Schröder, *Numerische Simulationen zur Thermodynamik magnetischer Strukturen mittels deterministischer und stochastischer Wärmebadankopplung*, PhD thesis, University of Osnabrück (1999)

Susceptibility $N = 3$



Dimer spin-spin autocorrelation function

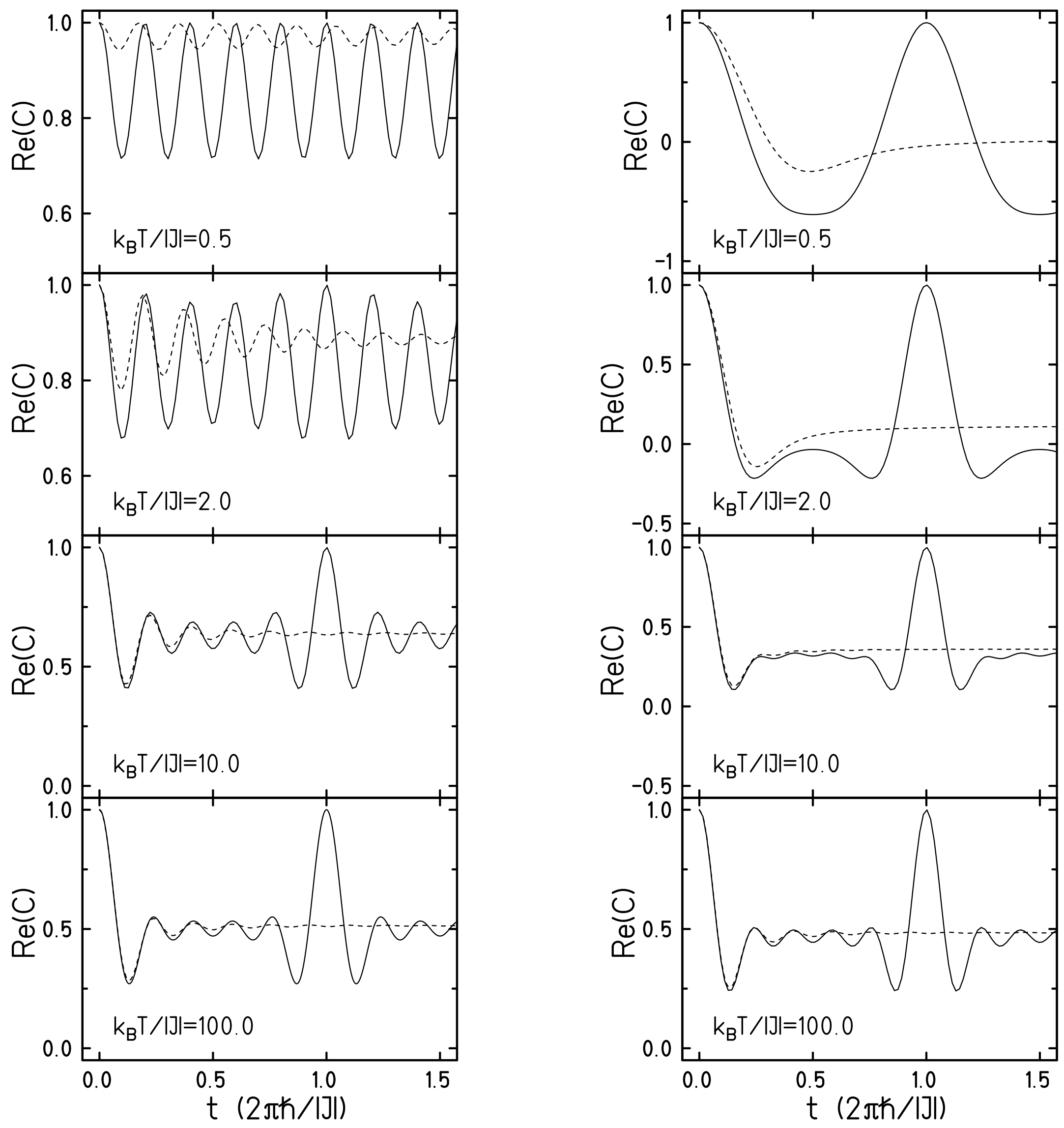


Figure 1: Normalized autocorrelation function $\mathrm{Re}\,(C(t))$ for a spin-$\frac{5}{2}$-dimer for four different temperatures (solid lines). The left panels display our results for the ferromagnetic dimer, the right panels the antiferromagnetic case. The dashed lines show the classical result.

Dimer spin-spin autocorrelation function

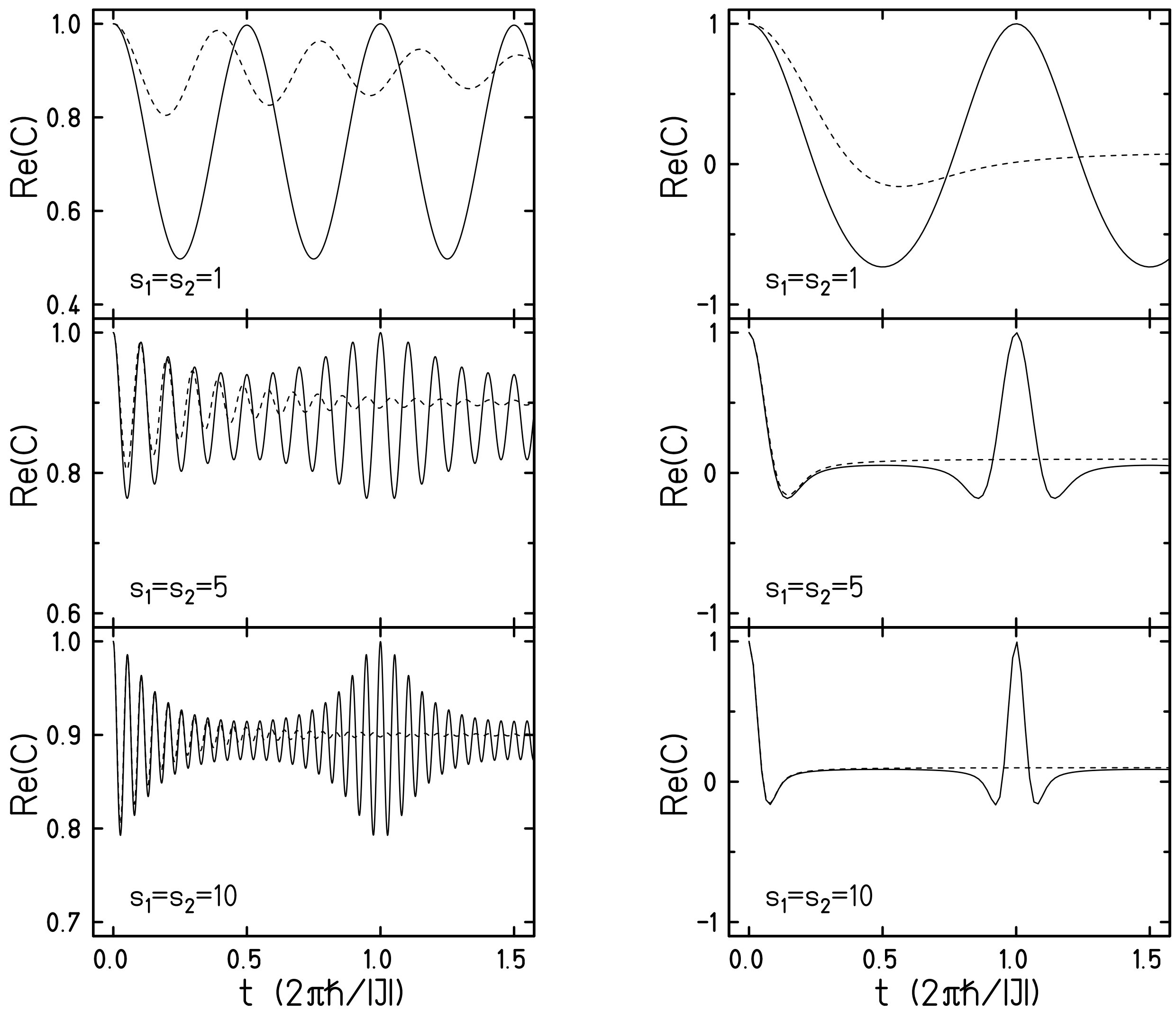


Figure 2: Normalized autocorrelation function for three different spins at the temperature $k_B\,T/(J\,s\,(s+1)) = 0.2$. The left panels displays the ferromagnetic dimer, the right panels the antiferromagnetic one. The solid lines show the quantum result, the dashed lines the classical.

Quantum Heisenberg model

Be all $s(x) = s$ and isotropic next neighbour interaction

$$\underset{\sim}{H} \quad = \quad -J \sum_{x=1}^{N} \underset{\sim}{\vec{s}}(x) \cdot \underset{\sim}{\vec{s}}(x+1) + g\,\mu_B\, B \sum_{x}^{N} \underset{\sim}{s}^{3}(x)$$

Symmetry about the 3-axis, good quantum number M

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

Rotational symmetry, good quantum number S

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

Translational symmetry of rings

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

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

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

Eigenvalues of $\underset{\sim}{T}$, good quantum number k

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

Evaluation of eigenvalues and eigenstates of the Hamilton operator in Hilbert suspaces $\mathcal{H}(S,M,k)$ with good quantum numbers S, M and k.

Relevant dimension for spin rings

s	N=2	3	4	5	6	7	8	9
$\frac{1}{2}$	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: Upper rows – only invariance with respect to rotations, lower rows – also invariance with respect to cyclic shifts.

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	$E_0/(NJ)$
	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
$\frac{1}{2}$	4.0	3.0	2.0	2.236	1.369	2.098	1.045	1.722	0.846	$\Delta E/\lvert J\rvert$
	3	4	3	2	3	8	3	8	3	deg
	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
1	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	deg
	0	0	0	0	0	0	0	0	0	S
	0	0	0	0	0	0	0	0	0	k
1	4.0	2.0	2.0	1.929	1.441	1.714	1.187	1.540	1.050	$\Delta E/\lvert J\rvert$
	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
$\frac{3}{2}$	7.5	3.5	6	4.973	5.798	5.338	5.732	5.477	$5.704^{\dagger\dagger}$	$E_0/(NJ)$
	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
$\frac{3}{2}$	4.0	3.0	2.0	2.629	1.411	2.171	1.117	1.838	$0.938^{\dagger\dagger}$	$\Delta E/\lvert J\rvert$
	3	16	3	8	3	8	3	8	3	deg
	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
2	12	6	10	8.456	9.722	9.045	9.630	$9.263^{\dagger\dagger}$	$9.590^{\dagger\dagger}$	$E_0/(NJ)$
	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
2	4.0	2.0	2.0	1.922	1.394	1.652	1.091	$1.431^{\dagger\dagger}$	$0.906^{\dagger\dagger}$	$\Delta E/\lvert J\rvert$
	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
$\frac{5}{2}$	17.5	8.5	15	12.434	14.645	13.451	$14.528^{\dagger}$	$13.848^{\dagger\dagger}$	$14.475^{\dagger\dagger}$	$E_0/(NJ)$
	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. † – O. Waldmann, private communication. †† – projection method.

Ground State Properties of Heisenberg rings with isotropic af next neighbour interaction

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; $\Rightarrow$ frustration ???
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;

Lieb-Mattis-Theorem

Lieb-Mattis-Theorem for spin rings[a]

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.

Then

- 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

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

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

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

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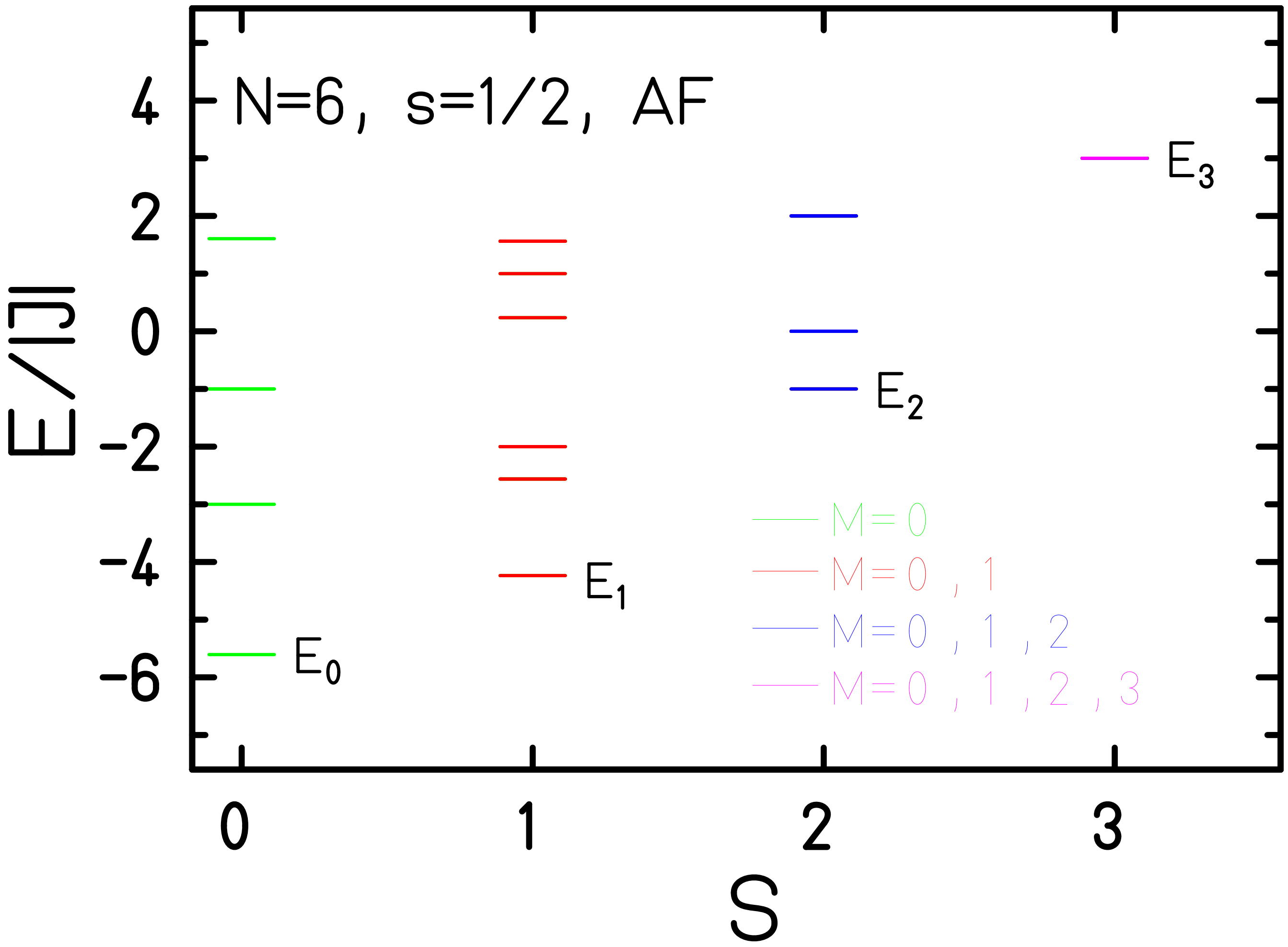
[a] E.H. Lieb, T.D. Schultz, D.C. Mattis, Ann. Phys. (N.Y.) **16** (1961) 407; E.H. Lieb, D.C. Mattis, J. Math. Phys. **3** (1962) 749

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

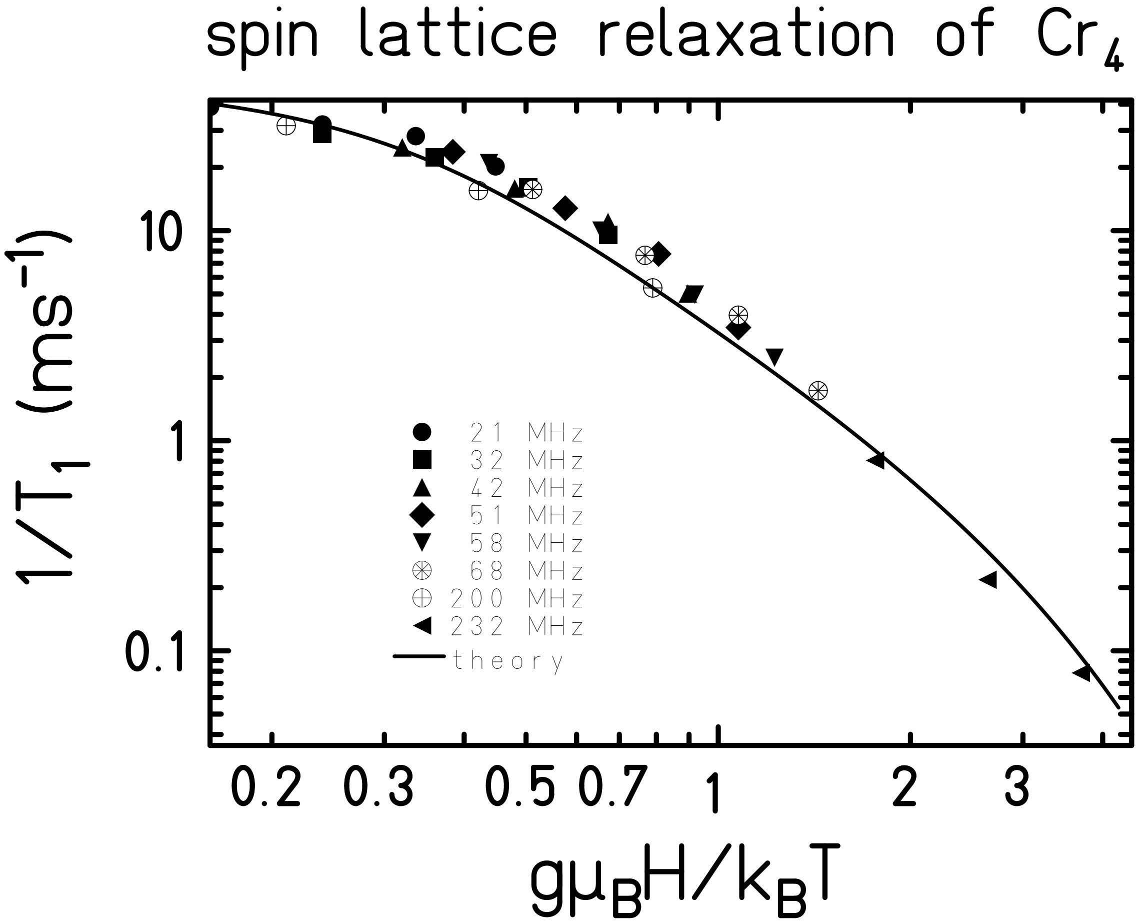


Odd rings

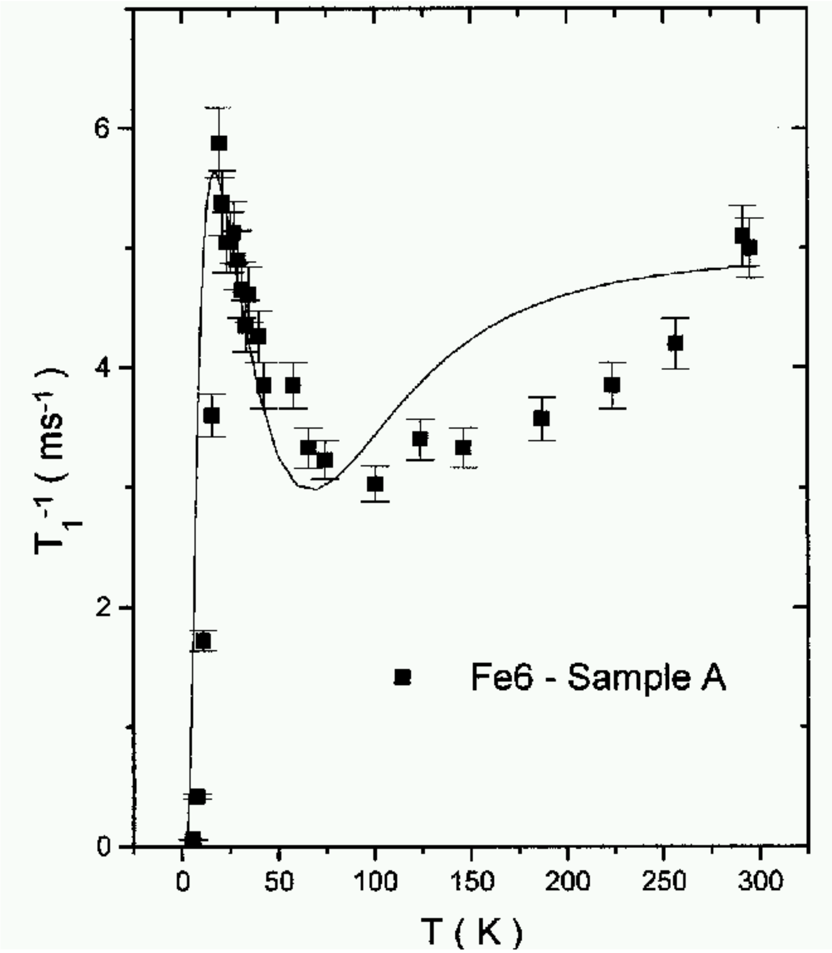
- Spin rings with an odd number of sites and half integer spin are interesting, at least for theorists, because they show unusual properties.
- Up to now there are no such molecules except trimers.

Spin-lattice relaxation rate

Ferromagnetic Cr_4 molecules, $s = 3/2$



Spin-lattice relaxation rate



A. Lascialfari, D. Gatteschi, F. Borsa, A. Cornia, Phys. Rev. B **55**, 14341 (1997)

Summary

Summary

- Heisenberg model with isotropic next neighbour interaction describes the spectrum of magnetic molecules with very good accuracy;
- additional terms seem to be rather small;
- with the help of symmetries the Hamiltonian of small systems can be diagonalized;
- ground states and first excited states show systematic properties; helpful to understand low T behaviour;

Open problems or in progress

- approximations to the full quantum density of states;
- better understand NMR data;
- goto neutron scattering to see a wider frequency range;
- Where to get students?