

Frustration-induced exotic properties of magnetic molecules

Jürgen Schnack

Department of Physics – University of Osnabrück – Germany

<http://obelix.physik.uni-osnabueck.de/~schnack/>

Spin- and charge-correlations in molecule-based materials
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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);
- M. Luban, P. Kögerler, D. Vaknin (Ames Lab, Iowa, USA);
J. Musfeldt (U. of Tennessee, USA);
- 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. Tenant (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 taught 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

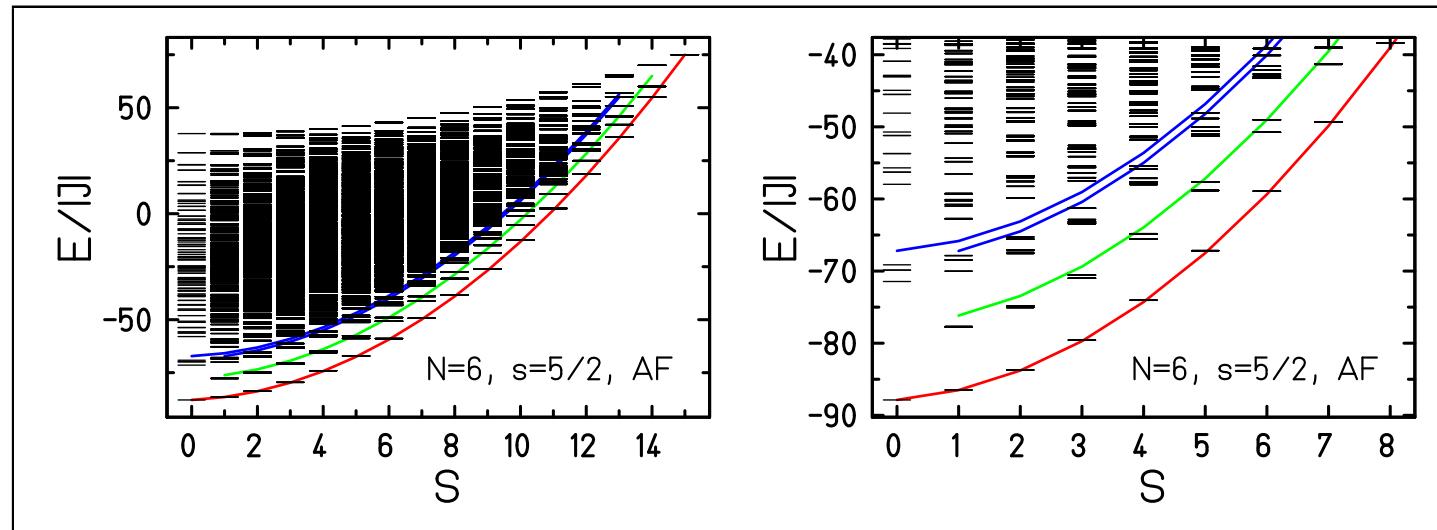
Model Hamiltonian – Heisenberg-Model

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 $\sum_{i,j} \vec{s}(i) \cdot \mathbf{D}_{ij} \cdot \vec{s}(j)$.

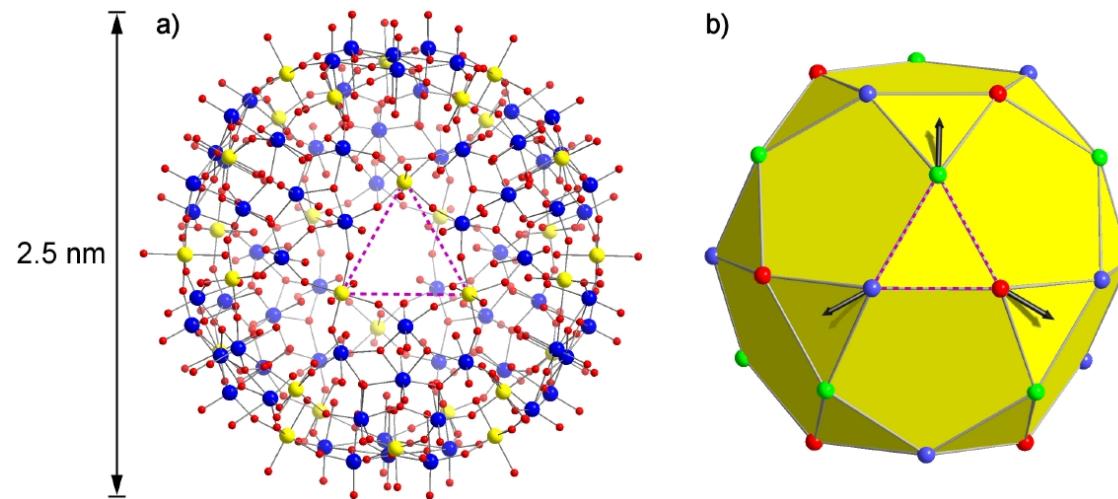
Rotational bands in antiferromagnets I



- 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).

{Mo₇₂Fe₃₀} – a molecular brother of the kagome lattice and an archetype of geometric frustration

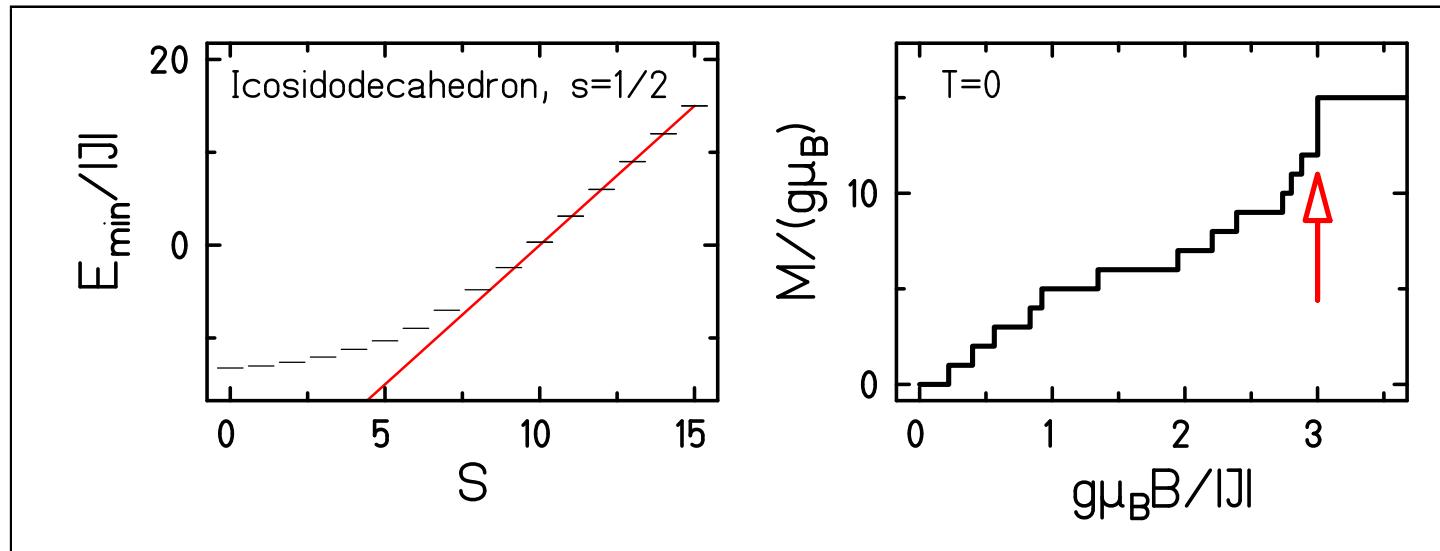


- Giant magnetic Keplerate molecule;
- Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).
- Classical ground state of {Mo₇₂Fe₃₀} : three sublattice structure, coplanar spins (2);
- Quantum mechanical ground state $S = 0$ can only be approximated, e.g. by 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: $E_{\min}(S)$ 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);

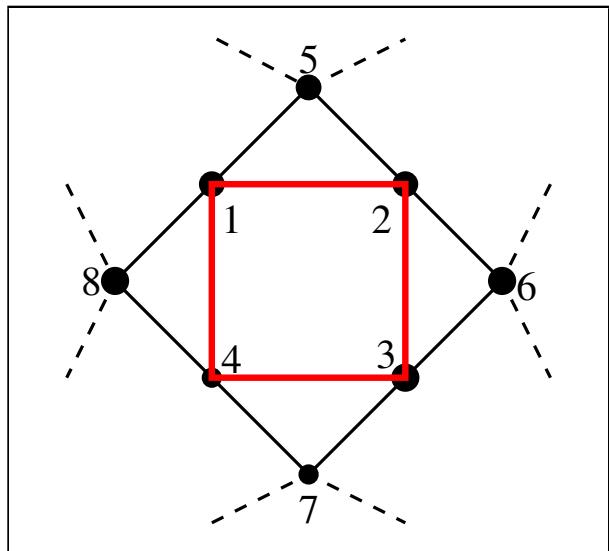
(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

(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

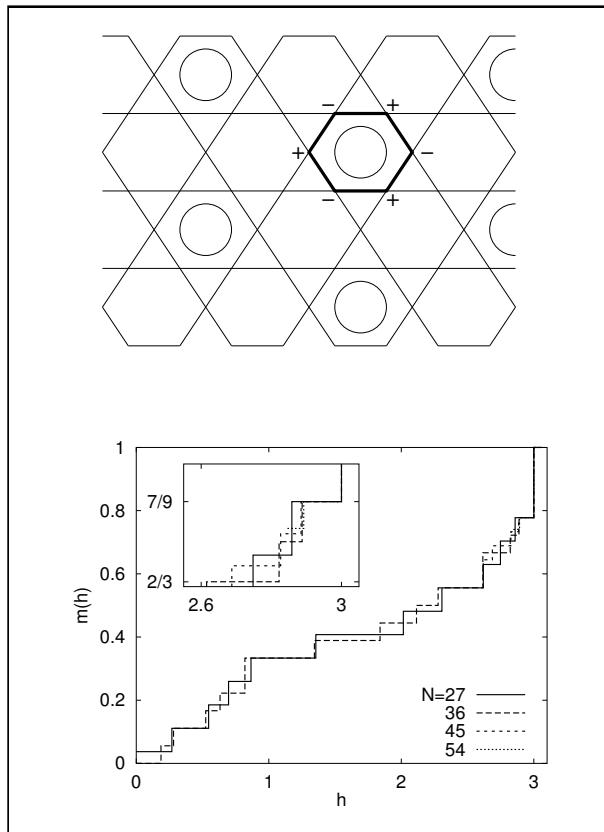
Localized Magnons



- $|\text{localized magnon}\rangle = \frac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle)$
- $|1\rangle = \tilde{s}^-(1)|\uparrow\uparrow\uparrow\dots\rangle$ etc.
- $\tilde{H}|\text{localized magnon}\rangle \propto |\text{localized magnon}\rangle$
- 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)

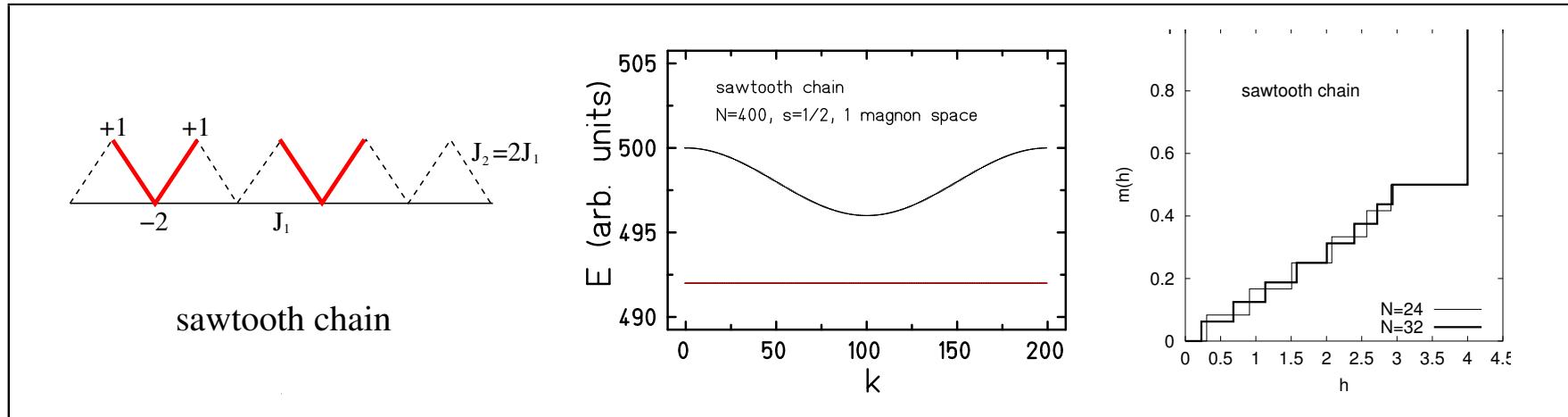
Giant magnetization jumps in frustrated antiferromagnets III Kagome Lattice



- 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
⇒ 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

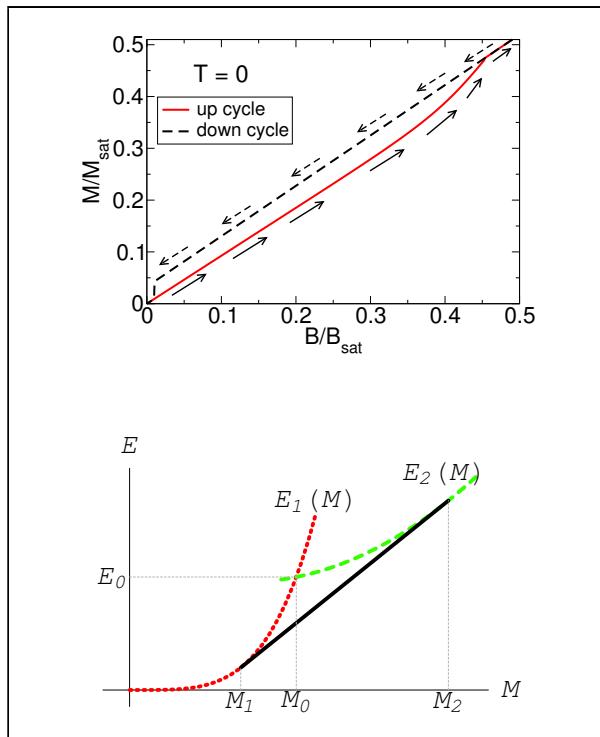


- Flat band of minimal energy in one-magnon space, i. e. high degeneracy of ground state energy in $\mathcal{H}(M = Ns - 1)$;
- Localized magnons can be built from those eigenstates of the translation operator, that belong to the flat band;
- Sawtooth chain exceptional since degeneracy is $N/2$ (very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

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

Metamagnetic phase transition I

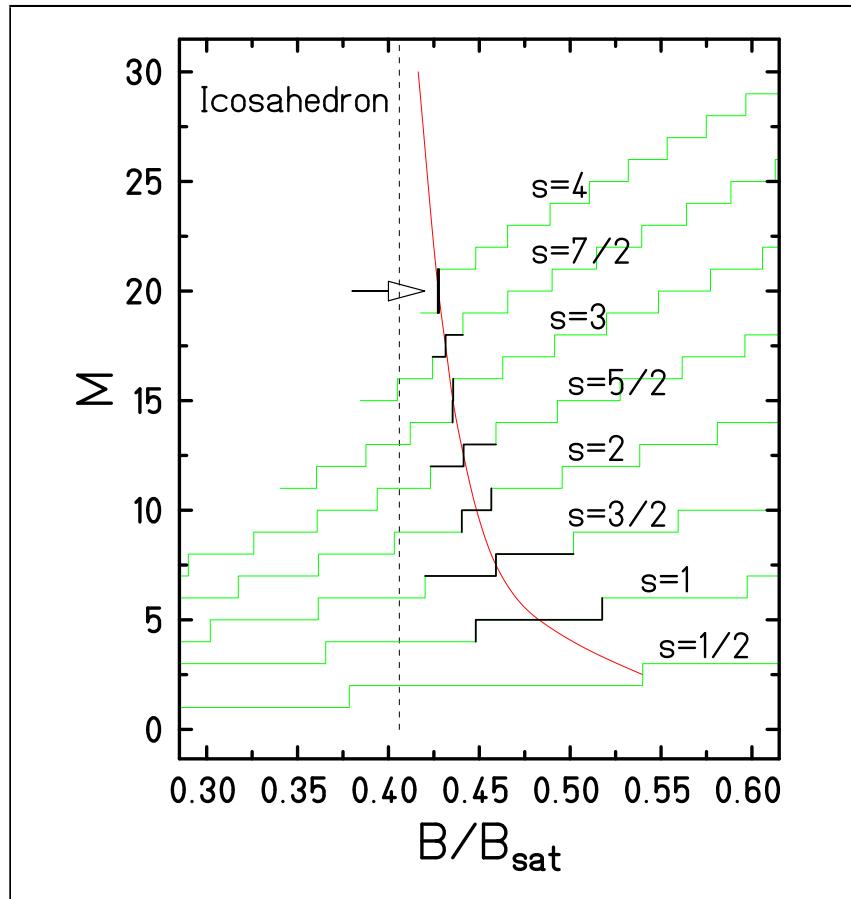
Hysteresis without anisotropy



- 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

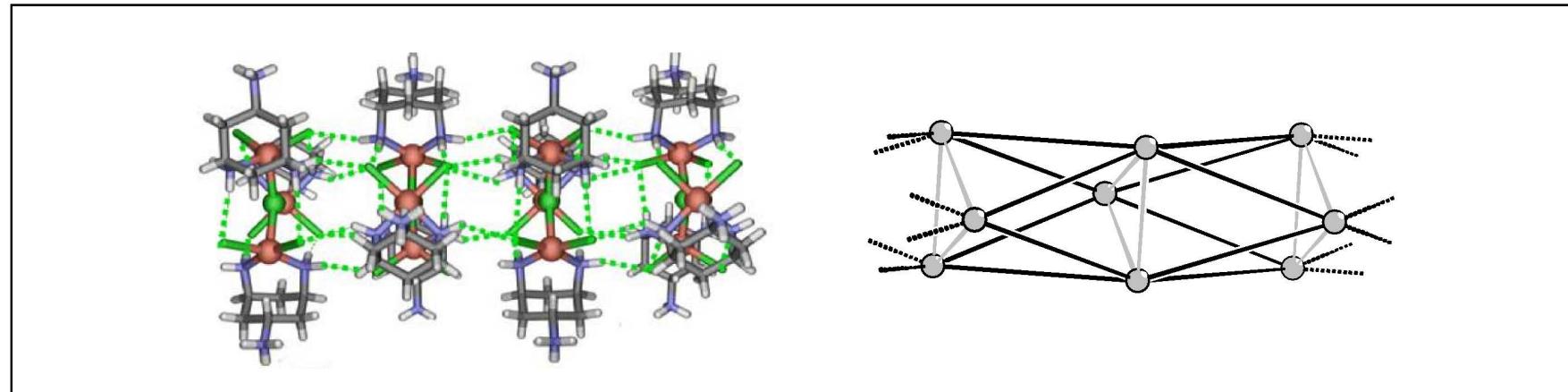


- Quantum analog:
Non-convex minimal energy levels
⇒ magnetization jump of $\Delta M > 1$.
- Lanczos diagonalization for various s .
- True jump of $\Delta M = 2$ for $s = 4$.
- Polynomial fit in $1/s$ yields the classically observed transition field.

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

no more time option

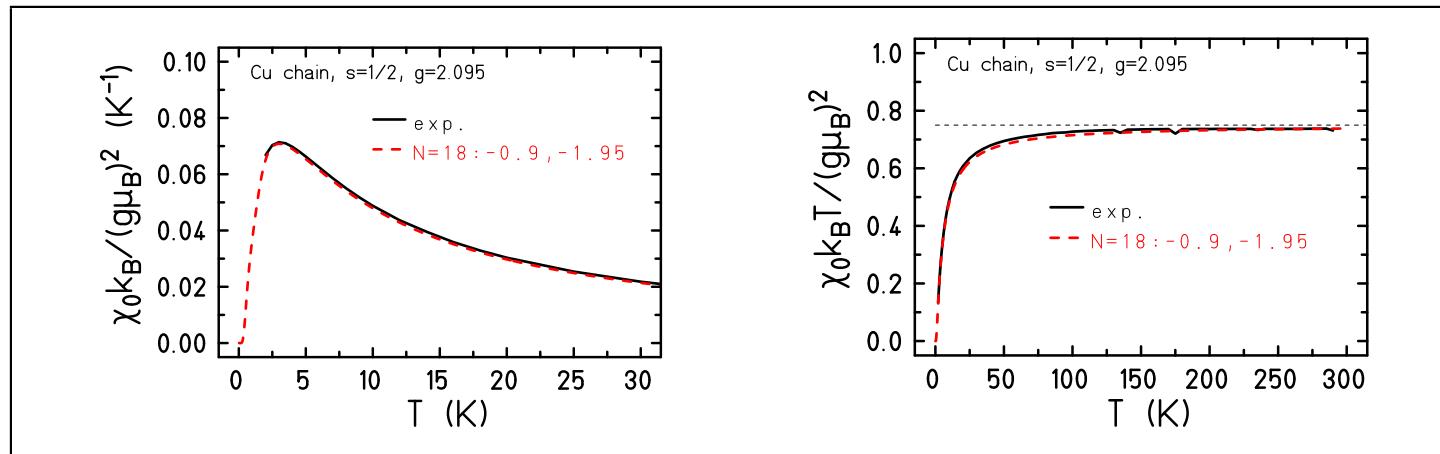
A frustrated triangular Cu chain



- $[(\text{CuCl}_2\text{tachH})_3\text{Cl}]\text{Cl}_2$, 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).

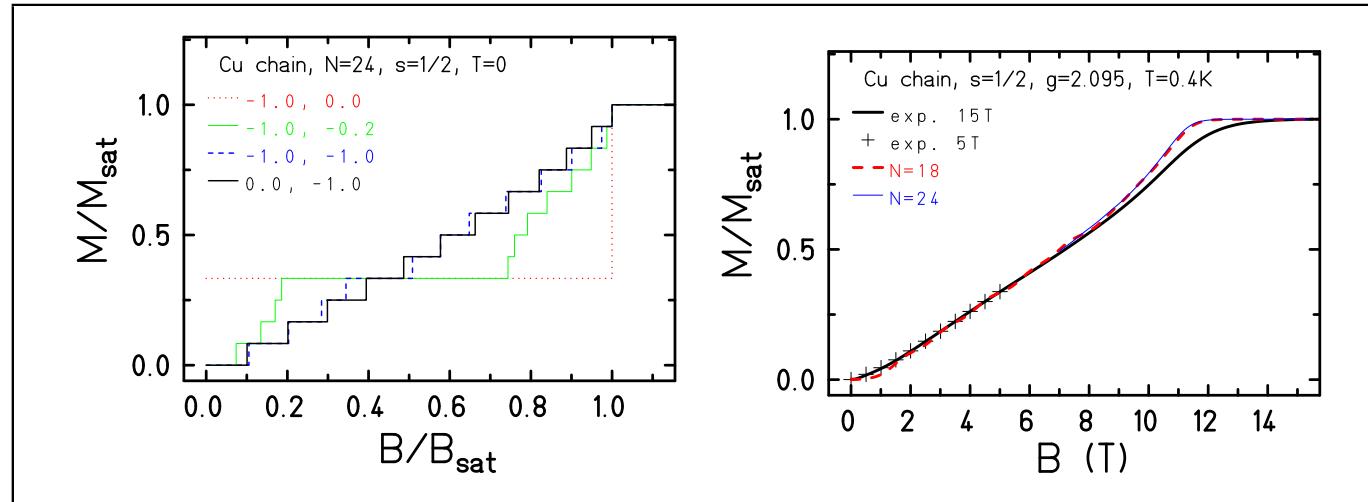
Triangular Cu chain: susceptibility



- 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!**

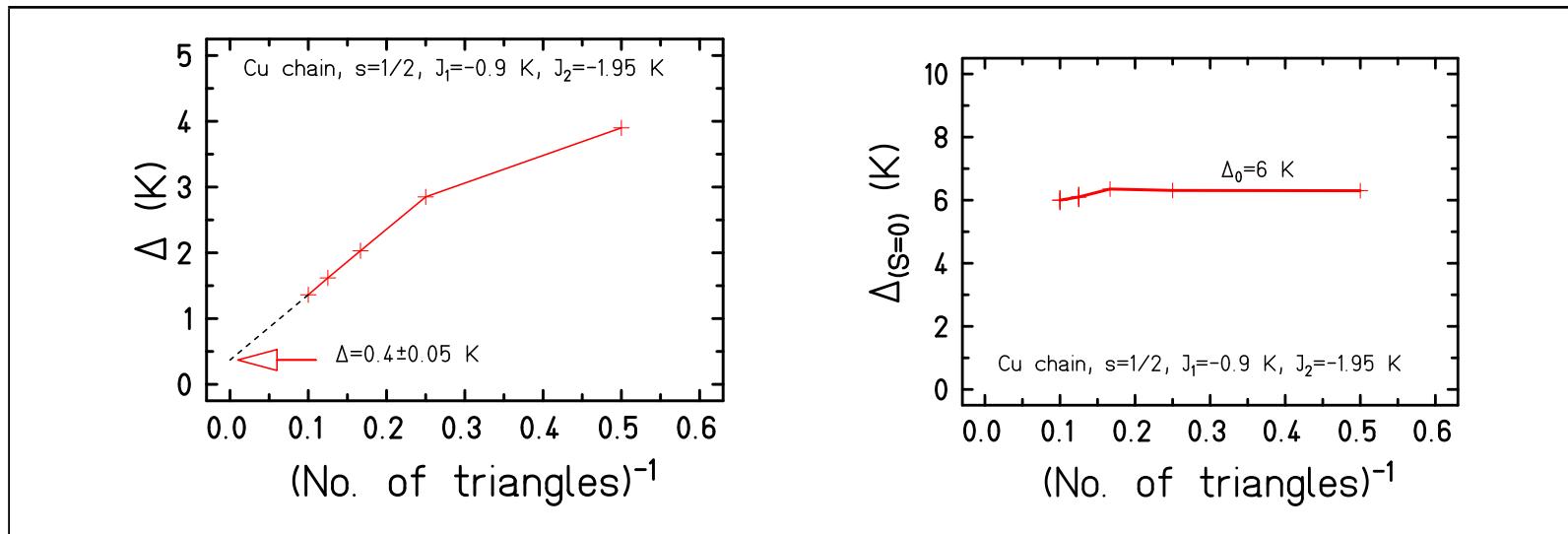
(1) J. Schnack, Hiroyuki Nojiri, P. Kögerler, G.J.T. Cooper, L. Cronin, Phys. Rev. B **70**, 174420 (2004)

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.

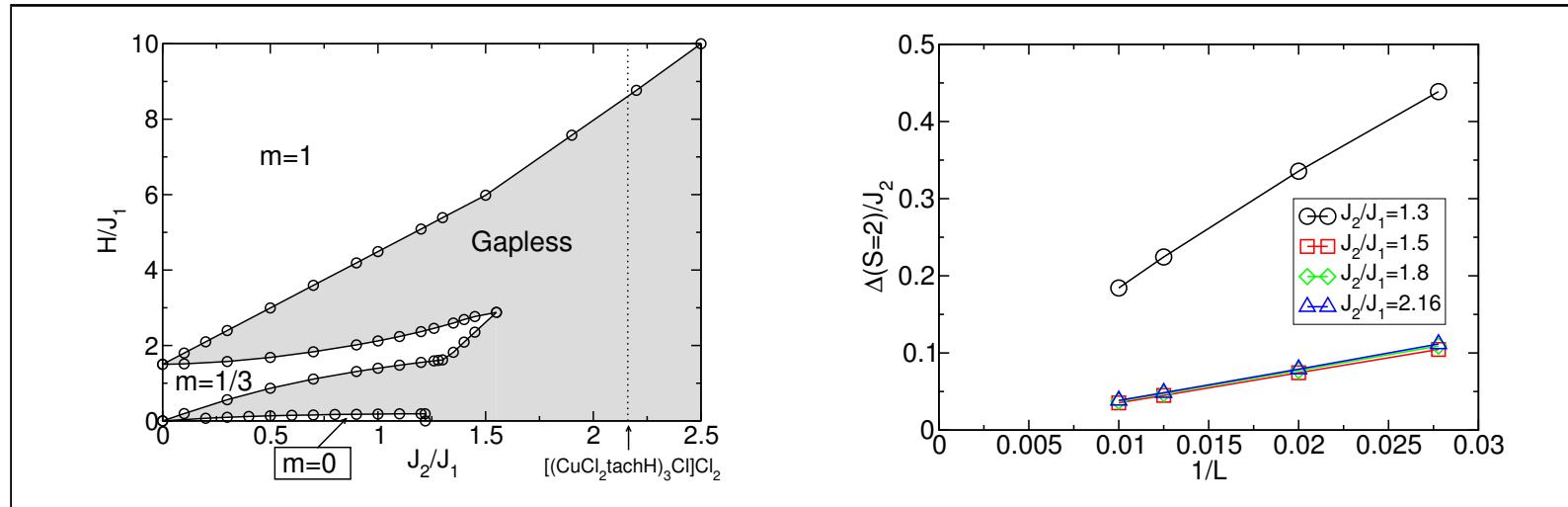
Triangular Cu chain: **our** gaps



- Ground state non-degenerate (1), whereas should be twofold degenerate for weakly coupled triangles (2).
- Singlet-triplet gap $\Delta_{0-1} \gtrsim 0.4$ 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!



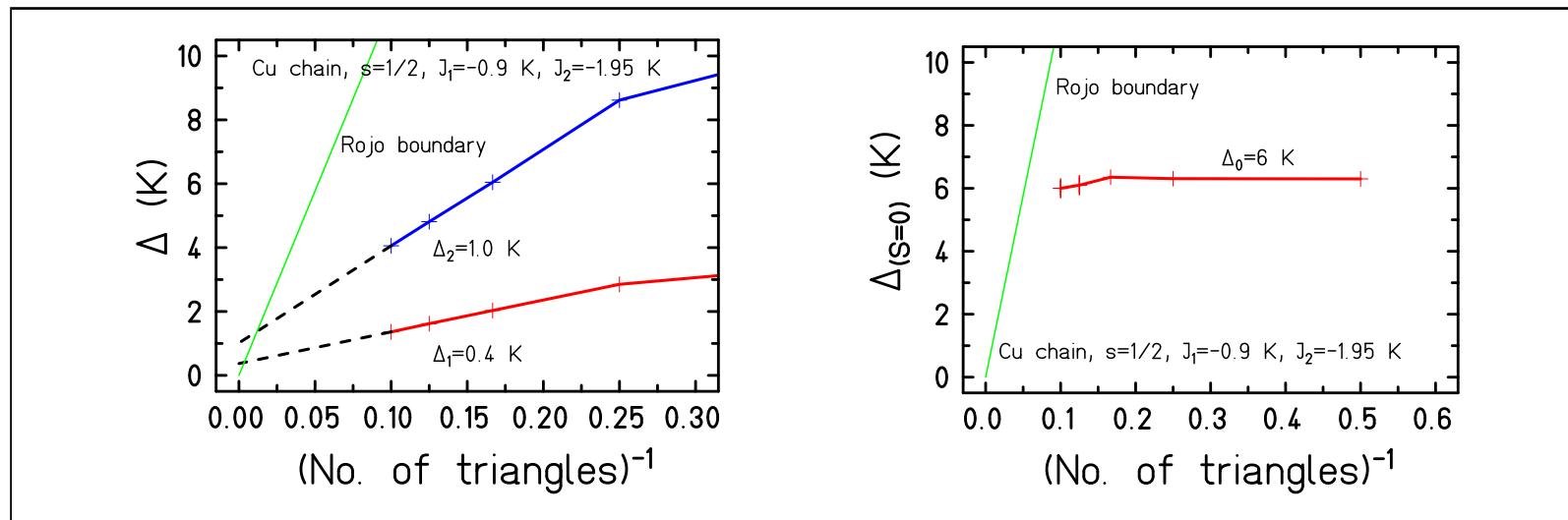
- Chain can be mapped on either effective $s = 1/2$ chain with chirality for weak intertriangle coupling (degenerate ground state) or on a gapless effective $s = 3/2$ chain for strong intertriangle coupling (2). In addition, all three-lag ladders with half-integer spin are gapless or have a degenerate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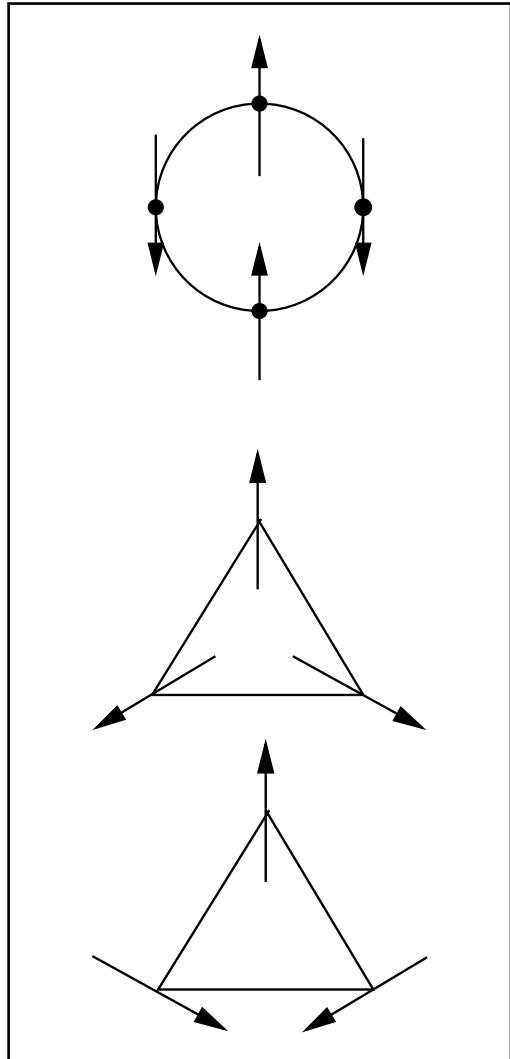
This was a great workshop.

Let's thank the organizers!

It's your turn, clap your hands.

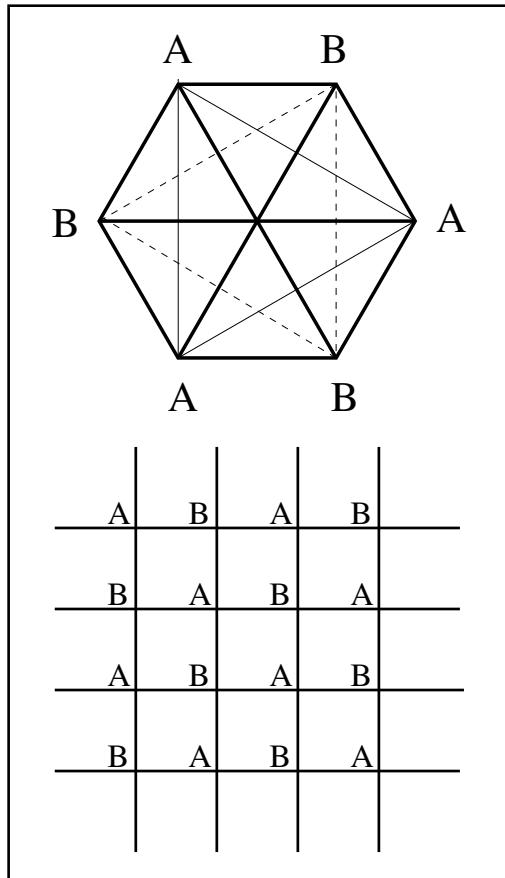
Appendix

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

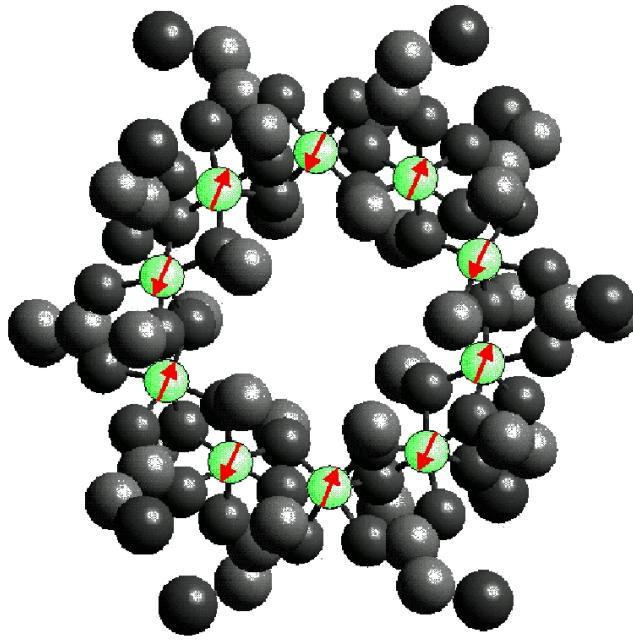


- Definition: A non-bipartite system is called frustrated.
- Bipartite: If the system can be decomposed into subsystems A and B such that the coupling constants fulfil $J(x_A, y_B) \leq g^2$, $J(x_A, y_A) \geq g^2$, $J(x_B, y_B) \geq g^2$, the system is called bipartite (1,2).
- Simple bipartite cases: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

Fe₁₀

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

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

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

N	s	a									
		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. Müller, 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)