The end is (not) in sight: exact diagonalization, Lanczos, and DMRG

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http://www.physik.uni-osnabrueck.de/makrosysteme/

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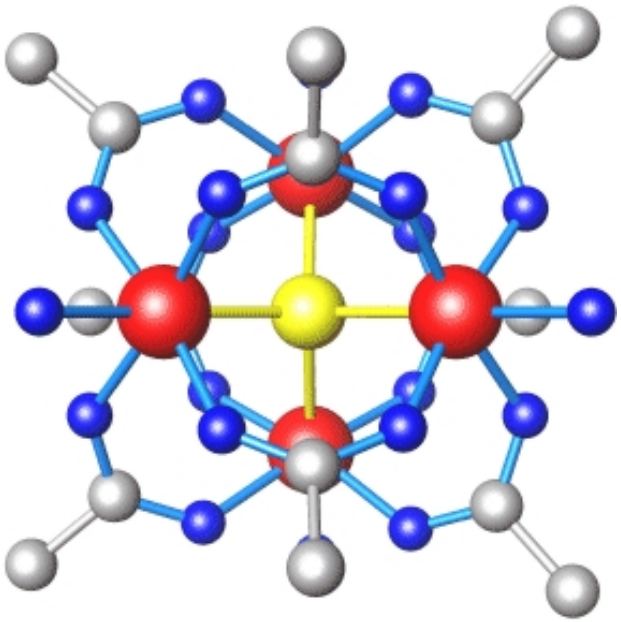
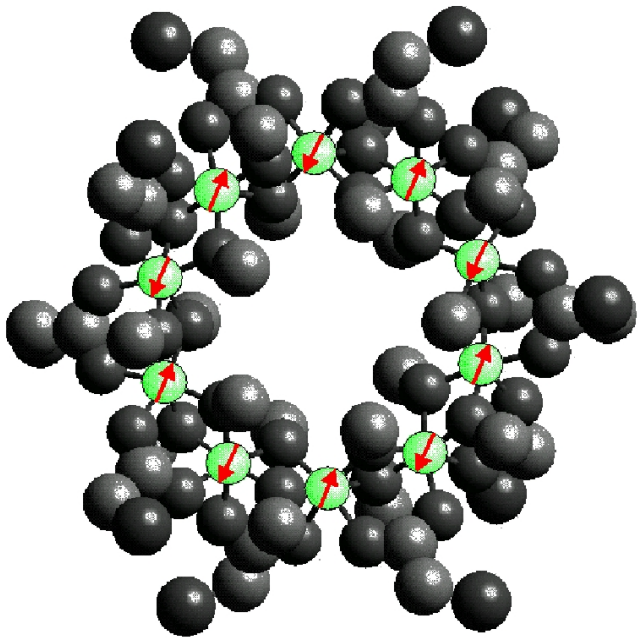
What are magnetic molecules?



Cr_4

- macro molecules (polyoxometalates etc.): consist of constituents like Hydrogen (H), Carbon (C), Oxygen (O), and diamagnetic ions (e.g. Mo) as well as paramagnetic ions like Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni) or Manganese (Mn);
- pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- single spin quantum number $1/2 \leq s \leq 7/2$;
- intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

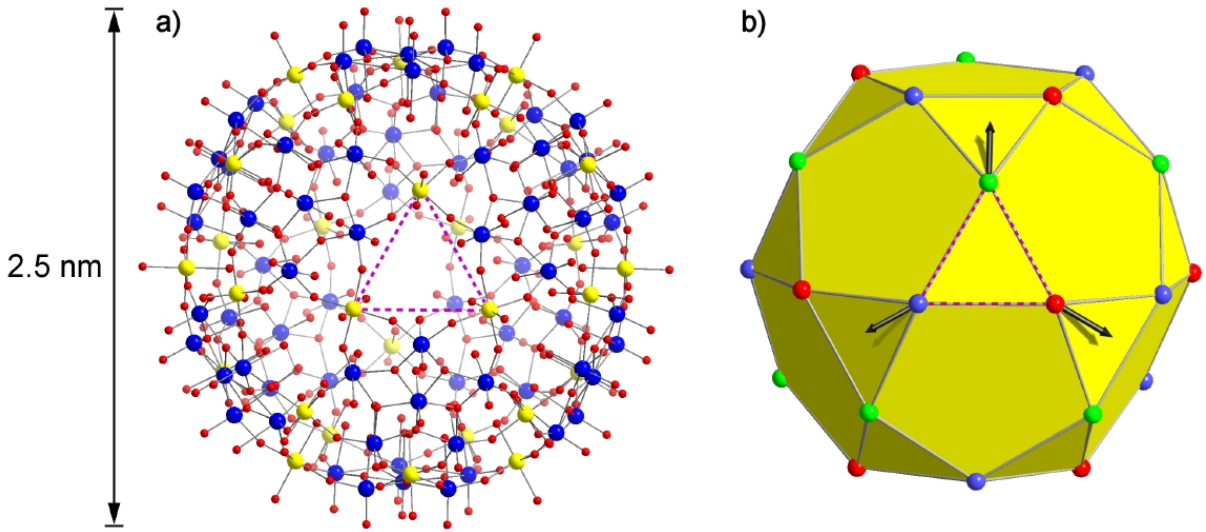
Structure of magnetic molecules



Fe_{10}

- dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, ...);
- complex structures (Mn_{12}) – drosophila of molecular magnetism;
- soccer balls, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- chain like and planar structures of interlinked magnetic molecules.

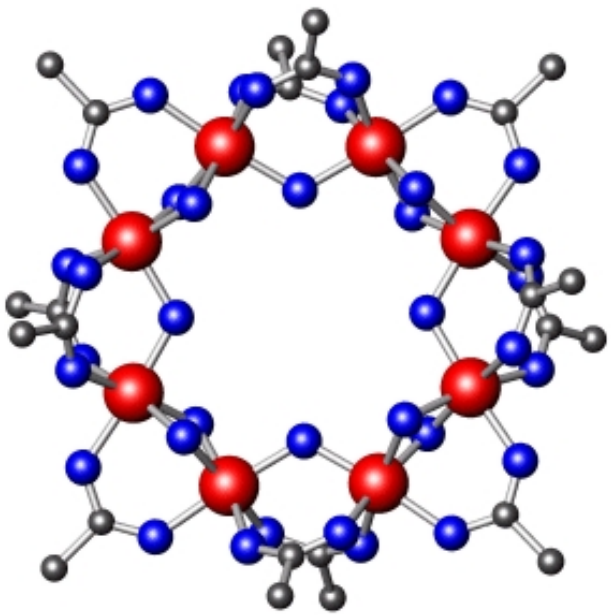
Example of magnetic macro molecules $\{Mo_{72}Fe_{30}\}$



- structure of $\{Mo_{72}Fe_{30}\}$: 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, dimension 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)

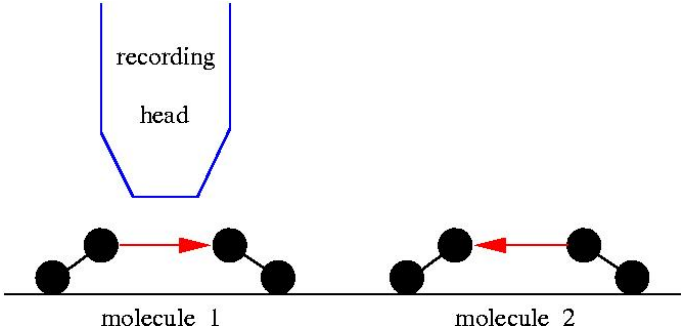
Why study magnetic molecules?

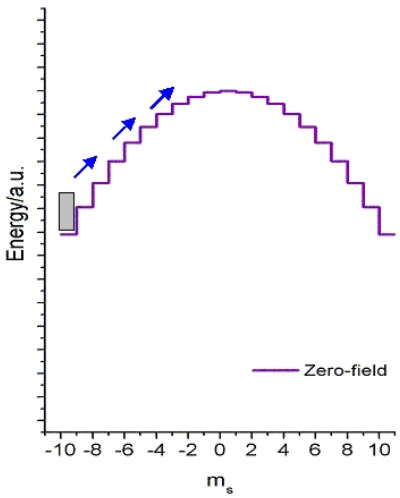


Cr_8

- transition few-spin system $\Rightarrow$ many-spin system, contribution to understanding of bulk magnetism;
- transition quantum spin system $(s = 1/2)$ $\Rightarrow$ classical spin system (Fe: $s = 5/2$, Gd: $s = 7/2$);
- easy to produce, single crystals with $> 10^{17}$ identical molecules can be synthesized and practically completely characterized;
- speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.

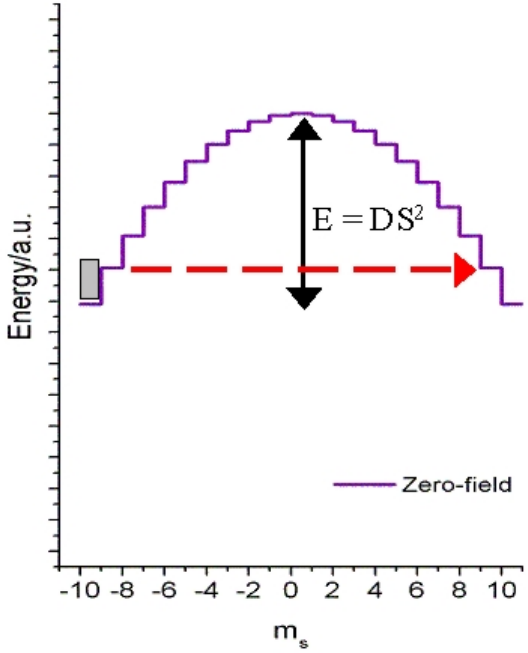
Magnetic molecules as storage media?





- Single Molecule Magnet (SMM): magnetic molecule with high ground state spin and hysteresis (usually due to large anisotropy);
- every molecule is a domain of its own; very weak intermolecular interactions; high density and nevertheless good separation of magnetic moments;
- high ground state spin possible, e.g. $S = 10$ for Mn_{12};
- theoretically possible storage density: **40 Tbits per square inch**, today: 20 Gbits per square inch (IBM), 300GB per square inch (Fujitsu 05/2002)

Magnetic molecules as storage media?



Disadvantages:

- magnetization tunneling – stabilisation by appropriate substrate?
  Prof. Blügel, Osnabrück/Jülich,
  http://www.flapw.de
- often very small coupling ($J \approx 10$ K), i.e. thermally unstable at room temperature;
- recording head must be very small and needs precise guide.

http://www.people.man.ac.uk/∼mbdssrew/winpeny_intro3.html

Model Hamiltonian – Heisenberg-Model

$$\underset{\sim}{H} = -\sum_{i,j} J_{ij} \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j)$$

The Heisenberg model, sometime augmented with anisotropy and dipol-dipol interaction terms as well as a Zeeman term, describes the magnetic spectrum of many molecules with high accuracy, although its derivation by means of *ab initio* calculations (DFT?) remains a challenge.

In the following we will only consider system with $s(i) = s \forall i$. Since the dimension of Hilbert space equals $(2s+1)^N$ the Hamiltonian can be diagonalized completely for small molecules. For larger ones approximate methods are used.

Dimension of the problem

Product basis, total dimension: $\dim(\mathcal{H}) = (2s+1)^N$

$$\underset{\sim}{s}_z(u)\,|\,m_1,\ldots,m_u,\ldots,m_N\,\rangle = m_u\,|\,m_1,\ldots,m_u,\ldots,m_N\,\rangle$$

These states span the Hilbert space and are used to construct symmetry-related basis states.

Symmetries of the Heisenberg model

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

Additional (point group) symmetries are possible.

Decomposition into mutually orthogonal subspaces

Hilbert space $\mathcal{H}$ can be decomposed into mutually orthogonal subspaces $\mathcal{H}(M)$ with $M = \sum_u m_u$ (M is the quantum number belonging to $\underset{\sim}{S}_z$)

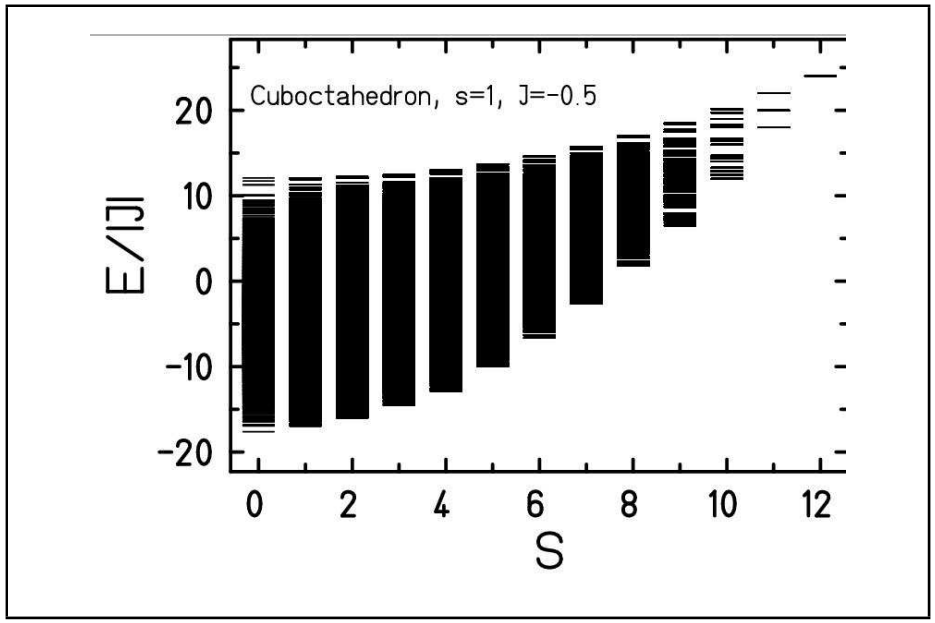
$$\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0 \quad : \quad \mathcal{H} = \bigoplus_{M=-S_{\text{max}}}^{+S_{\text{max}}} \mathcal{H}(M) \ , \quad S_{\text{max}} = Ns$$

dimension of $\mathcal{H}(M)$ (de Moivre)

$$\begin{aligned} \dim\left(\mathcal{H}(M)\right) &= f(N, 2s+1, S_{\text{max}} - M) \\ \text{with} \quad f(N,\mu,\nu) &= \sum_{n=0}^{\lfloor \nu/\mu \rfloor} (-1)^n \binom{N}{n} \binom{N-1+\nu-n\mu}{N-1} \end{aligned}$$

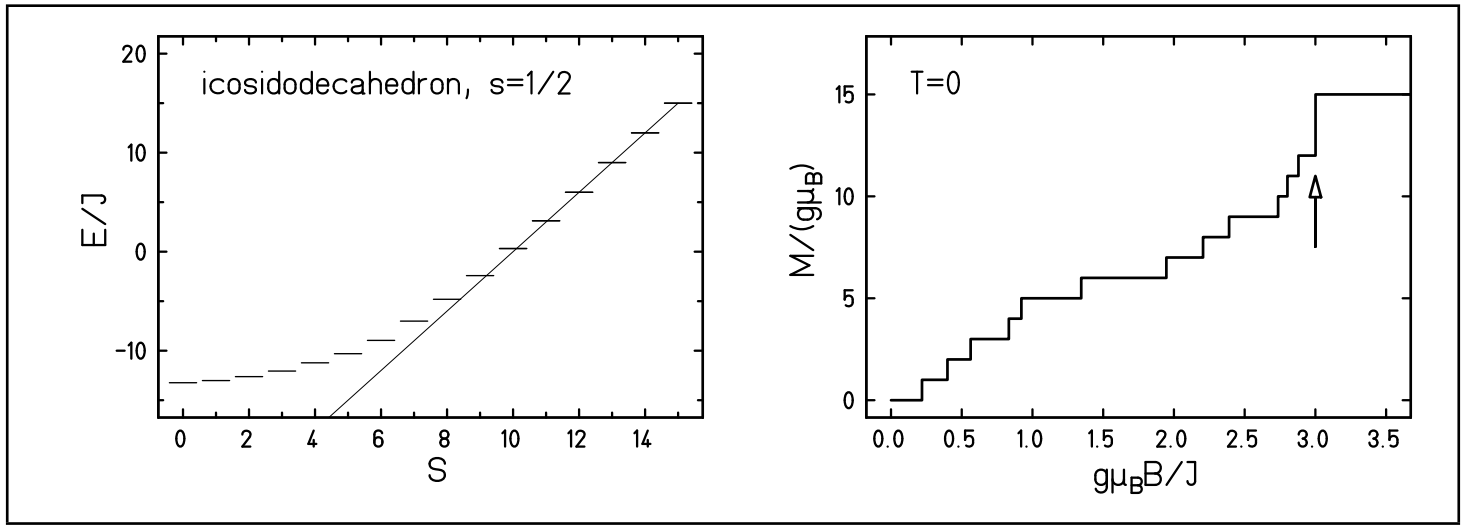
The dimension of the largest subspace is relevant. If more symmetries apply this dimension will be further reduced.

Exact diagonalization



- Numerically exact diagonalization feasible up to RAM size;
- Example: 10,000x10,000 complex*16, 1.6 GB RAM needed;
- Not much we can do at this point, wait for more RAM ;-)

The best we can do: Low-lying states



- Low-lying states sufficient for low-temperature physics;
- Low-lying states important for quantum phase transitions, e.g. magnetization jumps.
- Several methods available to obtain extreme eigenvalues: projection, Lánczos, DMRG.

Lanczos method

Construct tridiagonal matrix starting with an arbitrary vector $|\,\psi_1\,\rangle$

$$
\begin{aligned}
|\,\psi'_{k+1}\,\rangle &= (1 - |\,\psi_k\,\rangle\langle\,\psi_k\,| - |\,\psi_{k-1}\,\rangle\langle\,\psi_{k-1}\,|\,)\,\underset{\sim}{H}\,|\,\psi_k\,\rangle \\
|\,\psi_{k+1}\,\rangle &= \frac{|\,\psi'_{k+1}\,\rangle}{\sqrt{\langle\,\psi'_{k+1}\,|\,\psi'_{k+1}\,\rangle}}
\end{aligned}
$$

- New Lanczos vector by construction orthogonal all previous Lanczos vectors;
- Extremal eigenvalues of tridiagonal matrix converge quickly against true extremal eigenvalues;
- Example: ground state energy approximated to 10 figures with about 300 Lanczos steps although dimension of Hilbert space 10^8;
- Three Lanczos vectors needed: RAM!

Density Matrix Renormalization Group technique

Procedure to construct subspaces that contain low-lying trial states
Developed to calculate groundstate properties of (infinite) 1D spin systems (S. White 1992)

- Split system into subsystems (e.g. spin chain into single spin sites)
- Iteratively increase system size but keep only a fixed number of states

→ Truncation of the Hilbert space

- Question: Which states are best suited to be kept?

→ Use density matrix of "target state" to determine most important states

- Calculate physical properties in reduced Hilbert spaces

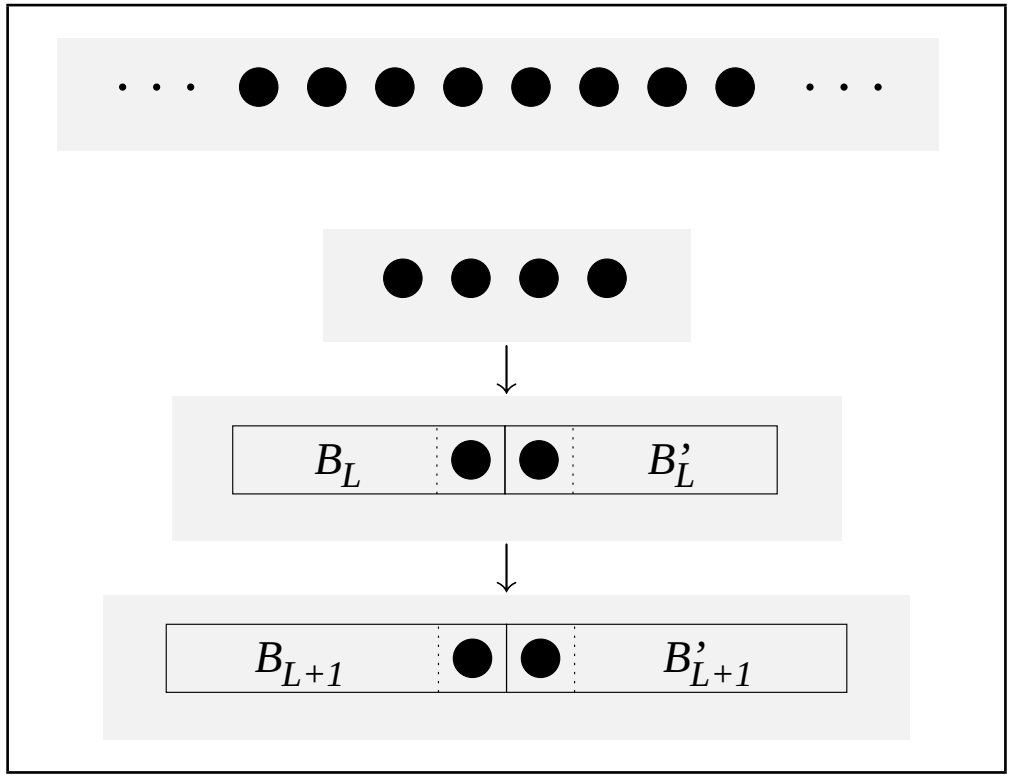
Standard DMRG algorithm schematically

Algorithm was developed and first used to study groundstate properties of infinite systems (1-dimensional)

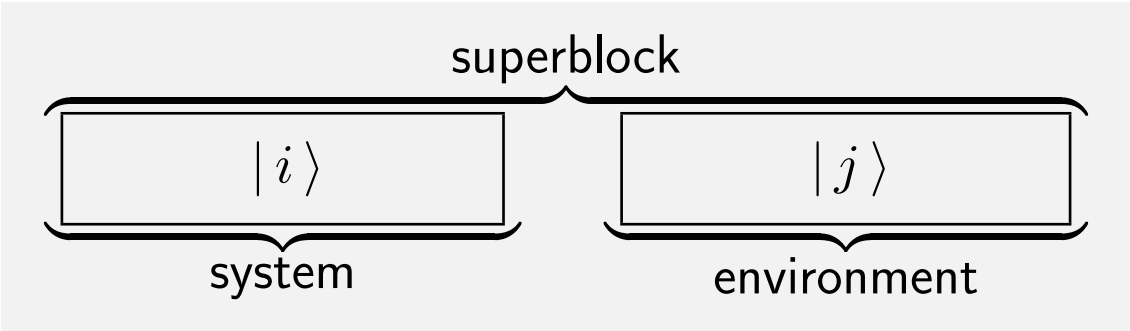
Example: infinite spin chain

1. Begin with 4-spin superblock
2. Combine block B_L and one spin to block B_{L+1}
3. Truncate block B_{L+1} to m states
4. continue with step 2.

$\longrightarrow$ System size increases by 2 spins after each step



Density matrix projection and basis truncation



- Find "target state" (groundstate) $|\, \psi^{\mathrm{SB}} \,\rangle$ of superblock
- Calculate partial trace of corresponding density operator $\rho^{\mathrm{SB}} = |\, \psi^{\mathrm{SB}} \,\rangle\langle\, \psi^{\mathrm{SB}} \,|$

$\longrightarrow$ Reduced density matrix ρ describes the weights of the system states in the decomposition of $|\, \psi^{\mathrm{SB}} \,\rangle$

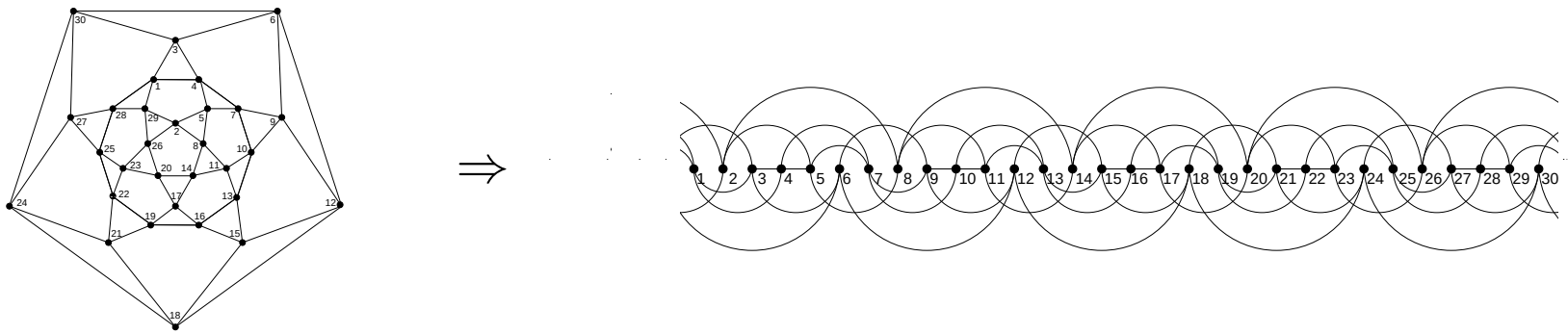
- Keep only the m "most important" states as truncated basis of the system
- Parameter m controls accuracy and computational cost of the method

- For many 1D systems, errors decrease exponentially with m
- Very good accuracy can be achieved, e.g. $\Delta E/E \approx 10^{-6}$ in the groundstate energy (infinite $s = \frac{1}{2}$ chain, nn-interaction, S. White 1992)

DMRG for 2D systems

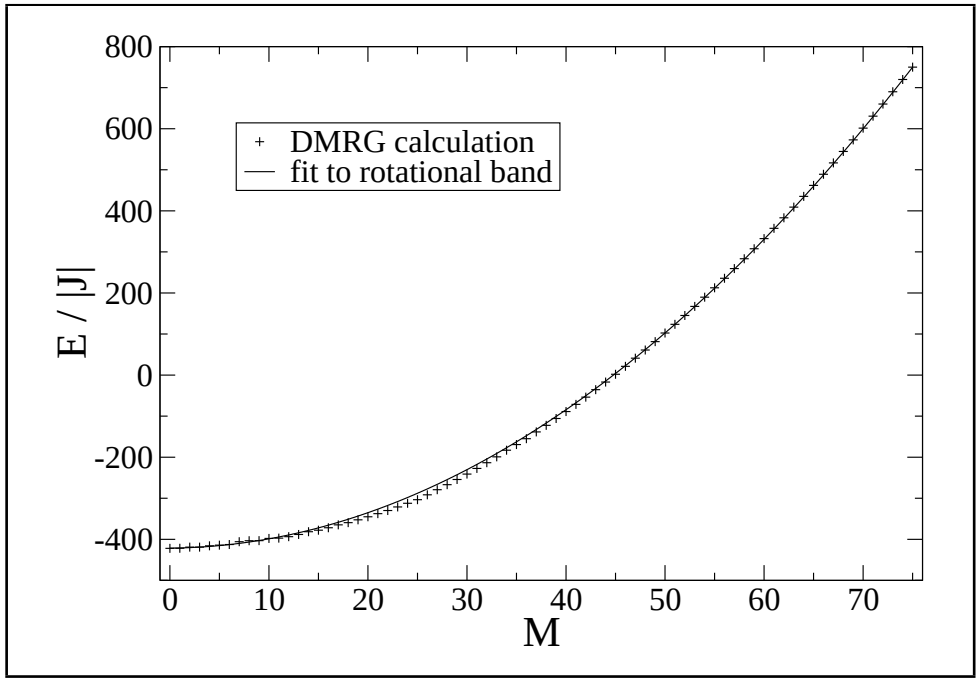
How to apply method to 2D systems?

- Map 2D structure to 1D chain with long-range interactions



- Perform standard algorithm
- Accuracy not as good as in 1D case
- $\Delta E/E \propto 1/m$ for the icosidodecahedron ($s = 1/2$, $\{\mathrm{Mo}_{72}\mathrm{Fe}_{30}\}$)

$\{Mo_{72}Fe_{30}\}$ - lowest rotational band with DMRG



- Rotational band hypothesis predicts quadratic sequence of $\mathcal{H}(M)$ ground-states
- Consistent with DMRG calculations
- Difficult to calculate since quasi two-dimensional and finite
- Accuracy tested with an icosidodecahedron of $s = 1/2$ ($\Delta E/E \approx 1\%$ for $m = 200$)

M. Exler, J. Schnack, Phys. Rev. B **67**, 094440 (2003)

Spin-coherent states

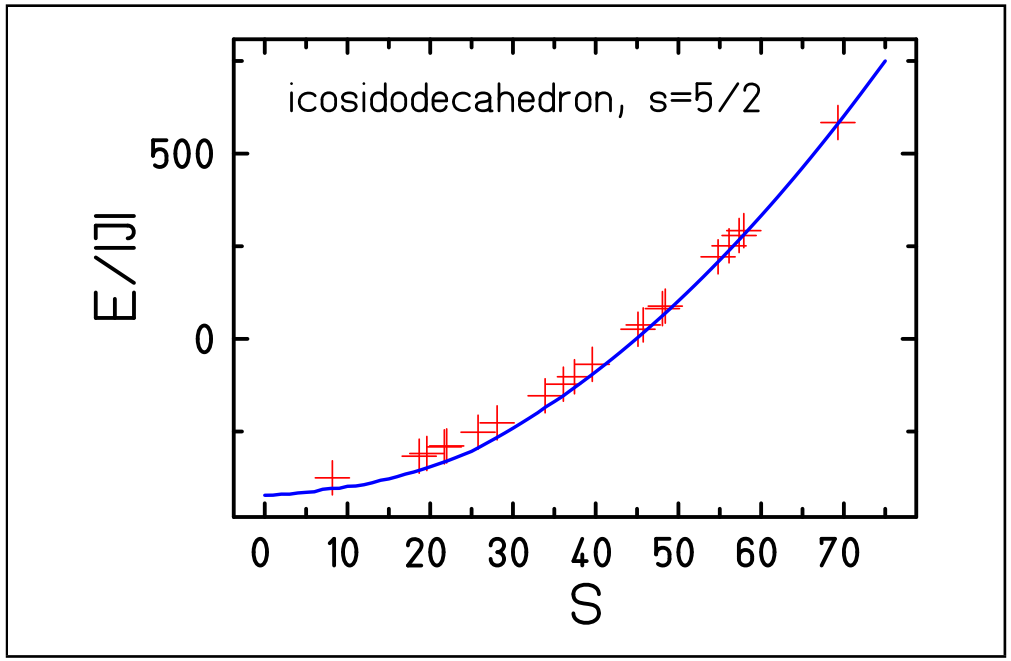
Overcomplete set of "basis" states

$$
\begin{aligned}
|\,\theta,\phi\,\rangle &= \sum_{p=0}^{2s} \sqrt{\binom{2s}{p}}\,[\cos(\theta/2)]^{(2s-p)}\,\left[e^{i\phi}\sin(\theta/2)\right]^{p}\,|\,s,m=s-p\,\rangle \\
\langle\,\theta,\phi\,|\,\underset{\sim}{\vec{s}}\,|\,\theta,\phi\,\rangle &= s\begin{pmatrix}\sin(\theta)\cos(\phi)\\ \sin(\theta)\sin(\phi)\\ \cos(\theta)\end{pmatrix}
\end{aligned}
$$

- Spin-coherent states intuitiv due to classical correspondence;
- Use reduced set of trial states to approximate low-lying levels.

Outlook

- DMRG for finite systems? DMRG for two- or three-dimensional systems?
- How to choose optimal set of spin-coherent states?



Thank you very much for your attention.

Collaboration

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