Frustration-induced exotic properties of magnetic molecules

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Spin- and charge-correlations in molecule-based materials
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Deutsche Forschungsgemeinschaft DFG

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"The worldwide Ames group"

- K. Bärwinkel, H.-J. Schmidt, J. S., M. Allalen, M. Brüger, D. Mentrup, M. Exler, P. Hage, F. Hesmer, K. Jahns, F. Ouchni, R. Schnalle, P. Shechelokovskyy, S. Torbrügge (Uni Osnabrück);
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- Chr. Schröder (FH Bielefeld & Ames Lab, Iowa, USA);
- R.E.P. Winpenny (Man U); L. Cronin (University of Glasgow);
- H. Nojiri (Tohoku University, Japan); N. Dalal (Florida State, USA);
- J. Richter, J. Schulenburg, R. Schmidt (Uni Magdeburg);
- S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (Uni Braunschweig).
- E. Rentschler (Uni Mainz); U. Kortz (IUB); A. Tennant (HMI Berlin).

General results on frustrated magnetic molecules

1. Extension of Lieb, Schultz, and Mattis: k–rule for odd rings
2. Rotational bands in antiferromagnets
3. What the Icosidodecahedron tought us about magnetism
   (a) Giant magnetization jumps
   (b) Enhanced magnetocaloric effect
   (c) Magnetization plateaus and susceptibility minima
4. Hysteresis without anisotropy
5. A special triangular molecule-based spin tube

Model Hamiltonian – Heisenberg-Model

$$\underset{\sim}{H} = -\sum_{i,j} J_{ij} \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) \qquad + \qquad g \, \mu_B \, B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

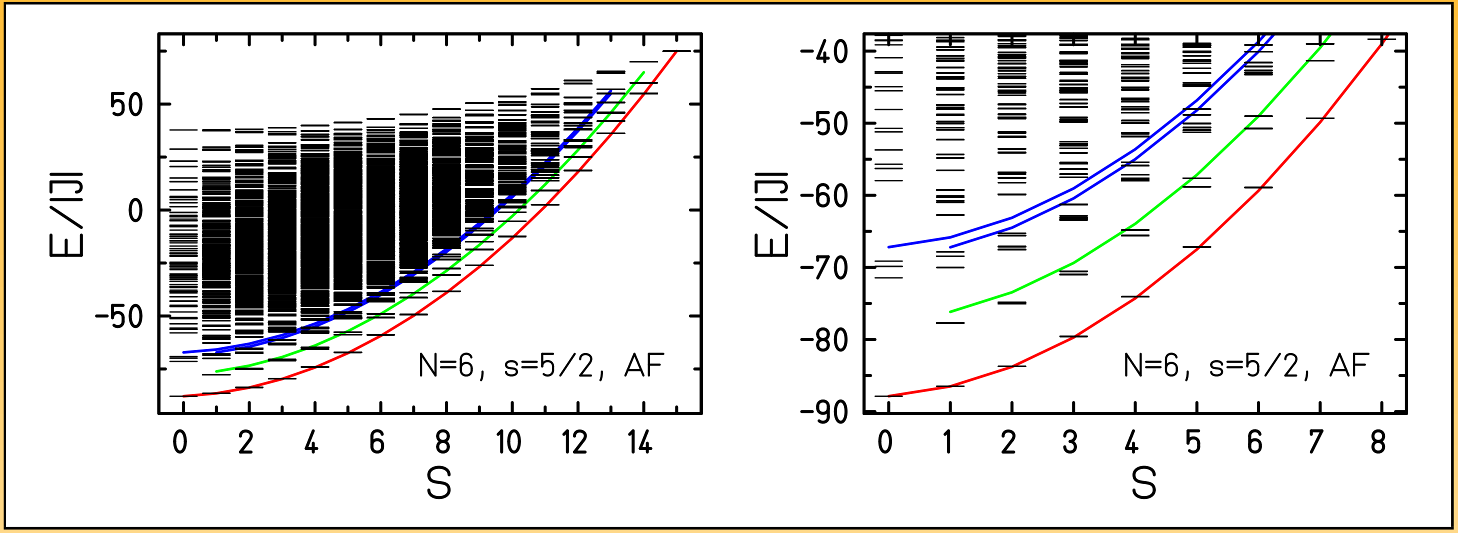
Heisenberg Zeeman

The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations.

$J < 0$: antiferromagnetic coupling.

Very often additional terms – dipolar, anisotropic – are utterly negligible. If needed they can be cast in the form $\sum_{i,j} \underset{\sim}{\vec{s}}(i) \cdot \mathbf{D}_{ij} \cdot \underset{\sim}{\vec{s}}(j)$.

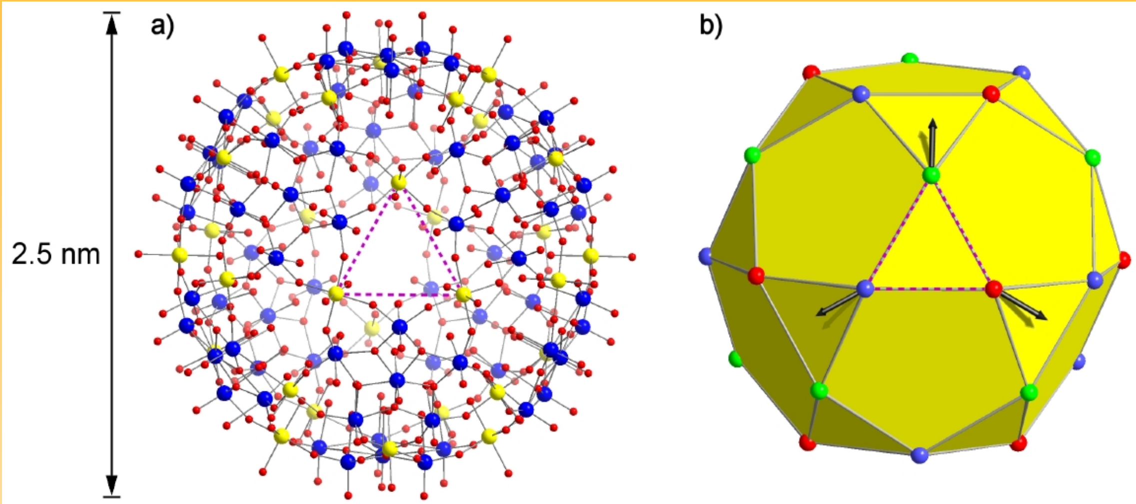
Rotational bands in antiferromagnets I



- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- Most pronounced for bipartite systems (2,3),
  might be a good approximation for more general systems;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(1) A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996), G. L. Abbati *et al.*, Inorg. Chim. Acta **297**, 291 (2000)
(2) J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2001)
(3) O. Waldmann, Phys. Rev. B **65**, 024424 (2002)
(4) P.W. Anderson, Phys. Rev. B **86**, 694 (1952), O. Waldmann *et al.*, Phys. Rev. Lett. **91**, 237202 (2003).

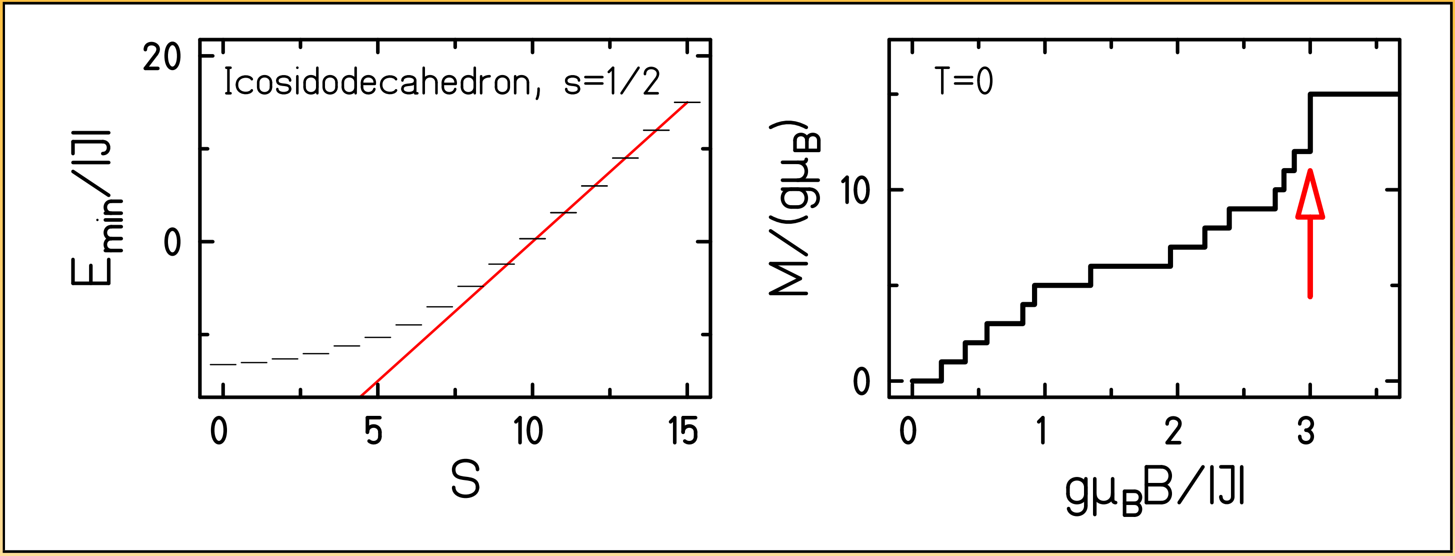
$\{Mo_{72}Fe_{30}\}$ – a molecular brother of the kagome lattice and an archetype of geometric frustration



- Giant magnetic Keplerate molecule;
- Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).
- Classical ground state of $\{Mo_{72}Fe_{30}\}$: three sublattice structure, coplanar spins (2);
- Quantum mechanical ground state $S = 0$ can only be approximated, e.g. by DMRG (3), dim. of Hilbert space $(2s + 1)^N \approx 10^{23}$.

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001) , (2) M. Axenovich and M. Luban, Phys. Rev. B **63**, 100407 (2001) , (3) M. Exler, J. Schnack, Phys. Rev. B **67**, 094440 (2003)

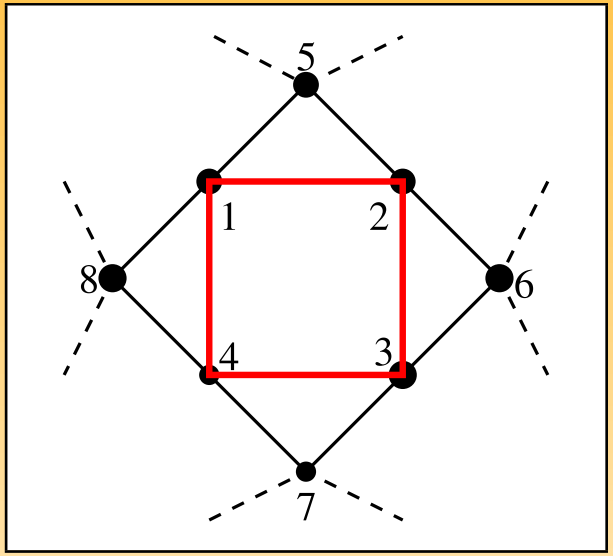
Giant magnetization jumps in frustrated antiferromagnets I Icosidodecahedron with $s = 1/2$



- Close look: $E_{\text{min}}(S)$ linear in S for high S instead of being quadratic (1);
- Heisenberg model: property depends only on the structure but not on s (2);
- Alternative formulation: independent localized magnons (3);

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)
(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)
(3) J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons

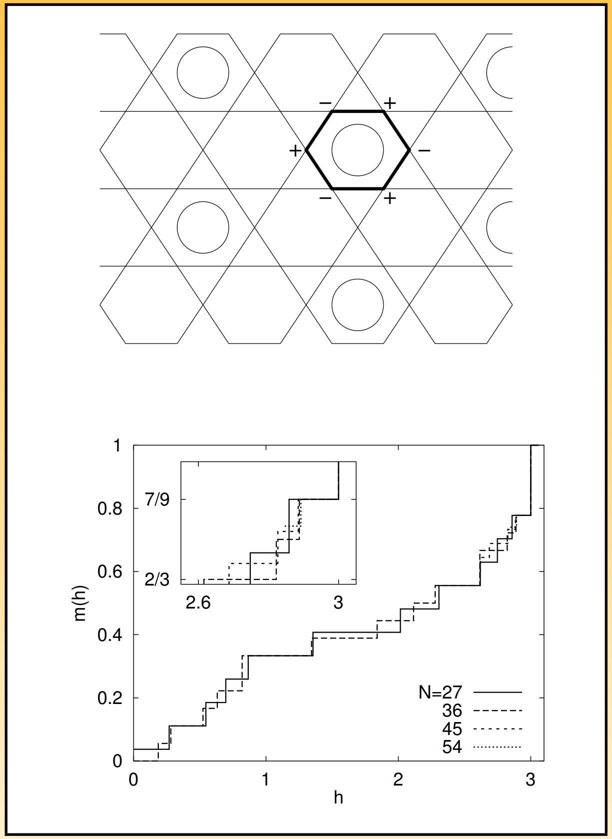


- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}\left(\,|\,1\,\rangle - \,|\,2\,\rangle + \,|\,3\,\rangle - \,|\,4\,\rangle\right)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ \dots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto \,|\,\text{localized magnon}\,\rangle$
- Localized magnon is state of lowest energy (1,2).

- Triangles trap the localized magnon, amplitudes cancel at outer vertices.

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)
(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)

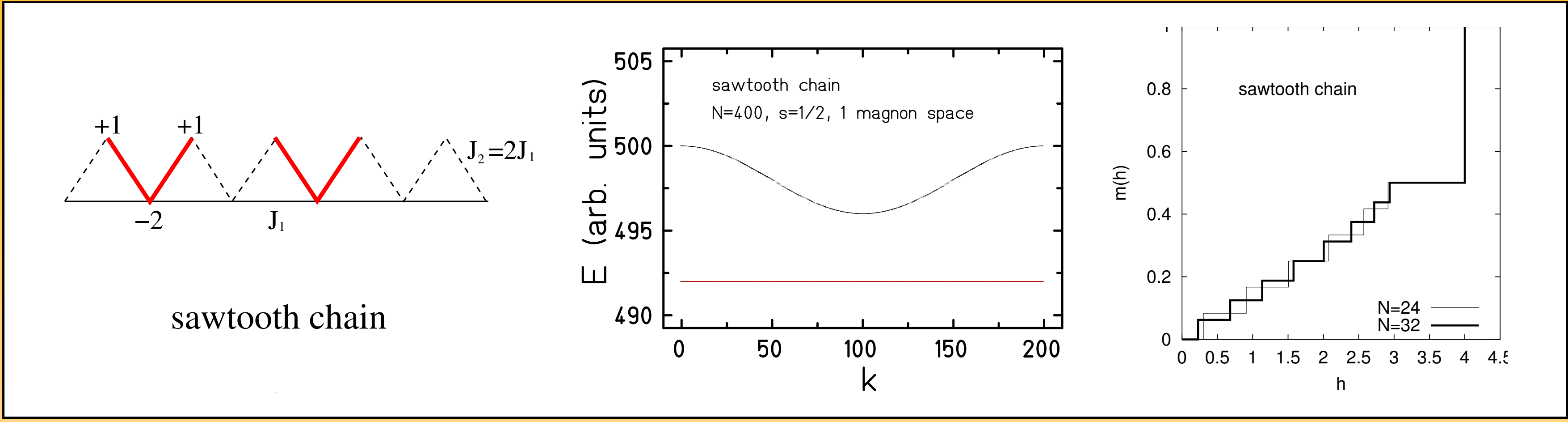
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$;
- Linear dependence of E_{min} on M
  $\Rightarrow$ magnetization jump;
- Maximal number of independent magnons: N/9;
- Jump is a macroscopic quantum effect!

J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
J. Richter, J. Schulenburg, A. Honecker, J. Schnack, H.-J. Schmidt, J. Phys.: Condens. Matter **16**, S779 (2004)

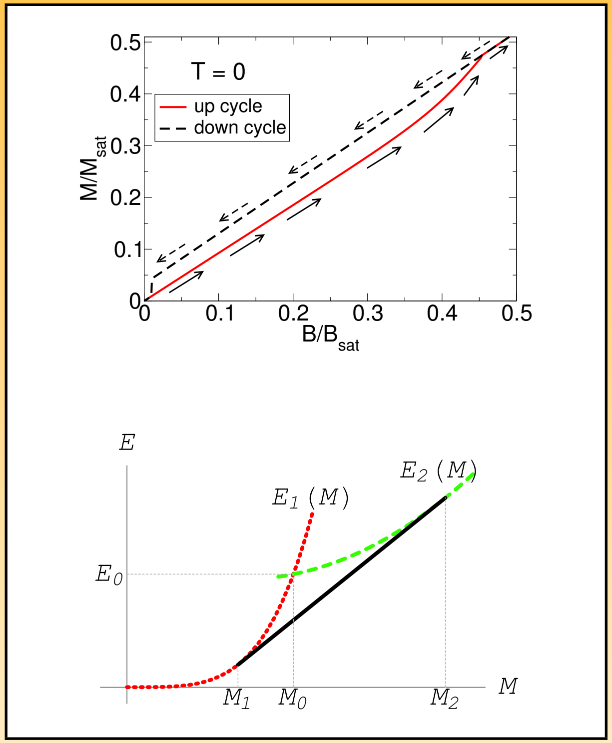
Condensed matter physics point of view: Flat band



- Flat band of minimal energy in one-magnon space, i. e. high degeneracy of ground state energy in $\mathcal{H}(M = Ns - 1)$;
- Localized magnons can be built from those eigenstates of the translation operator, that belong to the flat band;
- Sawtooth chain exceptional since degeneracy is $N/2$ (very high).

J. Richter, J. Schulenburg, A. Honecker, J. Schnack, H.-J. Schmidt, J. Phys.: Condens. Matter **16**, S779 (2004)

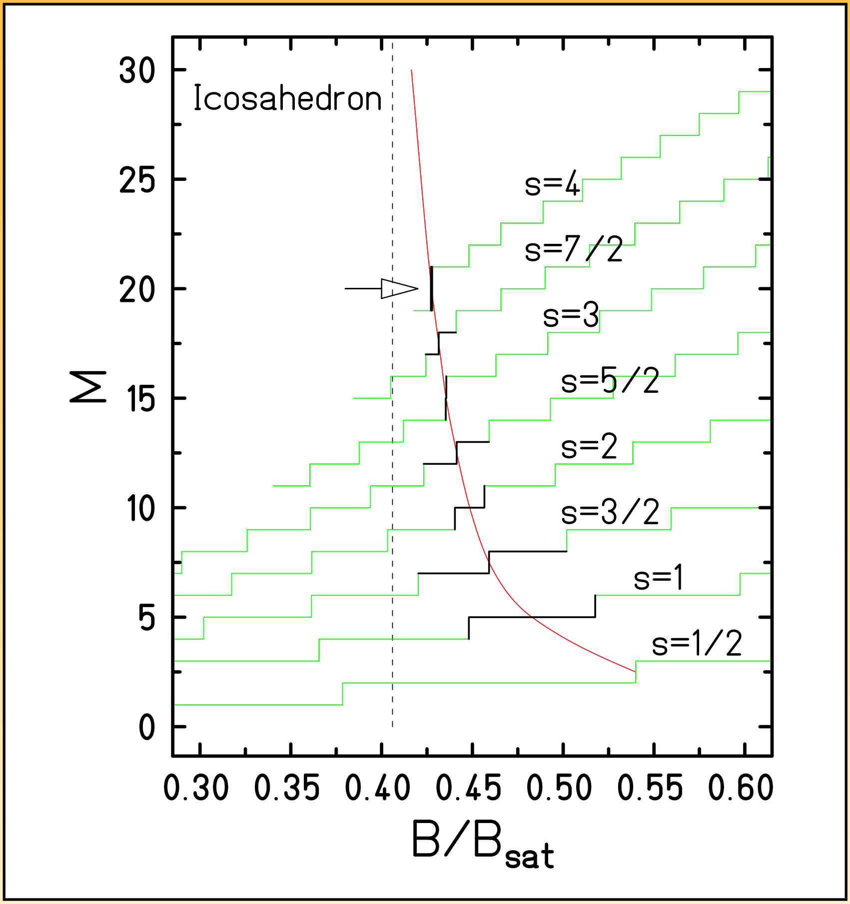
Metamagnetic phase transition I
Hyteresis without anisotropy



- Normally hysteretic behavior of Single Molecule Magnets is an outcome of magnetic anisotropy.
- The classical AF Heisenberg Icosahedron exhibits a pronounced hysteresis loop.
- It shows a first order phase transition at $T = 0$ as function of B.
- The minimal energies are realized by two families of spin configurations.
- The overall minimal energy curve is not convex $\Rightarrow$ magnetization jump.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)
D. Coffey and S.A. Trugman, Phys. Rev. Lett. **69**, 176 (1992).

Metamagnetic phase transition II

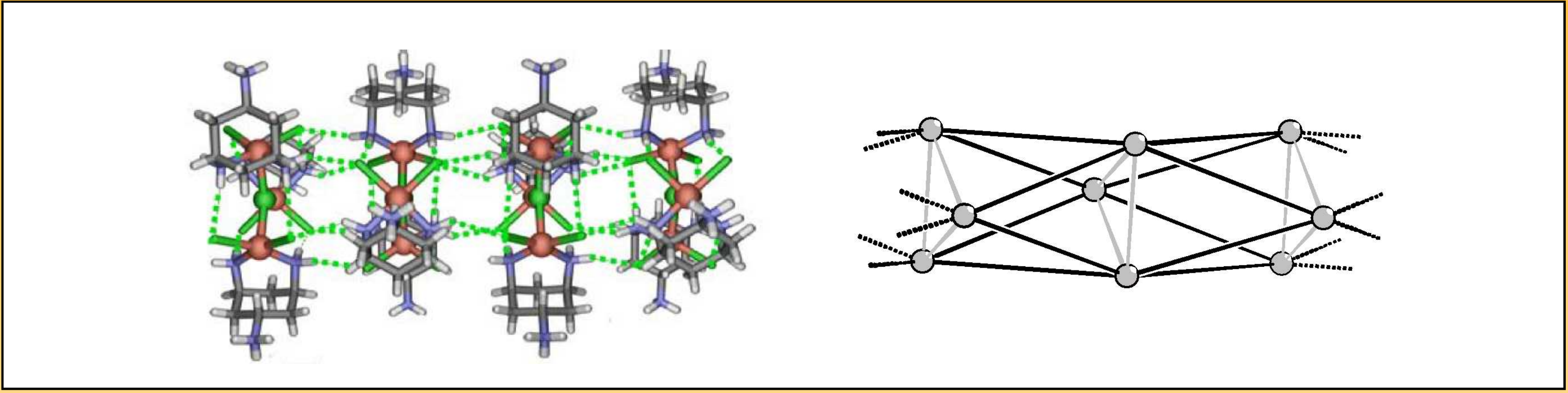


- Quantum analog:
  Non-convex minimal energy levels
  $\Rightarrow$ magnetization jump of $\Delta M > 1$.
- Lanczos diagonalization for various s.
- True jump of $\Delta M = 2$ for $s = 4$.
- Polynomial fit in $1/s$ yields the classically observed transition field.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)

no more time option

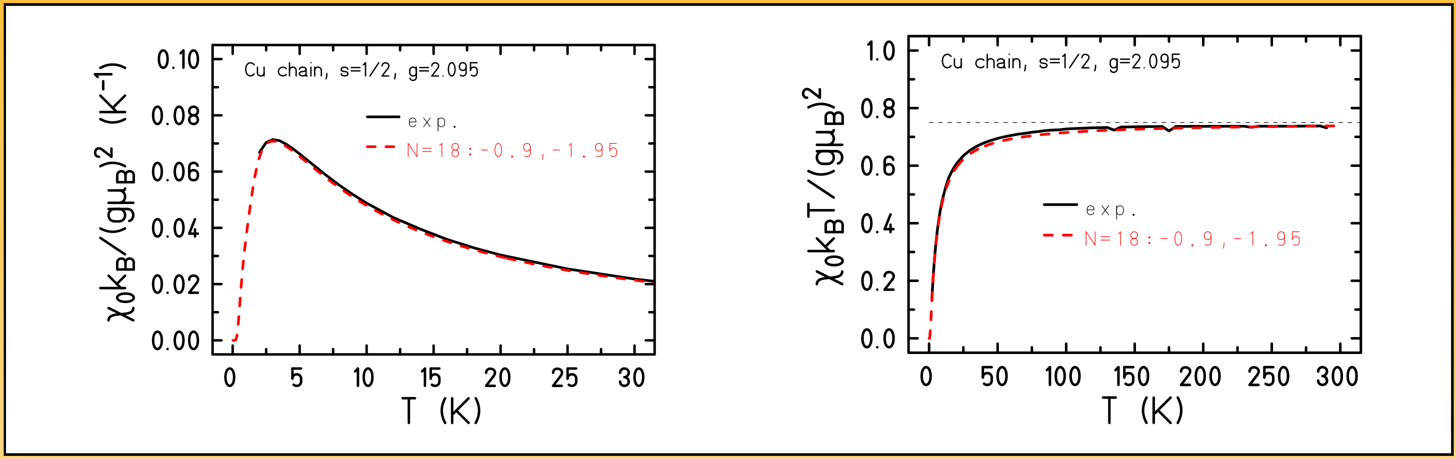
A frustrated triangular Cu chain



- $[(CuCl_2tachH)_3Cl]Cl_2$, tach $=$ *cis,trans*-1,3,5-triamino-cyclohexane (1)
- One-dimensional stack of antiprisms of af coupled equilateral copper(II) triangles: three-leg ladder with frustrated rung boundary condition.
- Intra-triangle couplings J_1 – grey lines, inter-triangle couplings J_2 – black lines.

(1) G. Seeber, P. Kögerler, B.M. Kariuki, and L. Cronin, Chem. Commun. (Cambridge) **2004**, 1580 (2004).

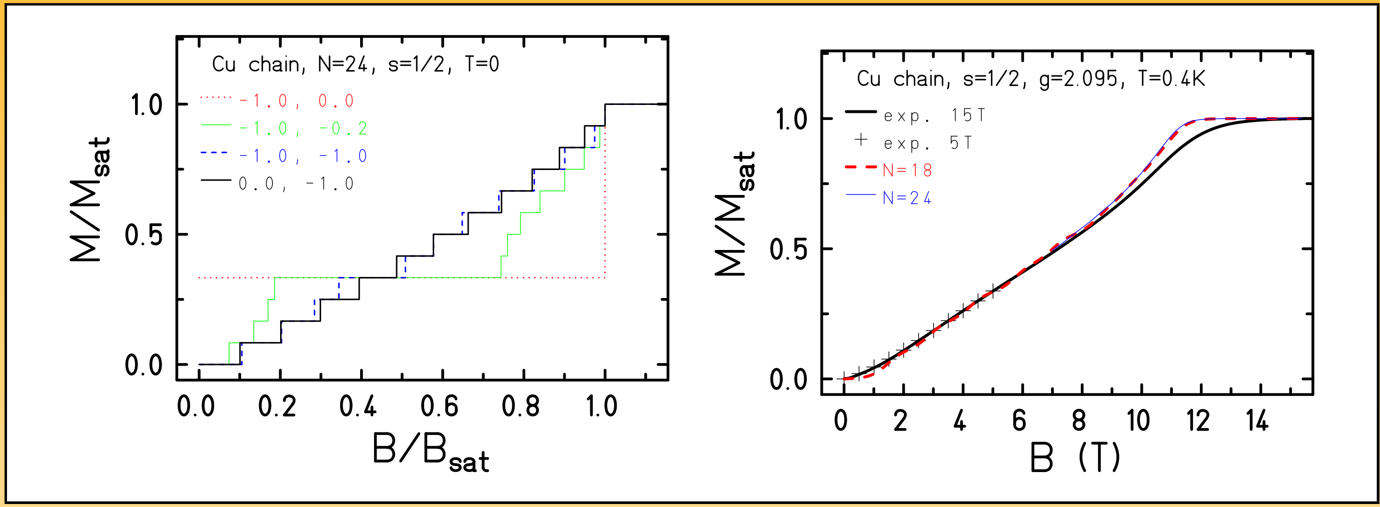
Triangular Cu chain: susceptibility



- Intra-triangle exchange J_1: bridging chloro ligand and hydrogen bonds; Cu-Cu distance is 4.46 Å.
- Inter-triangle exchange J_2: hydrogen-bonded Cu-Cl$\cdots$H-N-Cu super-exchange; Cu-Cu distance is 6.82 Å.
- Conjecture: weakly coupled triangles, i. e. $|J_2| \ll |J_1|$ $\Rightarrow$ independent triangles at high T; effective spin-$1/2$ chain at low T: wrong!

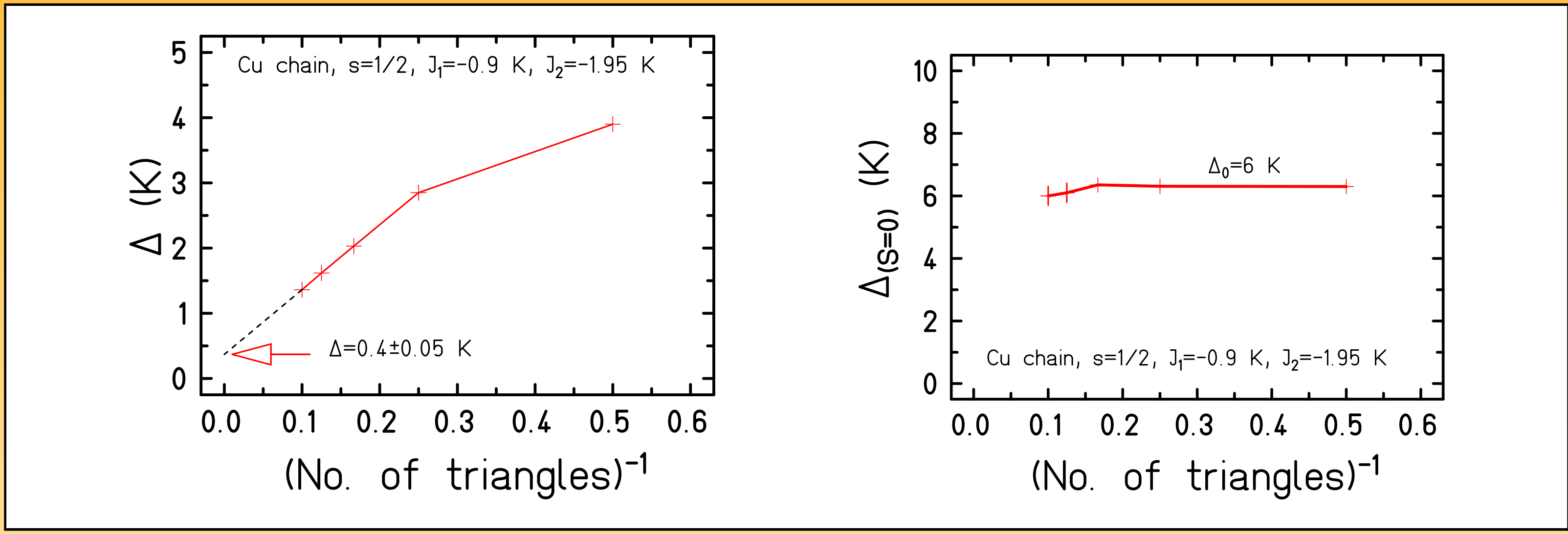
(1) J. Schnack, Hiroyuki Nojiri, P. Kögerler, G.J.T. Cooper, L. Cronin, Phys. Rev. B **70**, 174420 (2004)

Triangular Cu chain: magnetization



- Weakly coupled triangles: pronounced plateau at $1/3$ of the saturation magnetization. Magnetization measurement shows no plateau.
- Solution: isotropic Heisenberg model with antiferromagnetic exchange parameters $J_1 = -0.9$ K and $J_2 = -1.95$ K and $g = 2.095$ (average of small g-anisotropy).
- Deviations at high field: g-anisotropy and DM-interaction (?); deviations at low field: singlet-triplet gap overestimated in finite systems.

Triangular Cu chain: our gaps

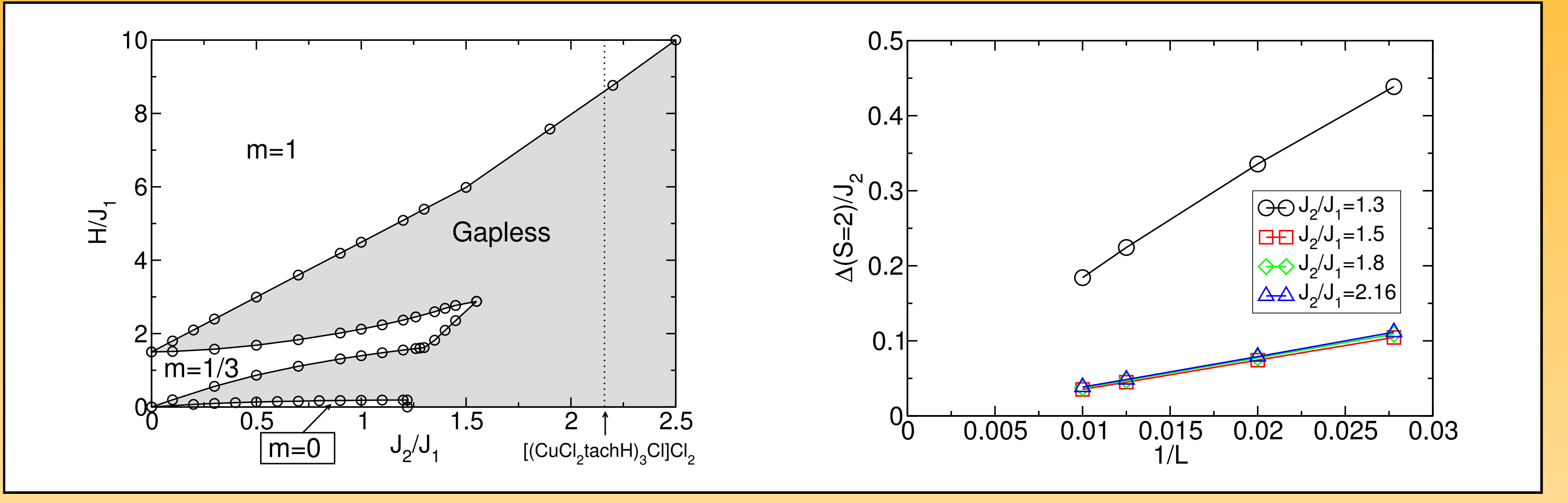


- Ground state non-degenerate (1),
  whereas should be twofold degenerate for weakly coupled triangles (2).

- Singlet-triplet gap $\Delta_{0-1} \gtrapprox 0.4$ K; singlet-singlet gap $\Delta_{0-0} \approx 6$ K

(1) J. Schnack, Hiroyuki Nojiri, P. Kögerler, G.J.T. Cooper, L. Cronin, Phys. Rev. B **70**, 174420 (2004)
(2) A. Lüscher, R. M. Noack, G. Misguich, V. N. Kotov, and F. Mila, Phys. Rev. B **70**, 060405(R) (2004)

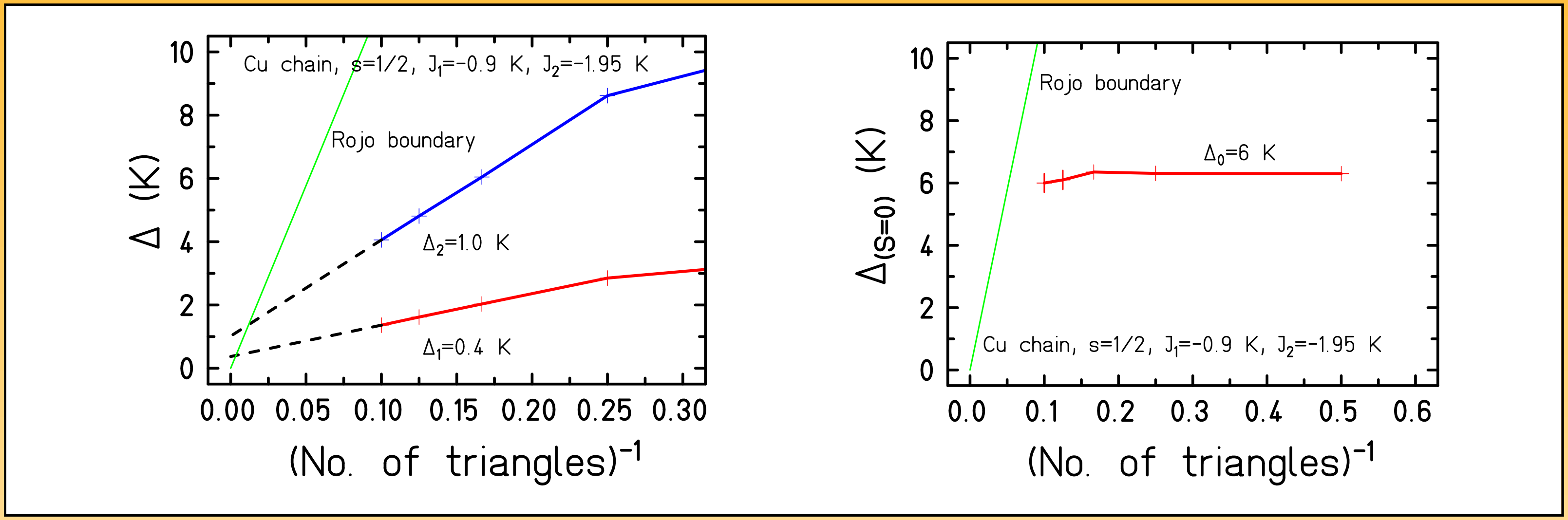
Triangular Cu chain: their gaps – no gaps!



- Chain can be mapped on either effective $s = 1/2$ chain with chirality for weak intertriangle coupling (degenerate ground state) or on a gapless effective $s = 3/2$ chain for strong intertriangle coupling (2). In addition, all three-lag ladders with half-integer spin are gapless or have a degenerate ground state (3)!

(1) J.-B. Fouet, A. Läuchli, S. Pilgram, R.M. Noack, F. Mila, cond-mat/0509217
(2) A. Lüscher, R.M. Noack, G. Misguich, V.N. Kotov, and F. Mila, Phys. Rev. B **70**, 060405(R) (2004)
(3) A.G. Rojo, Phys. Rev. B **53**, 9172 (1996)

Triangular Cu chain: our gaps II



- Finite size extrapolation problem?
- Rojo boundary (1) can be numerically tested for singlet-singlet gap $\Delta_{0-0} \approx 6$ K.
- Apart from the these poblems the real chain will be further investigated experimentally.

(1) A.G. Rojo, Phys. Rev. B **53**, 9172 (1996)

Summary

Geometric frustration of interacting spin systems is the driving force of a variety of fascinating phenomena in low-dimensional magnetism.

Therefore . . .

Frustrated or not frustrated

Frustrated, or not frustrated; that is the question:
Whether it's nobler in the mind to suffer
The difficulties and pain of competing interactions,
Or to take arms against the intractable antiferromagnets?
And by diagonalizing the Hamiltonian? To know;
No more; and to say we understand
The gaps, the plateaus, and the giant jumps

. . .

W.S., Hamlet, early version, about 1599

Thank you very much for your attention.

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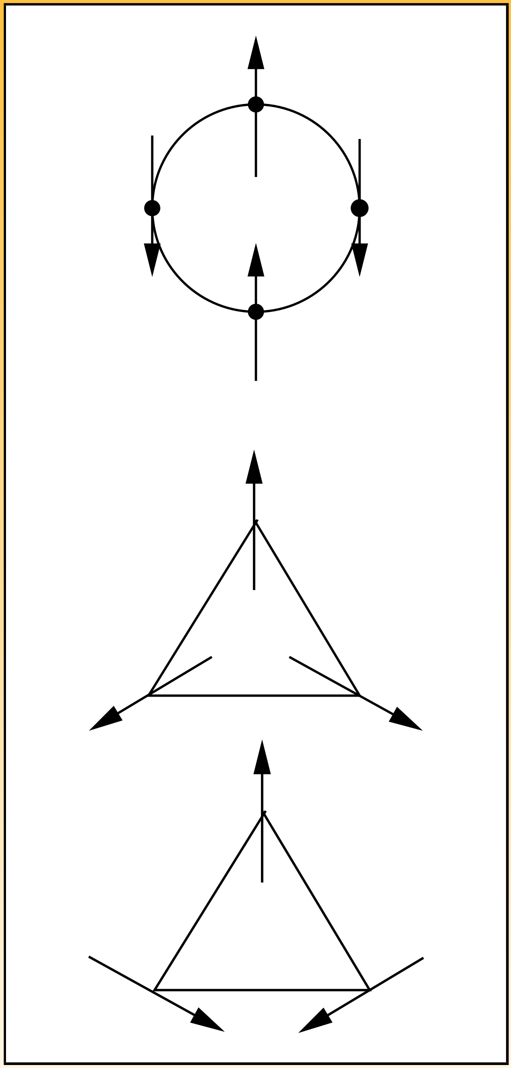
This was a great workshop.

Let’s thank the organizers!

It’s your turn, clap your hands.

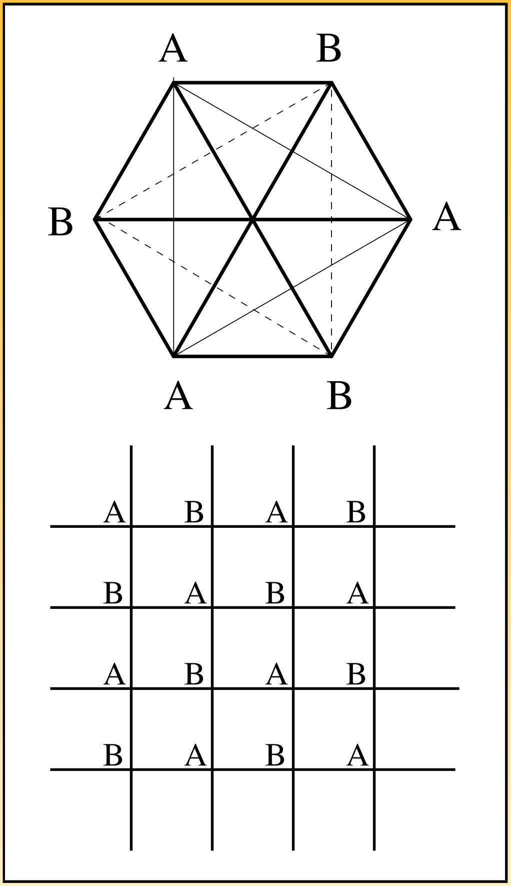
Appendix

Classical definition of frustration



- Definition: A quantum spin system is frustrated if the corresponding classical system is frustrated, i. e. if neighboring classical spins are not aligned antiparallel.
- Problem: Need to know the corresponding classical system.

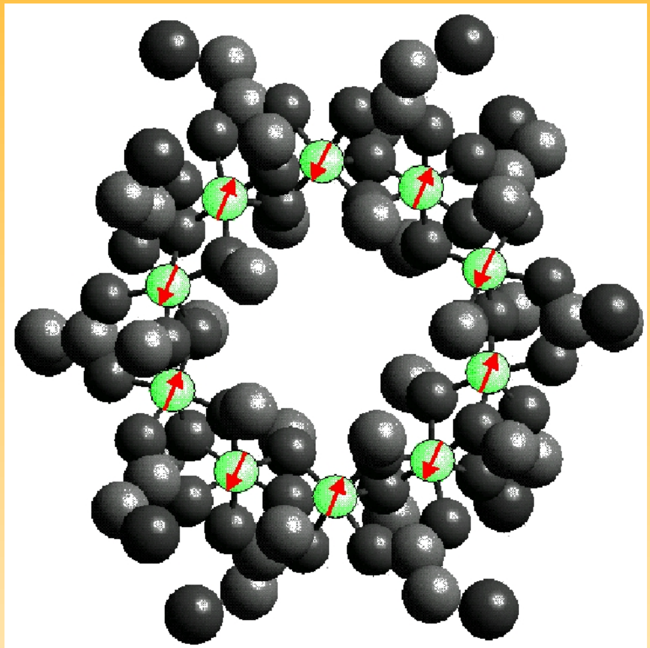
Advanced definition of frustration



- Definition: A non-bipartite system is called frustrated.
- Bipartite: If the system can be decomposed into subsystems A and B such that the coupling constants fulfil $J(x_A, y_B) \leq g^2$, $J(x_A, y_A) \geq g^2$, $J(x_B, y_B) \geq g^2$, the system is called bipartite (1,2).
- Simple bipartite cases: there are only antiferromagnetic interactions between spins of different sublattices.

(1) E.H. Lieb, T.D. Schultz, and D.C. Mattis, Ann. Phys. (N.Y.) **16**, 407 (1961)
(2) E.H. Lieb and D.C. Mattis, J. Math. Phys. **3**, 749 (1962)

Extension of Lieb, Schultz, and Mattis I
k–rule for even rings



Fe$_{10}$

- Goal: general properties of the magnetic spectrum depending on the structure, e.g. ground state quantum numbers.
- Properties of certain low-lying states known for bipartite spin systems (Marshall, Peierls, Lieb, Schultz, Mattis).
- For AF Heisenberg rings of even N thus the momentum quantum number k is known for relative ground states of subsapces $\mathcal{H}(M)$.

- Translational (shift) operator $\underset{\sim}{T}$ moves ring by one site: $\left[\underset{\sim}{H}, \underset{\sim}{T}\right] = 0$,
  Eigenvalues of $\underset{\sim}{T}$: $\exp\left\{-i2\pi k_\nu/N\right\}$, $k_\nu = 0, \dots, N-1$.

Extension of Lieb, Schultz, and Mattis II
k–rule for odd rings

- An extended k-rule can be inferred from numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings

$$\text{If } N \neq 3 \quad \text{then} \quad k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N \ , \quad a = Ns - M$$

		a									
N	s	0	1	2	3	4	5	6	7	8	9
8	1/2	0	4	$8 \equiv 0$	$12 \equiv 4$	$16 \equiv 0$	-	-	-	-	-
9	1/2	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	-	-	-	-	-
9	1	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

K. Fabricius, U. Löw, K.-H. Mütter, and P. Ueberholz, Phys. Rev. B **44**, 7476 (1991)
M. Karbach, Ph. D. thesis, Universität Wuppertal (1994)
K. Bärwinkel, H.-J. Schmidt, and J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
J. Schnack, Phys. Rev. B **62**, 14855 (2000)
K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)