Magnetic Molecules - A New Playground for the Heisenberg Model

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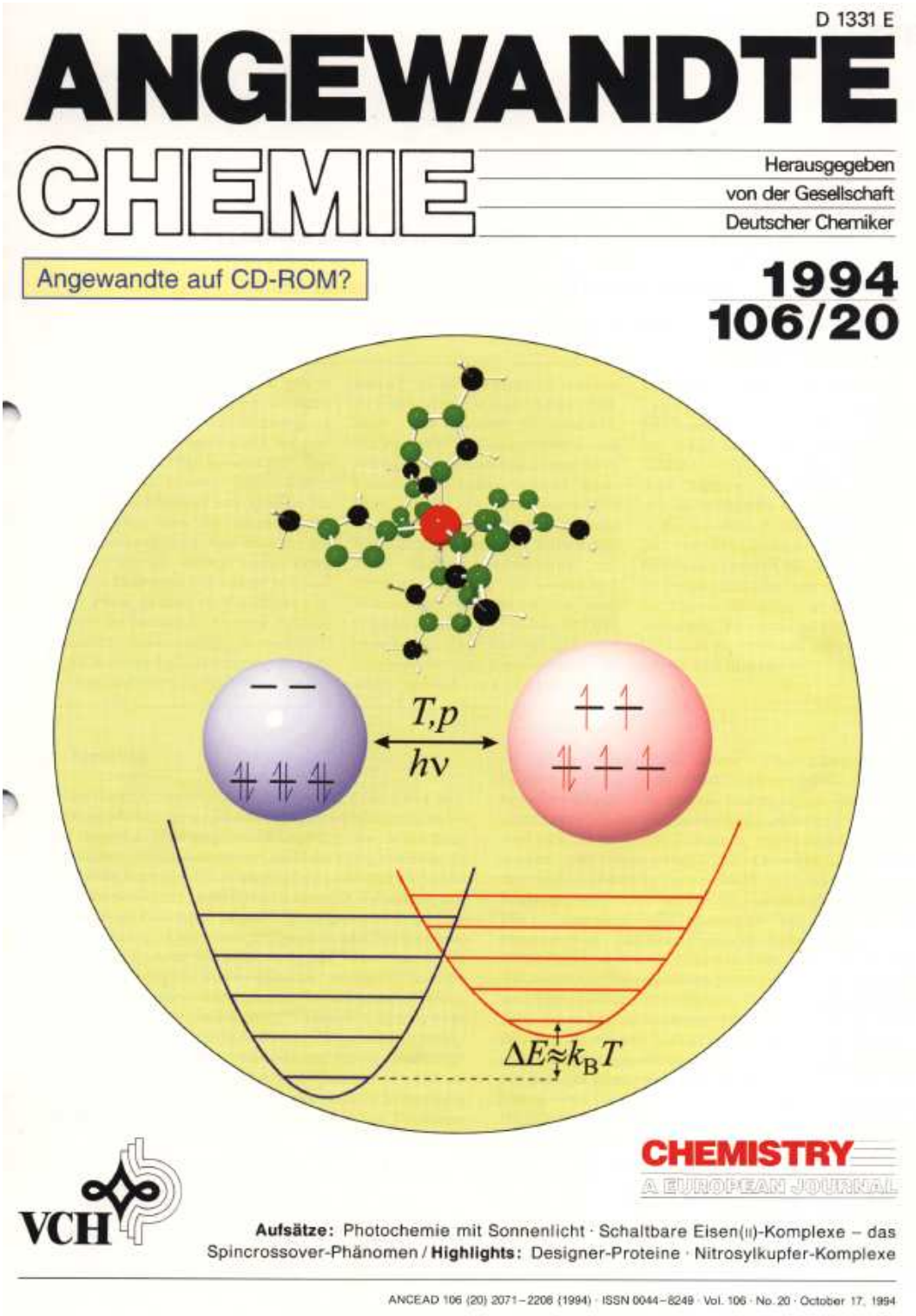
Magnetic molecules are an interesting new class of organo-metallic materials. A matrix of organic groups hosts paramagnetic ions. Very often the interaction of these ions ("spins") can be well described by the Heisenberg model.
The talk introduces some classes of molecules, their properties and modeling.

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

Properties of magnetic molecules

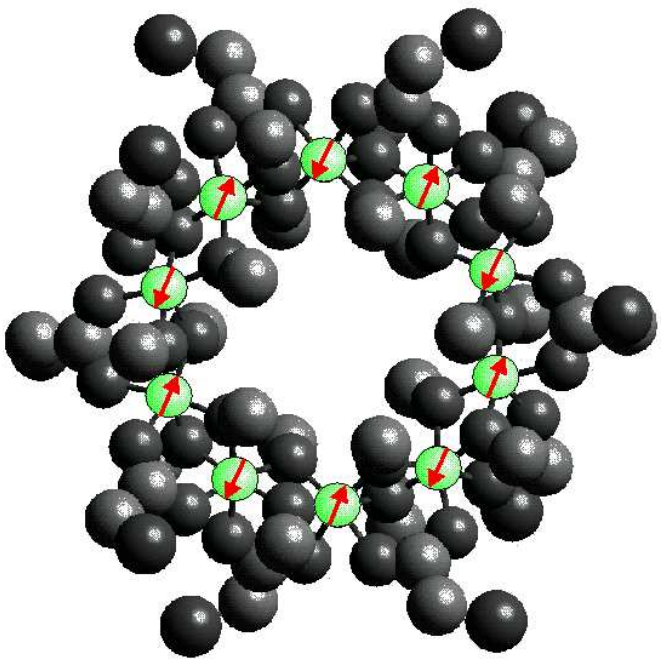
- new class of nanometer-size magnetic materials;
- molecules host from two up to thirty interacting paramagnetic ions;
- large number of nonmagnetic organic ligands;
- weak intermolecular interactions;
- measurements on a bulk sample reflect intramolecular interactions only;
- well described by the 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)

Light induced excited spin state trapping



Metastable excited state, structural and colour changes; light and temperature switching; P. Gütlich, A. Hauser, H. Spiering, *Thermisch und optisch schaltbare Eisen(II)-Komplexe*, Angew. Chem. **106** (1994) 2109.

Structure of magnetic molecules



- simple arrays 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 structures (Mn_{12})
- polytopes like the icosidodecahedron Fe_{30}
- typical spin quantum numbers: 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
- Electron Spin Resonance (ESR) $\equiv$ Electron Paramagnetic Resonance (EPR)
- NMR – spin-lattice-relaxation rates, neutron scattering cross section, torque magnetometry
- (macroscopic) tunneling of the magnetisation
- properties of ground and first excited state, general statements like those of the Lieb-Schultz-Mattis theorem

Heisenberg model

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

$$\underset{\sim}{H} = -\sum_{(u,v)} J(u,v) \left\{ \underset{\sim}{s}^3(u) \underset{\sim}{s}^3(v) + \frac{\gamma}{2} \left[\underset{\sim}{s}^+(u) \underset{\sim}{s}^-(v) + \underset{\sim}{s}^-(u) \underset{\sim}{s}^+(v) \right] \right\}$$

$$+ g\, \mu_B\, B \sum_u^N \underset{\sim}{s}^3(u)$$

$\gamma = 0$ – Ising model; $\gamma = 1$ – Heisenberg model.

Spin operators

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

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

$$\langle\langle \underset{\sim}{H} \rangle\rangle = \frac{1}{Z}\,\mathrm{tr}\left\{\underset{\sim}{H}\, e^{-\beta \underset{\sim}{H}}\right\} \quad , \quad Z = \mathrm{tr}\left\{e^{-\beta \underset{\sim}{H}}\right\} \quad , \quad \beta = \frac{1}{kT}$$

$$C = \frac{d}{dT}\,\langle\langle \underset{\sim}{H} \rangle\rangle = -\frac{1}{kT^2}\left(\langle\langle \underset{\sim}{H}^2 \rangle\rangle - \langle\langle \underset{\sim}{H} \rangle\rangle^2\right)$$

Magnetisation and magnetic susceptibility

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

$$\chi = \left(\frac{\partial\,\mathcal{M}}{\partial\,B}\right) = g^2\mu_B^2\beta\left(\langle\langle \left(\underset{\sim}{S}^3\right)^2 \rangle\rangle - \langle\langle \underset{\sim}{S}^3 \rangle\rangle^2\right)$$

Symmetries I

Heisenberg Hamilton operator & Zeeman term

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

Symmetry about the 3-axis, good quantum number M

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

Rotational symmetry, good quantum number S

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

Symmetries II
Translational invariance of rings

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

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

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

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

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

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

		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: Upper rows – only invariance with respect to rotations, lower rows – also invariance with respect to cyclic shifts.

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;
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;

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	$\Delta E/\|J\|$
	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	$\Delta E/\|J\|$
	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	$0.938^{\dagger\dagger}$	$\Delta E/\|J\|$
	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	$1.431^{\dagger\dagger}$	$0.906^{\dagger\dagger}$	$\Delta E/\|J\|$
	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.

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

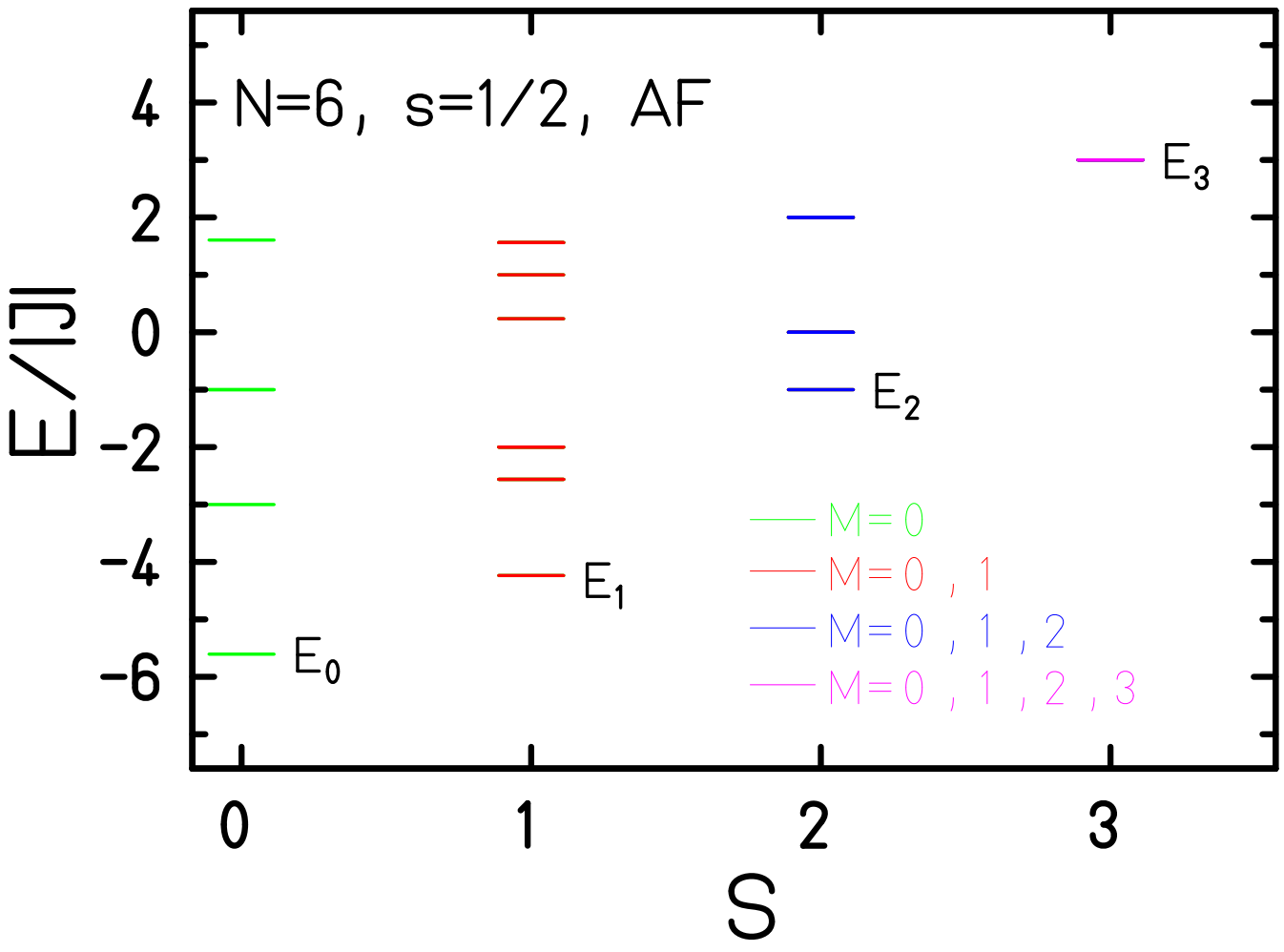
$$|\,\Psi_0\,\rangle = \sum_{\mathbf{m}} c(\mathbf{m})\;|\,\mathbf{m}\,\rangle \text{ with } \sum_{i=1}^{N} m_i = M$$

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

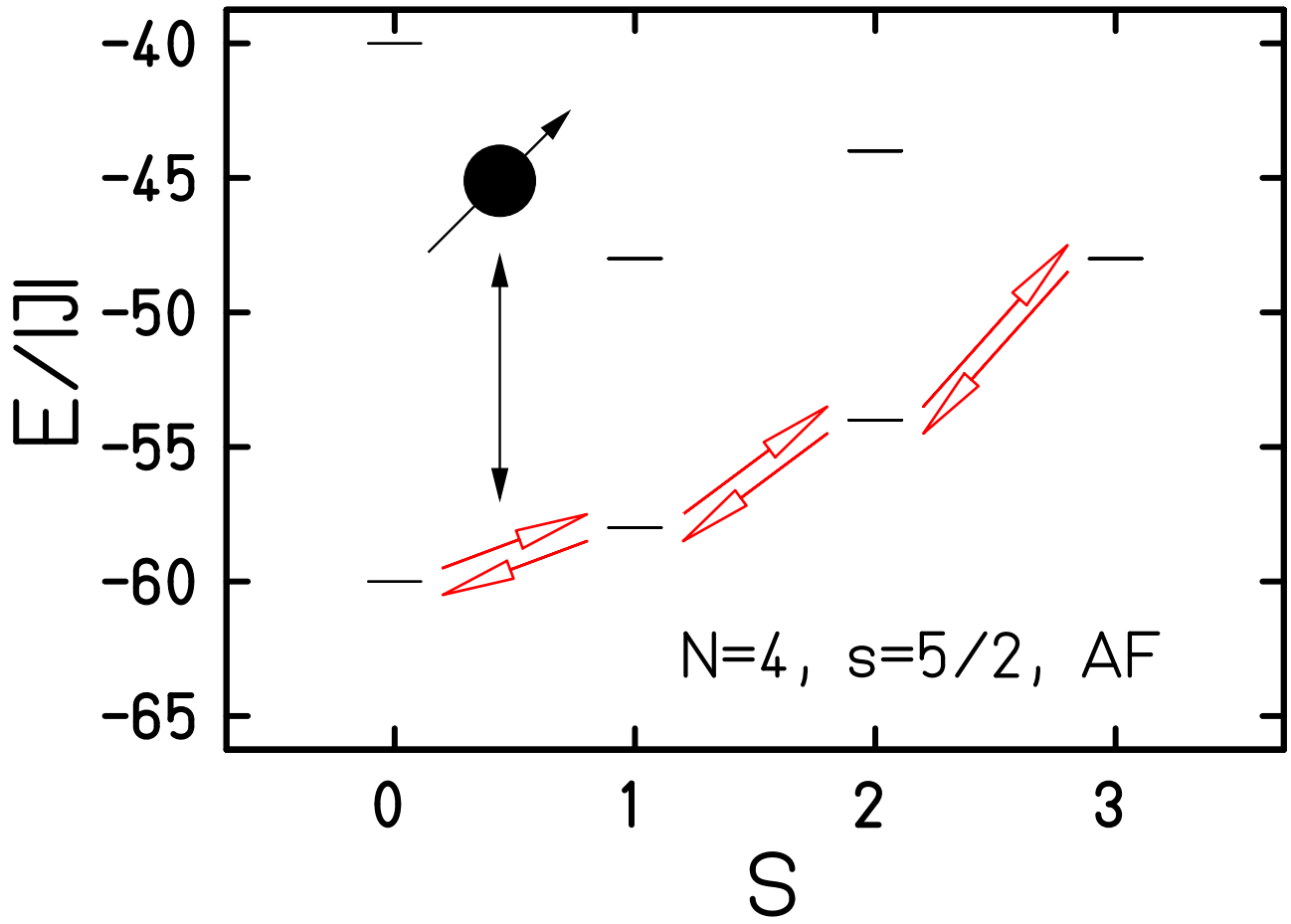
All $a(\mathbf{m})$ are non-zero, real and of equal sign.

[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

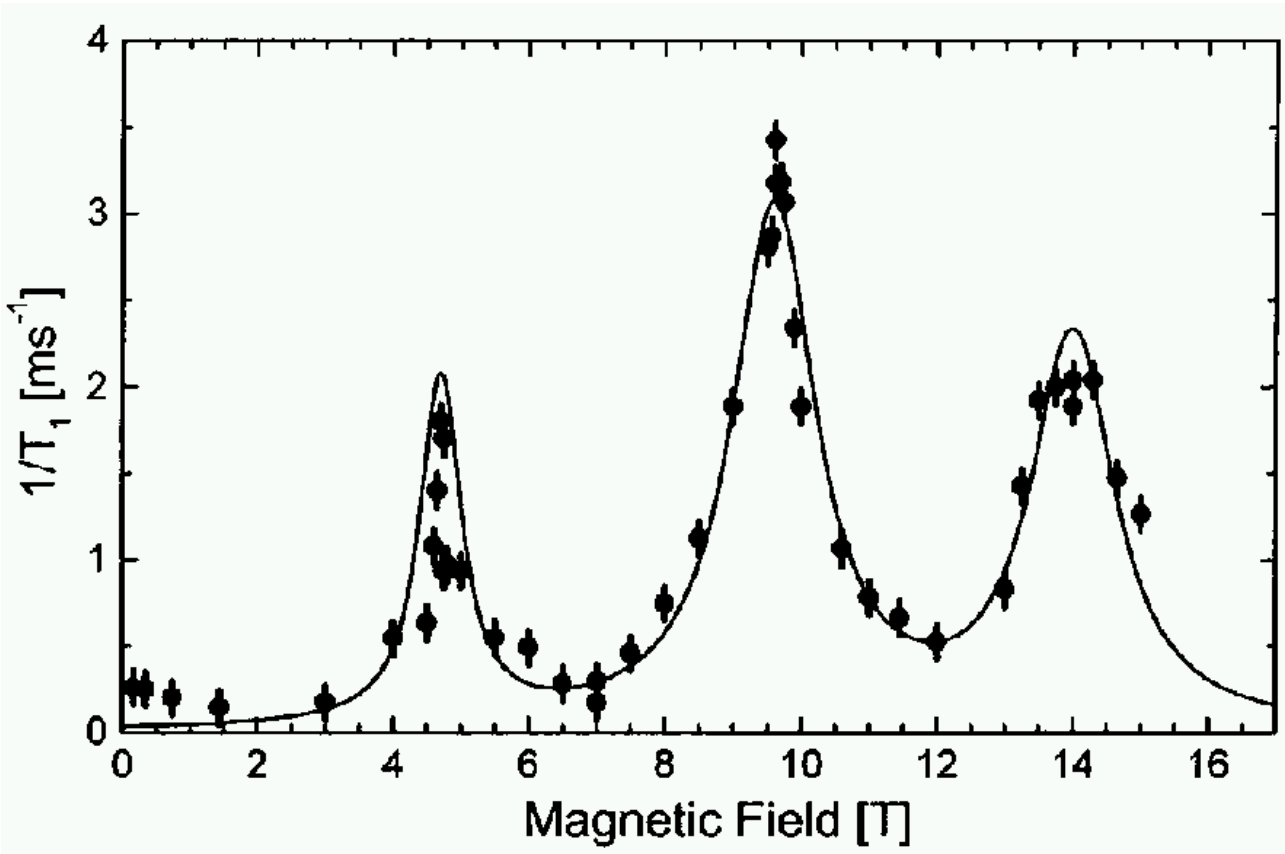
Spectrum $N = 6,\ s = 1/2,\ M \geq 0$



Spin-lattice relaxation rate I



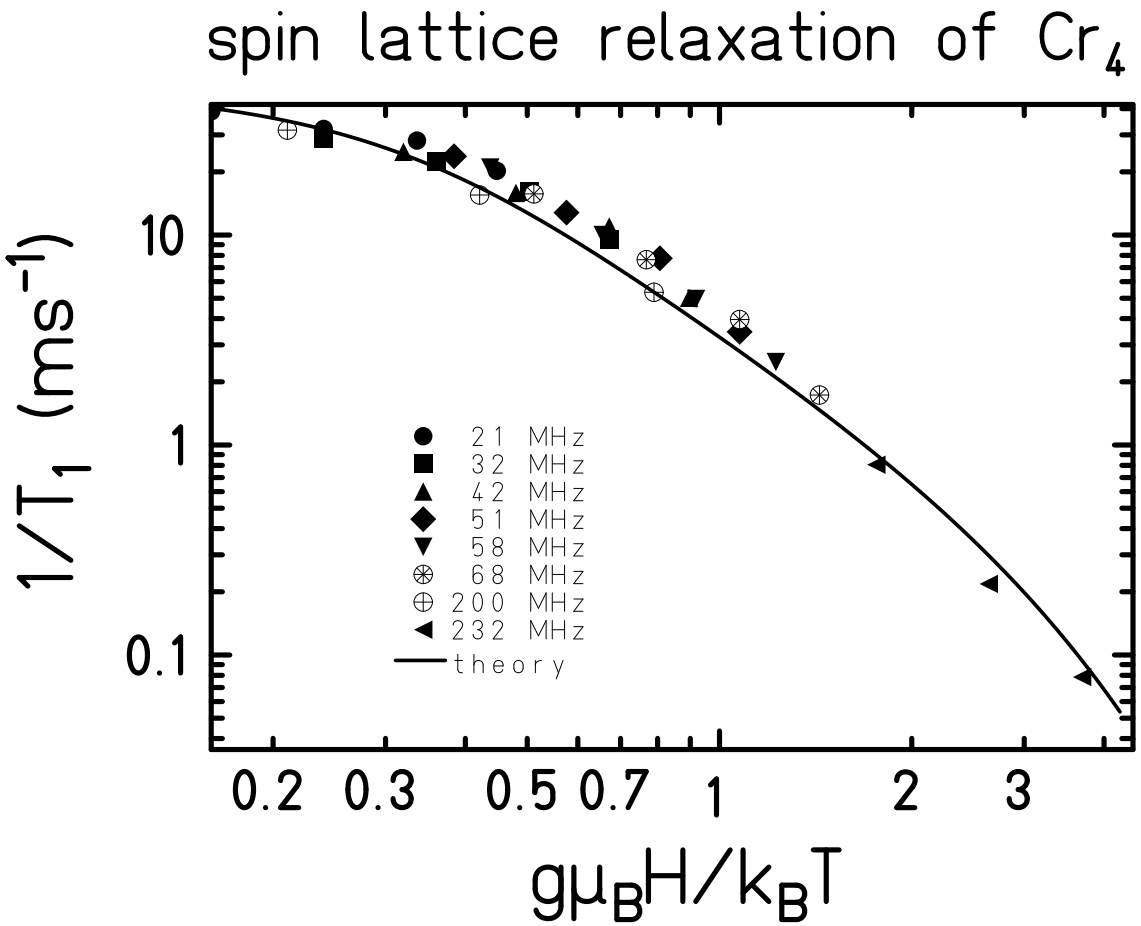
Spin-lattice relaxation rate II



The spin-lattice relaxation rate exhibits maxima at level crossings (M.-H. Julien et al., Phys. Rev. Lett. **83** (1999) 227).

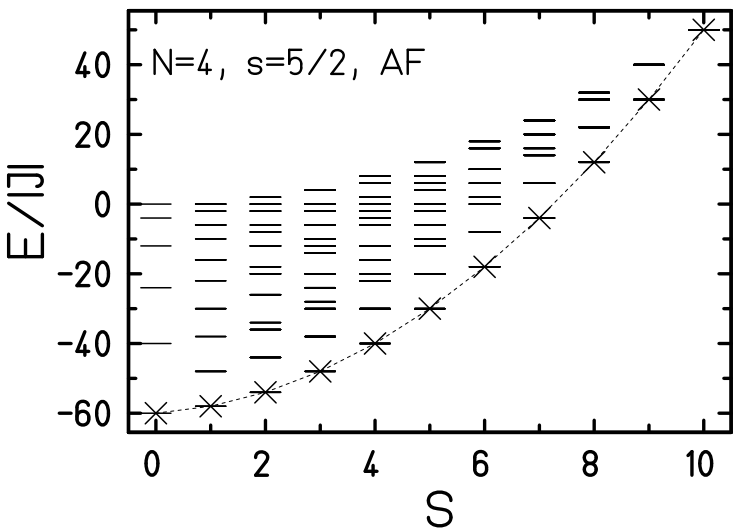
Spin-lattice relaxation rate III

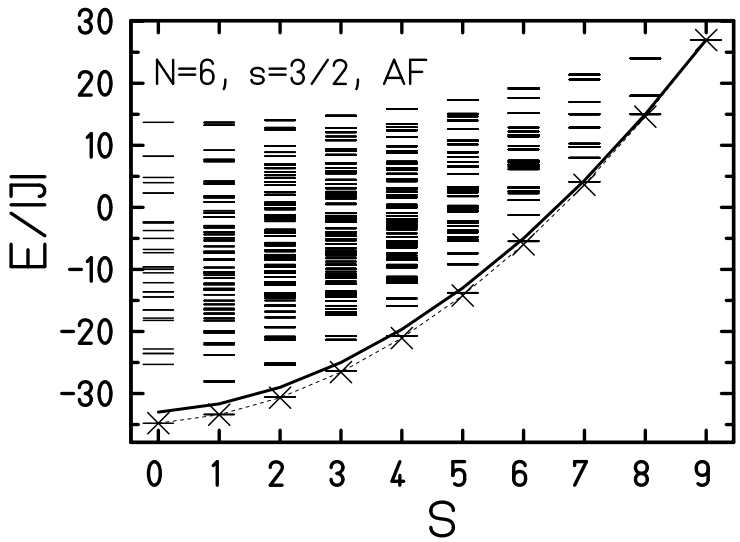
Ferromagnetic Cr_4 molecules, $s = 3/2$



Low-field behaviour of the spin-lattice relaxation rate (below the first level crossing), calculated in the $S = 6$-subspace (Y. Furukawa et al., Phys. Rev. B **61** (1999) 8635).

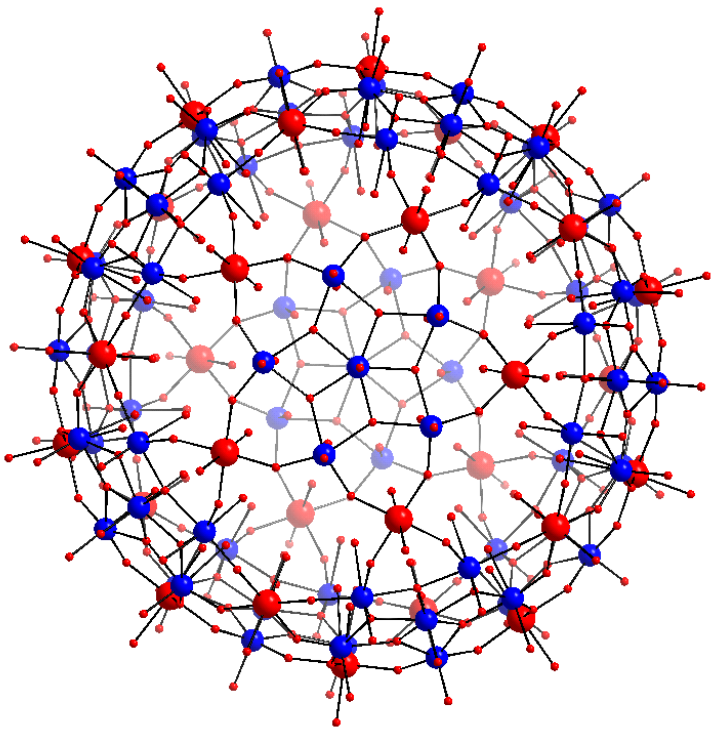
Approximations: Rotational band





$$
\begin{aligned}
E_{S,min} &\approx -J\,D(N,s)/N\;S(S+1) + E_a \\
&\approx -J\,D/N\left[S(S+1) - \sum_{j=1}^{N_{SL}} S_j(S_j+1)\right]
\end{aligned}
$$

Approximation – Rotational Hamiltonian

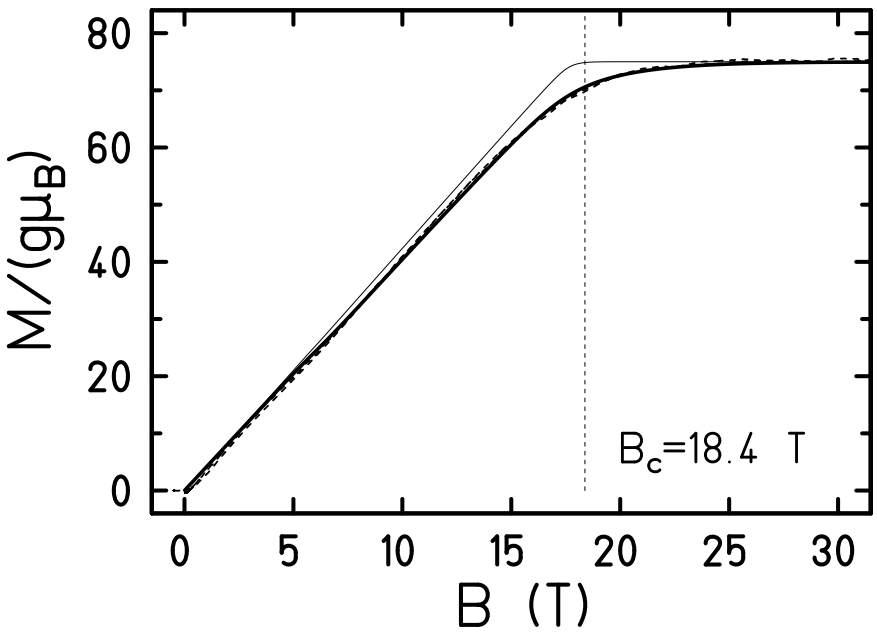


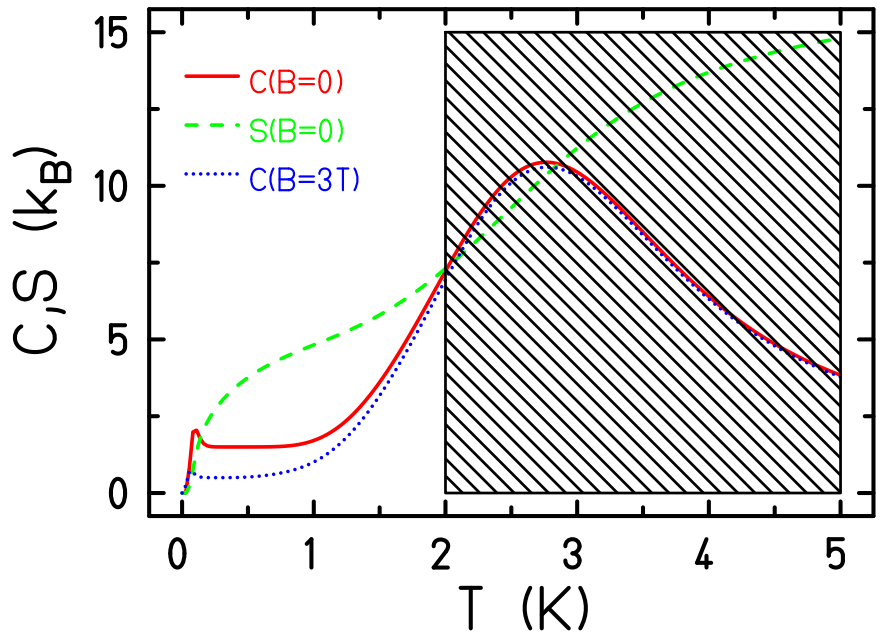
- Fe_{30} – one of the largest molecules synthesized to date (A. Müller et al., Angew. Chem. Int. Ed. **38** (1999), 3238)
- image: small red – O, big red – Fe, blue – Md
- Fe_{30} – dimension of the Hilbert space 6^{30}
- Fe_{30} – perfect icosidodecahedron
- Fe_{30} – rather small next neighbour coupling
- approximation of the low-lying spectrum with rotational bands

$$\underset{\sim}{H}^{\text{approx}} = -\frac{D\,J}{N}\left[\underset{\sim}{\vec{S}}^2 - \sum_{j=1}^{N_{SL}} \underset{\sim}{\vec{S}}_j^2\right]$$

unrealistic above the second band; combination with other approximations necessary

Rotational Hamiltonian for Fe_{30}





Limiting temperature!

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;
- rotational band structure;

Open problems or in progress

- approximations to the full quantum density of states;
- influence of the rotational bands on NMR data;
- goto neutron scattering to see a wider frequency range;