

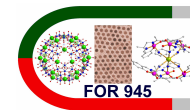
Modeling of time-dependent quantum processes

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Quantum Technology Meeting
12-15 January 2015 – The University of Manchester, UK



This talk follows the concept
of the famous
Course of Theoretical Physics
by Landau and Lifshitz

Lifshitz, who did the writing,
confessed that the books contain
“not a word of Landau
and not a thought of Lifshitz”

Contents for you today



$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. **Time evolution**
2. The dark horse
3. **Musings**

We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

Why time evolution?



- Study details of switching processes.
- Study influence of surrounding (bath).
- Ultimate goal: combined dynamics.
- Related: Magnetization dynamics, AC susceptibility, equilibration, μ SR.

Such calculations are complicated and rare!

Equation of motion

$$\frac{d}{dt} \underline{\rho}(t) = \frac{1}{i\hbar} \left[\underline{H}(t), \underline{\rho}(t) \right] + \hat{L} \underline{\rho}(t)$$

$\underline{\rho}(t)$ – density operator; generalization of states

$\underline{H}(t)$ – Hamiltonian; time-dependent, since $\vec{B}(t)$ time-dependent

\hat{L} – the UNKNOWN super operator (a very dark horse!)

Equation of motion II

Things you know: the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} | \Psi(t) \rangle = \underline{H}(t) | \Psi(t) \rangle$$

$| \Psi(t) \rangle$ – state vector of your quantum system

Be aware of the difference between state and state!

$\underline{H}(t)$ – Hamiltonian; time-dependent, since $\vec{B}(t)$ time-dependent

⇒ Unitary, coherent time-evolution of a single state vector, e.g. Landau-Zener.

Problems: 1. No decoherence.

2. What if your system does not start in a state vector?

Equation of motion III

Things you know: the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \underline{\underline{H}}(t) |\Psi(t)\rangle$$

is equivalent to

$$\frac{d}{dt} \underline{\underline{\rho}}(t) = \frac{1}{i\hbar} \left[\underline{\underline{H}}(t), \underline{\underline{\rho}}(t) \right]$$

with $\underline{\underline{\rho}}(t) = |\Psi(t)\rangle\langle\Psi(t)|$ being a pure state.

Equation of motion IV

Things you know, too: the equilibrium density matrix

$$\rho_{\sim}^{(\text{eq})}(T, B) = \frac{1}{Z(T, B)} \exp \left\{ -\beta \tilde{H} \right\}$$

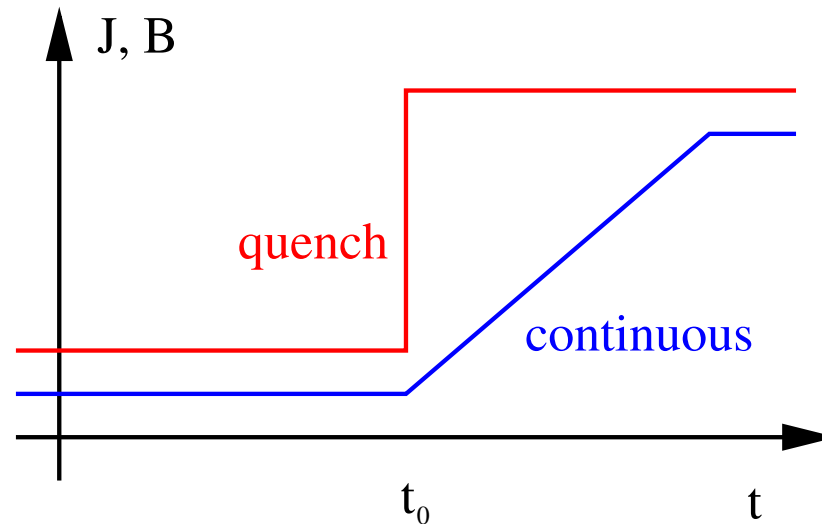
$$Z(T, B) = \text{Tr} \left(\exp \left\{ -\beta \tilde{H} \right\} \right) .$$

It could be that you start with this density matrix at $t = 0$, i.e. not in a single state vector, but a mixed state.

$$\rho_{\sim}(t = 0) = \rho_{\sim}^{(\text{eq})}(T, B) .$$

Equation of motion V

Protocols of time evolution

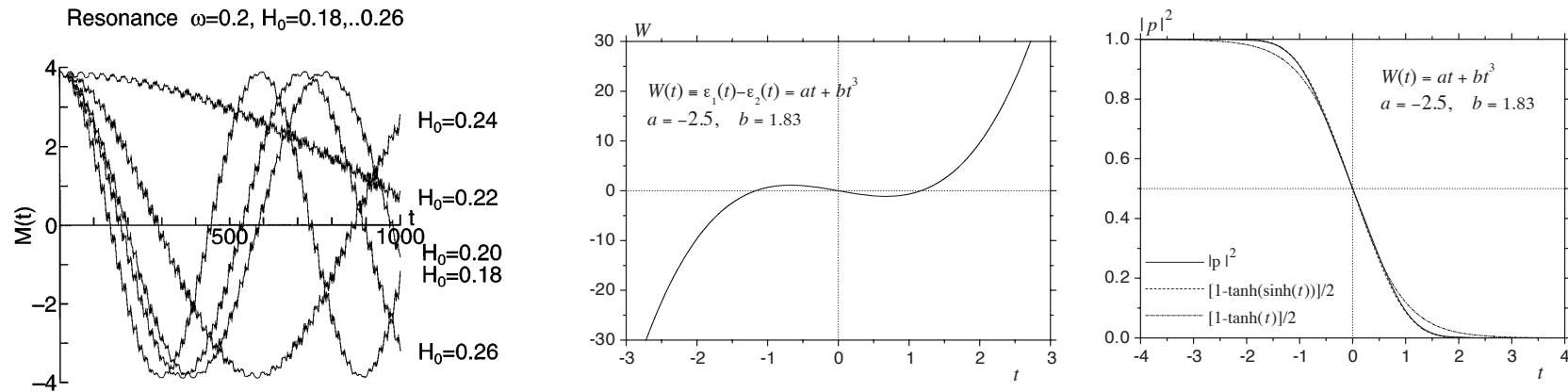


Magnetization dynamics with B being ramped up for $t > t_0$ (**Wolfgang!**).

$$\frac{d}{dt} \underline{\rho}(t) = \frac{1}{i\hbar} \left[\underline{H}(t), \underline{\rho}(t) \right], \quad \underline{\rho}(t = t_0) = \underline{\rho}^{(\text{eq})}(T, B(t < t_0)).$$

Equation of motion VI

Oscillating and non-linear $B(t)$

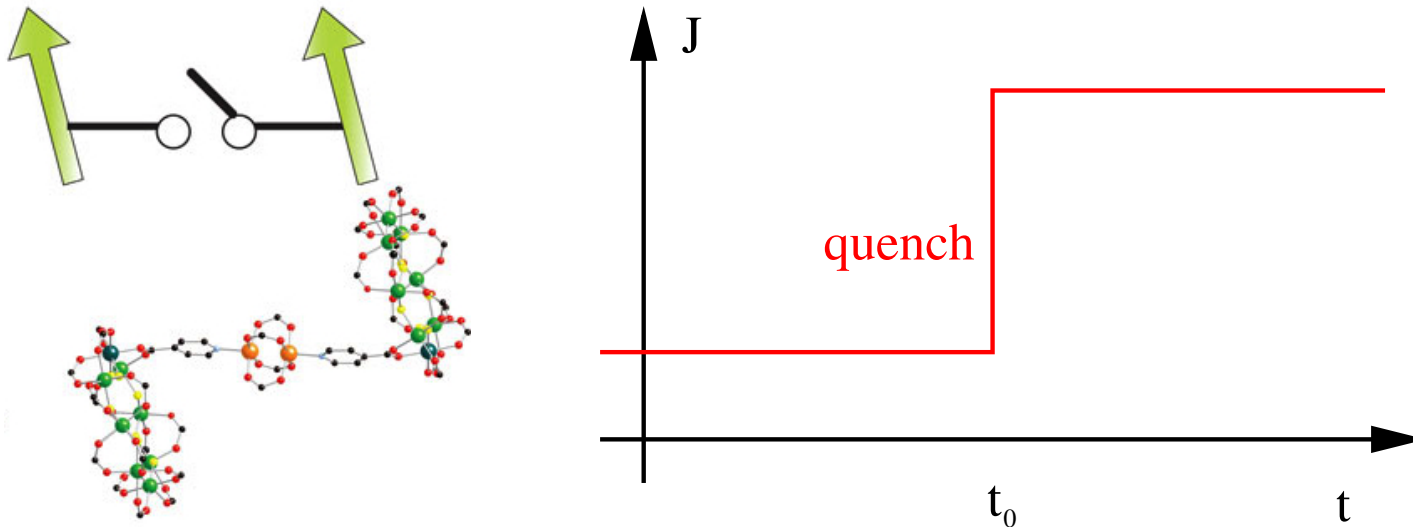


Magnetization dynamics with time-dependent B and pure states.
 R.h.s.: Non-linear $B(t)$ for full Landau-Zener switching (2).

- (1) S. Miyashita, K. Saito, and H. D. Raedt, Phys. Rev. Lett. **80**, 1525 (1998).
- (2) D. A. Garanin and R. Schilling, Europhysics Letters **59**, 7 (2002).

Equation of motion VII

Quantum quench of $J(t)$



Idea: switch interaction between Cr₇Ni rings by means of exciting the dimer in the middle from singlet to triplet (1).

(1) G. A. Timco *et al.*, Nature Nanotechnology **4**, 173 (2009).

Equation of motion VIII

Cr₇Ni–Cu₂–Cr₇Ni: more than a quench

$$\tilde{\rho}(t = 0) = \begin{pmatrix} \tilde{\rho}_{\text{Cr}_7\text{Ni, left}} & 0 & 0 \\ 0 & \tilde{\rho}_{\text{Cu}_2} & 0 \\ 0 & 0 & \tilde{\rho}_{\text{Cr}_7\text{Ni, right}} \end{pmatrix} .$$

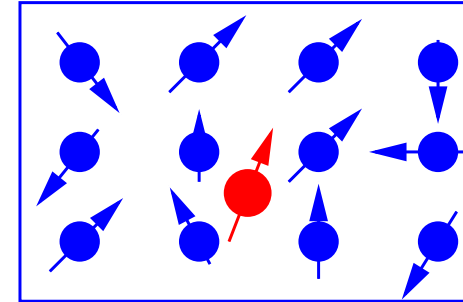
Idea: $B(t)$ would modify $\tilde{\rho}_{\text{Cu}_2}$ to have triplet character which then should initiate a non-trivial entanglement between l.h.s. and r.h.s. Cr₇Ni.

For $T > 0$ $\tilde{\rho}(t = 0)$ does not have block structure. What's the influence? In addition, what is the influence of dipolar interactions?

Equation of motion IX

We actually know this quench approach: μ SR

$$\tilde{\rho}(t = 0) = \begin{pmatrix} \tilde{\rho}_{\text{stuff}} & 0 \\ 0 & \tilde{\rho}_{\mu} \end{pmatrix} .$$



Idea: Muon implanted instantly, density matrix at $t = 0$ is a product of the equilibrium density matrix of the material and those of the polarized muon.

We should also solve this problem! The muon should develop into an entangled state with the material, but we don't treat it like this!

(1) Jonas Korenke, Diploma thesis, Bielefeld University (2013) & J. Korenke, J. Schnack, hopefully published some day.

The dark horse

Quantum master equation

$$\frac{d}{dt} \underline{\rho}(t) = \frac{1}{i\hbar} \left[\underline{H}(t), \underline{\rho}(t) \right] + \hat{L} \underline{\rho}(t)$$

\hat{L} – the UNKNOWN super operator (a very dark horse!) models the influence of the environment (bath) on the actual system; depends on the interactions and typ of bath. This term is responsible for thermalization, relaxation, decoherence.

The structure of \hat{L} is such, that the density matrix remains a density matrix (conservation of probability).

(1) N.V. Prokof'ev, P.C.E. Stamp, Rep. Prog. Phys. **63**, 669 (2000); Phys. Rev. Lett. **80**, 5794 (1998).

(2) Heinz-Peter Breuer, *The Theory of Open Quantum Systems*, Oxford University Press (2007).

A simple example

$$\frac{d}{dt} \rho_{\sim}(t) = \frac{1}{\tau} \left(\rho_{\sim}^{(\text{eq})}(T, B) - \rho_{\sim}(t) \right)$$

Describes an exponential relaxation towards thermal equilibrium with a single relaxation time τ . Fully phenomenological.

$$\rho_{\sim}(t) = \left(1 - e^{-\frac{t}{\tau}} \right) \rho_{\sim}^{(\text{eq})}(T, B) + e^{-\frac{t}{\tau}} \rho_{\sim}(0) .$$

Simple quantum dynamics with relaxation/decoherence

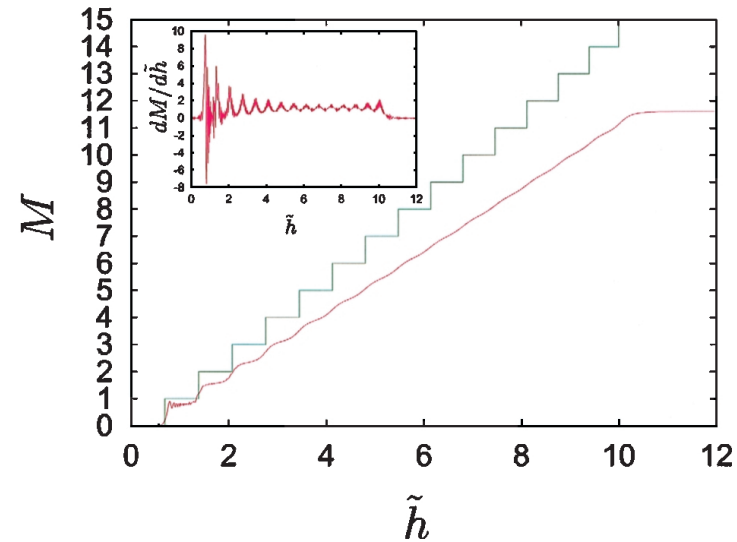
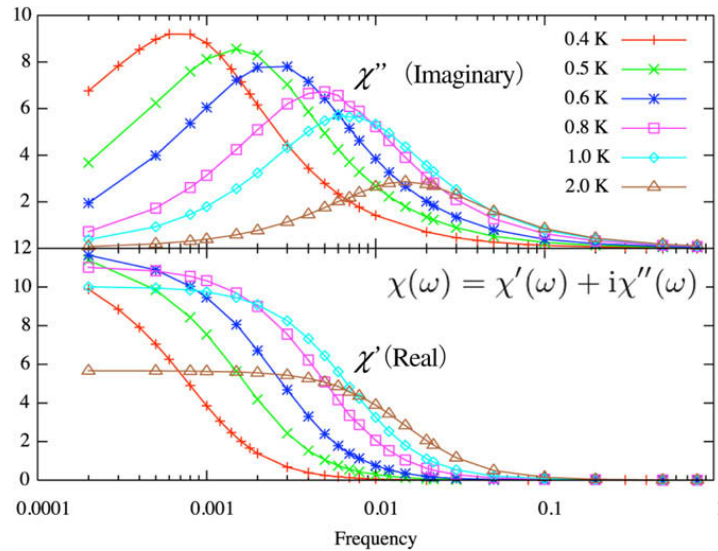
$$\frac{d}{dt} \tilde{\rho}(t) = \frac{1}{i\hbar} \left[\tilde{H}(t), \tilde{\rho}(t) \right] + \frac{1}{\tau} \left(\tilde{\rho}^{(\text{eq})}(T, B(t)) - \tilde{\rho}(t) \right)$$

Not a bad start to investigate coherent dynamics under the influence of a heat bath with a single relaxation time τ .

$\tilde{\rho}^{(\text{eq})}(T, B(t))$ is the equilibrium density matrix for the time-dependent magnetic field at fixed temperature.

related: P. Santini *et al.*, Phys. Rev. Lett. **94**, 077203 (2005).

Realistic bath



Interaction with phonons. AC-susceptibility of a single spin (1). Magnetization dynamics in a pulsed field (2).

(1) T. Kawakami *et al.*, Polyhedron **28**, 2092 (2009).

(2) H. Nakano and S. Miyashita, J. Phys. Soc. Jpn. **70**, 2151 (2001).

Why are such calculations so rare?

$$\frac{d}{dt} \underset{\sim}{\rho}(t) = \frac{1}{i\hbar} \left[\underset{\sim}{H}(t), \underset{\sim}{\rho}(t) \right] + \hat{L} \underset{\sim}{\rho}(t)$$

1. $\underset{\sim}{\rho}(t)$ has $\text{Dim}(\mathcal{H}) \times \text{Dim}(\mathcal{H})$ entries!

2. \hat{L} is not really known;

there are reasonable assumptions such as Lindblad form etc.

Very encouraging calculations along these lines concerning the question of robustness (1)!

(1) A. Chiesa, D. Gerace, F. Troiani, G. Amoretti, P. Santini, S. Carretta, Phys. Rev. A **89**, 052308 (2014).

Musings about things that I don't understand

in random order

Exact diagonalization required!



$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. For a trustworthy quantum dynamics you need exact diagonalization.
2. Initial state (pure or mixed) needs to be as accurate as possible.

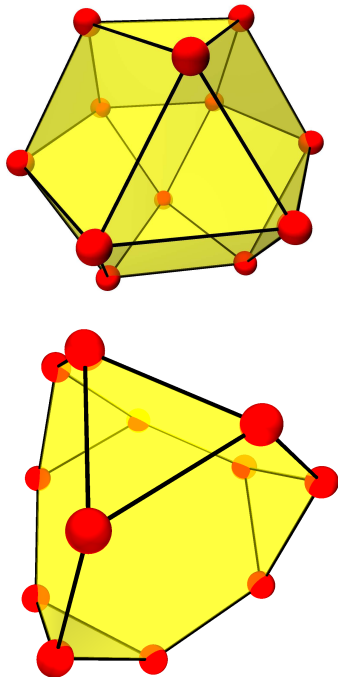
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Please send inquiries to jschnack@uni-bielefeld.de!

Complete diagonalization: SU(2) & point group symmetry

Quantum chemists need to be much smarter since they have smaller computers!

- (1) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).
- (2) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, *Inorg. Chem.* **38**, 6081 (1999).
- (3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Irreducible Tensor Operator approach



Spin rotational symmetry SU(2):

- $\underline{H} = -2 \sum_{i < j} J_{ij} \underline{\tilde{S}}_i \cdot \underline{\tilde{S}}_j + g\mu_B \underline{\tilde{S}} \cdot \underline{\tilde{B}} ;$

- Physicists employ: $[\underline{H}, \underline{\tilde{S}}_z] = 0;$

- Chemists employ: $[\underline{H}, \underline{\tilde{S}}^2] = 0, [\underline{H}, \underline{\tilde{S}}_z] = 0;$

Irreducible Tensor Operator (ITO) approach;
Free program MAGPACK (2) available.

(1) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).

(2) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, *Inorg. Chem.* **38**, 6081 (1999).

(3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Point Group Symmetry

$$|\alpha' S M \Gamma\rangle = \mathcal{P}^{(\Gamma)} |\alpha S M\rangle = \left(\frac{l_{\Gamma}}{h} \sum_R \left(\chi^{(\Gamma)}(R) \right)^* \mathcal{G}(R) \right) |\alpha S M\rangle$$

Method:

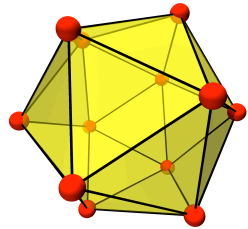
- Projection onto irreducible representations Γ of the point group (1,2);
- No free program, things are a bit complicated (3,4).

(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.

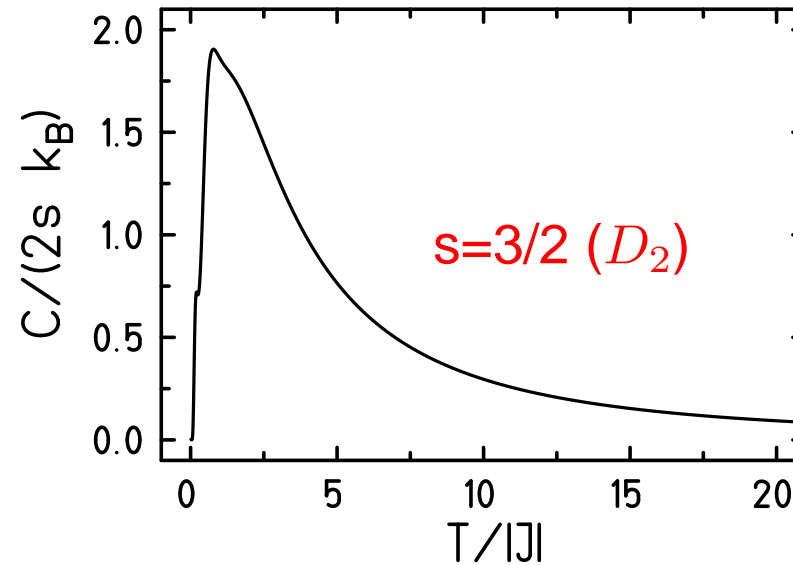
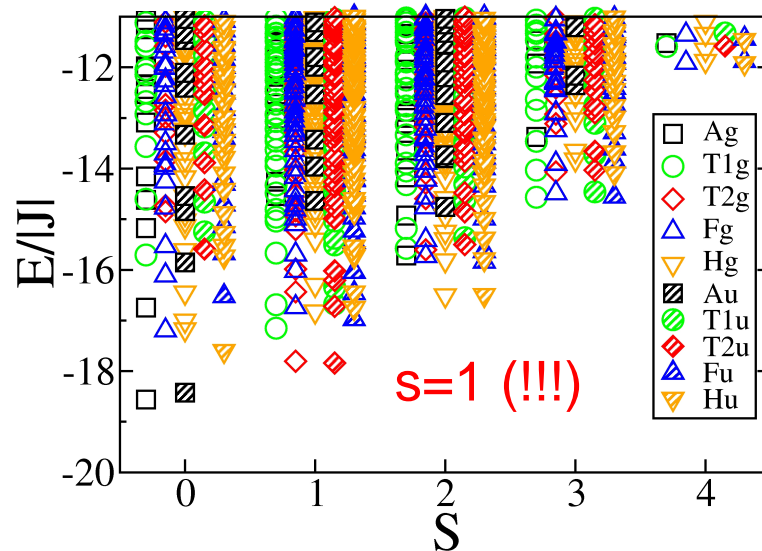
(2) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).

(3) O. Waldmann, *Phys. Rev. B* **61**, 6138 (2000).

(4) R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010) \Leftarrow contains EVERYTHING.



Example: Icosahedron



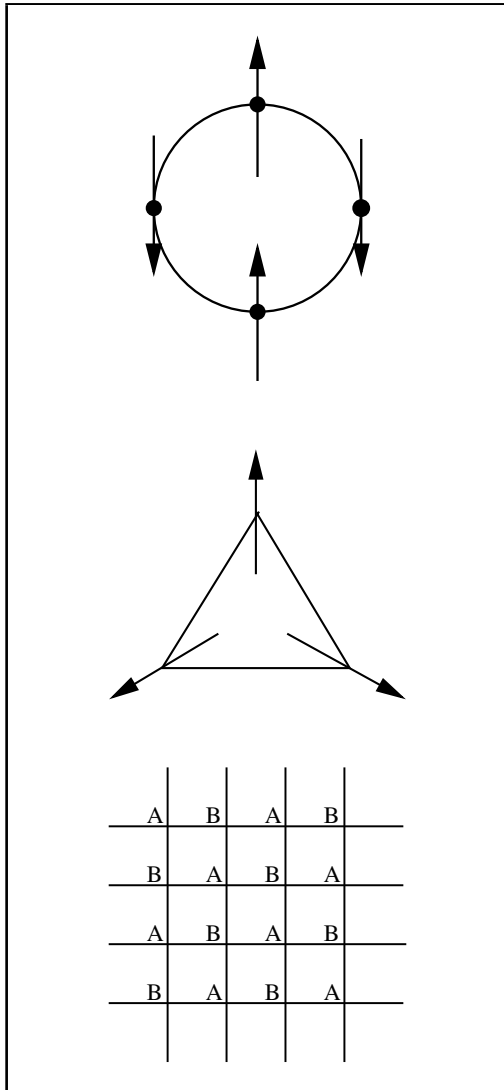
Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h ;
 Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

I love frustration, but

Frustration is probably not good

Definition of frustration



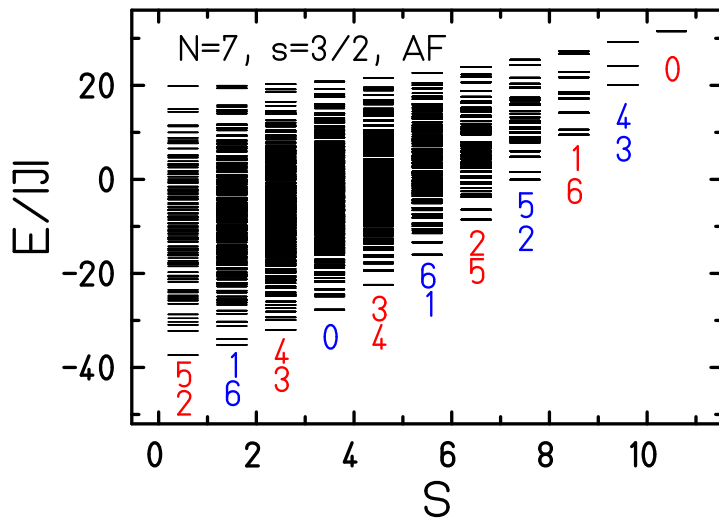
- Simple: A spin system is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.

- Advanced: A non-bipartite antiferromagnet is frustrated. A bipartite spin system can be decomposed into two sublattices A and B such that for all exchange couplings:

$$J(x_A, y_B) \leq g^2, J(x_A, y_A) \geq g^2, J(x_B, y_B) \geq g^2, \text{cmp. (1,2).}$$

(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)

Problem of frustrated systems



- For odd-membered spin rings and half integer s , i.e. $s = 1/2, 3/2, 5/2, \dots$ we find that (1)
 - ground state has total spin $S = 1/2$;
 - ground state energy **fourfold** degenerate (C_N).
- (Near) degeneracies may prevent accurate preparation.
- High density of low-lying states might easily mix in unwanted states during time evolution.

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Mater. **220**, 227 (2000).

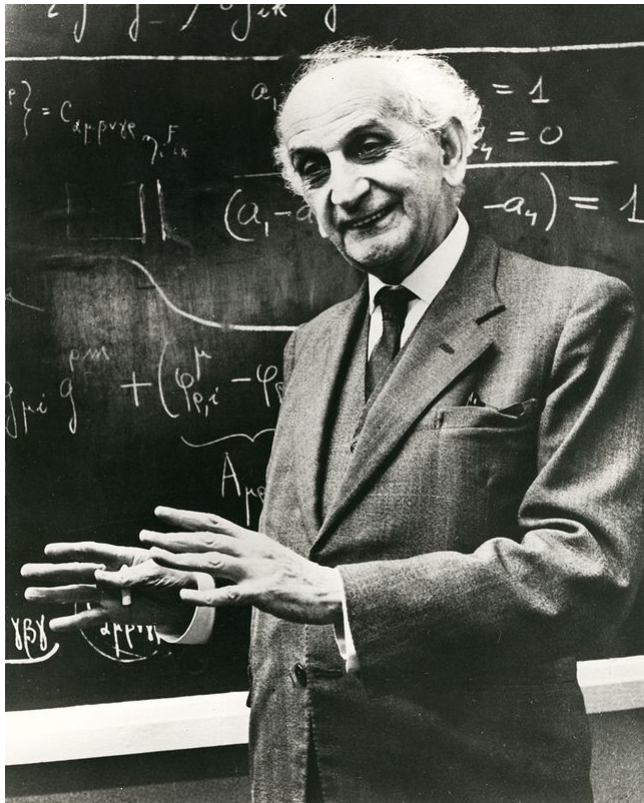
(2) J. Schnack, Dalton Trans. **39**, 4677 (2010); M. L. Baker *et al.*, Proceedings of the National Academy of Sciences **109**, 19113 (2012).

Finite-temperature Lanczos Method

(Good for dimensions up to 10^{10} .)

(Can also be used for time evolution!!!)

Lanczos – a Krylov space method



- Idea: exact diagonalization in reduced basis sets.
- But which set to choose???
- Idea: generate the basis set with the operator you want to diagonalize:
 $\{ |\phi\rangle, \tilde{H} |\phi\rangle, \tilde{H}^2 |\phi\rangle, \tilde{H}^3 |\phi\rangle, \dots \}$
- But which starting vector to choose???
- Idea: almost any will do!
- Cornelius Lanczos (Lánczos Kornél, 1893-1974)

(1) C. Lanczos, J. Res. Nat. Bur. Stand. **45**, 255 (1950).

Finite-temperature Lanczos Method I

$$Z(T, B) = \sum_{\nu} \langle \nu | \exp \left\{ -\beta \tilde{H} \right\} | \nu \rangle$$

$$\langle \nu | \exp \left\{ -\beta \tilde{H} \right\} | \nu \rangle \approx \sum_n \langle \nu | n(\nu) \rangle \exp \left\{ -\beta \epsilon_n \right\} \langle n(\nu) | \nu \rangle$$

$$Z(T, B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^R \sum_{n=1}^{N_L} \exp \left\{ -\beta \epsilon_n \right\} |\langle n(\nu) | \nu \rangle|^2$$

- $|n(\nu)\rangle$ n-th Lanczos eigenvector starting from $|\nu\rangle$
- Partition function replaced by a small sum: $R = 1 \dots 10, N_L \approx 100$.

J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Lanczos for unitary time evolution

$$\begin{aligned}
 |\Psi(t + \Delta t)\rangle &= \exp\left\{-\frac{i\Delta t}{\hbar} H\right\} |\Psi(t)\rangle \\
 &\approx \sum_{n=1}^{N_L} \exp\left\{-\frac{i\Delta t}{\hbar} \epsilon_n\right\} |n(\Psi)\rangle \langle n(\Psi)|\Psi\rangle
 \end{aligned}$$

- $|n(\Psi)\rangle$ n-th Lanczos eigenvector starting from $|\Psi\rangle$
- Time-evolution rather accurate, even for big systems, but formulated for pure states.

J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Is there more than
the Bloch sphere?

What about non-Bloch states?

Spin-coherent states for $s = 1/2$ (parameterized on the Bloch sphere)

$$|\theta, \phi\rangle = \cos\left(\frac{\theta}{2}\right) e^{-i\phi/2} |\uparrow\rangle + \sin\left(\frac{\theta}{2}\right) e^{+i\phi/2} |\downarrow\rangle$$

Spin-coherent states for $s = 1$ (parameterized on the Bloch sphere)

$$|\theta, \phi\rangle = \frac{1 + \cos(\theta)}{2} e^{-i\phi} |m = 1\rangle + \frac{\sin(\theta)}{\sqrt{2}} |m = 0\rangle + \frac{1 - \cos(\theta)}{2} e^{+i\phi} |m = -1\rangle$$

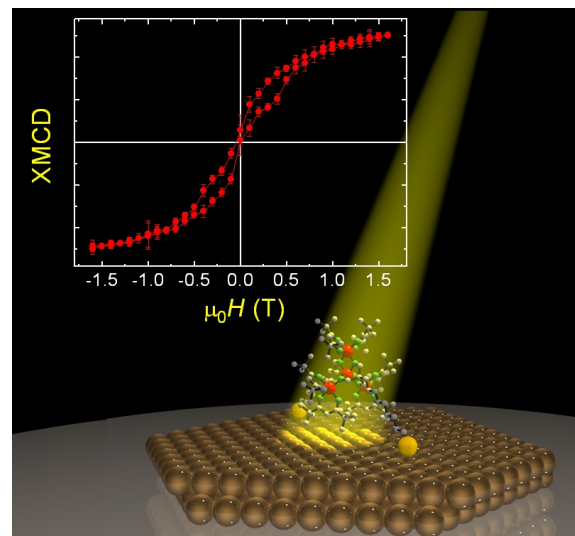
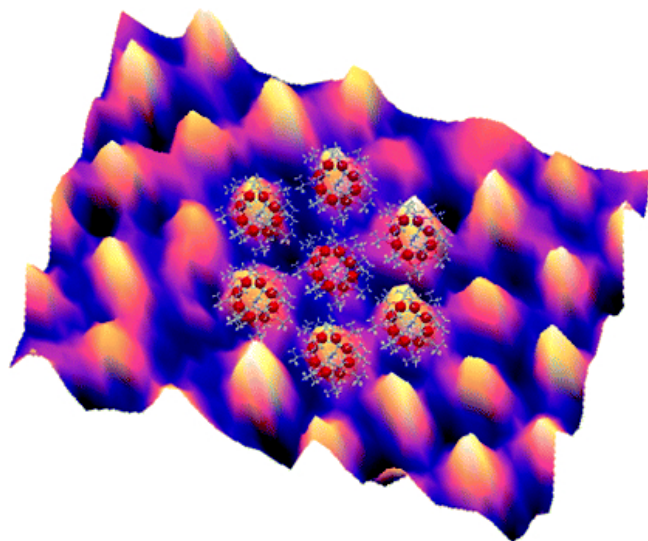
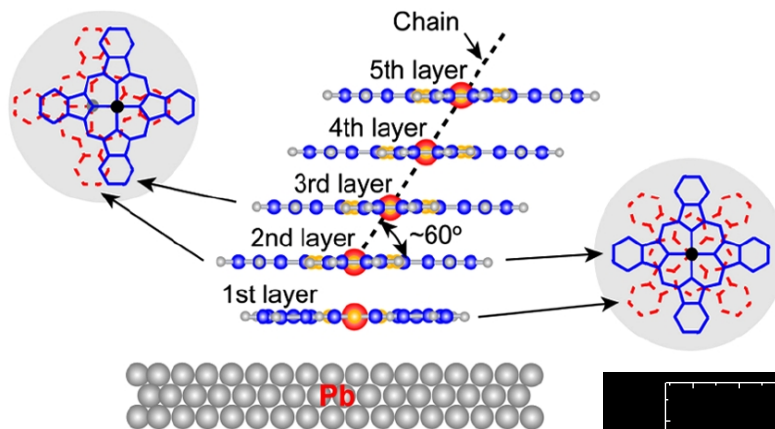
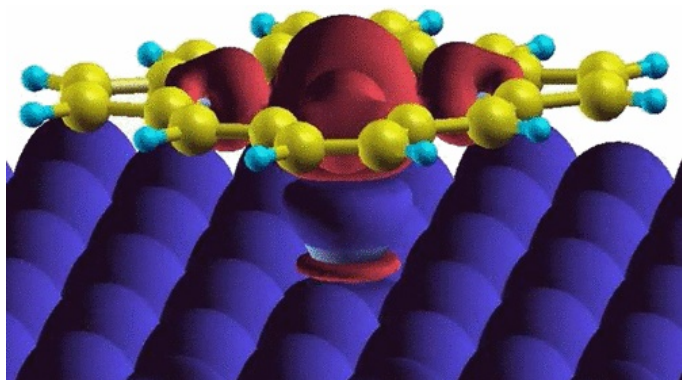
Do not exhaust all possible states, $|m = 0\rangle$ cannot be reached by a rotation of $|m = 1\rangle$, there are states such a spin-nematic states.

Can they be addressed? Do they form during time-evolution? Can they be read out?

Numerical Renormalization Group calculations

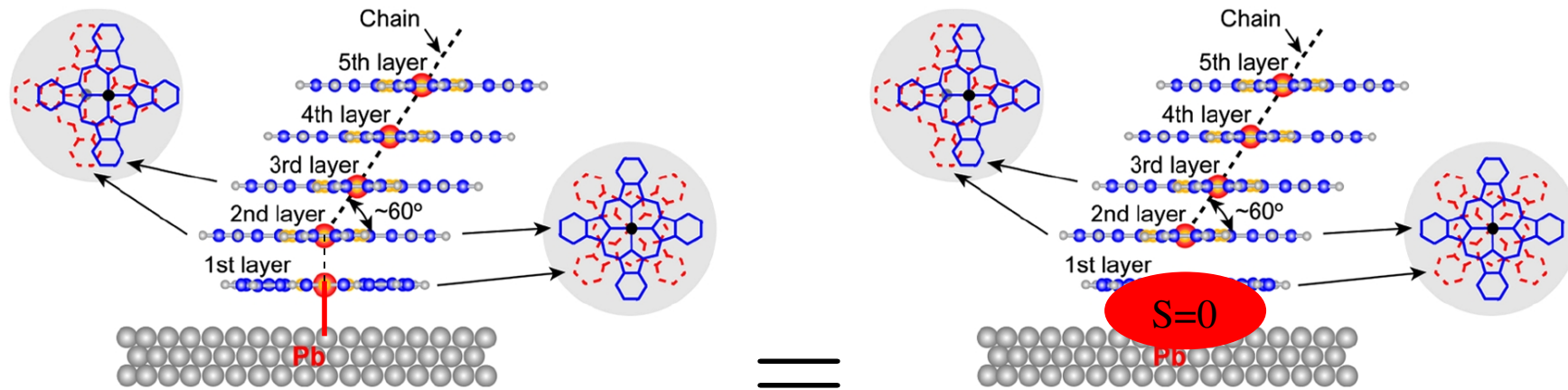
(Good for deposited molecules.)

You want to deposit a molecule



M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirriet *et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

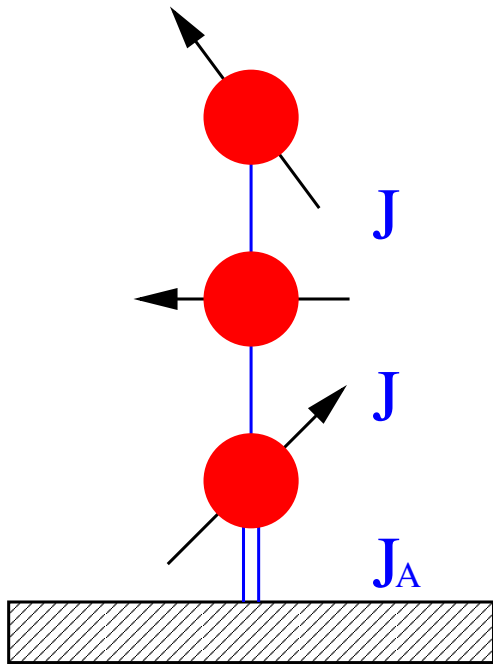


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
 Co^{2+} with spin $s = 1/2$.

Under which circumstances is the picture of total screening correct?

X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

NRG – minimal model (already an approximation!)



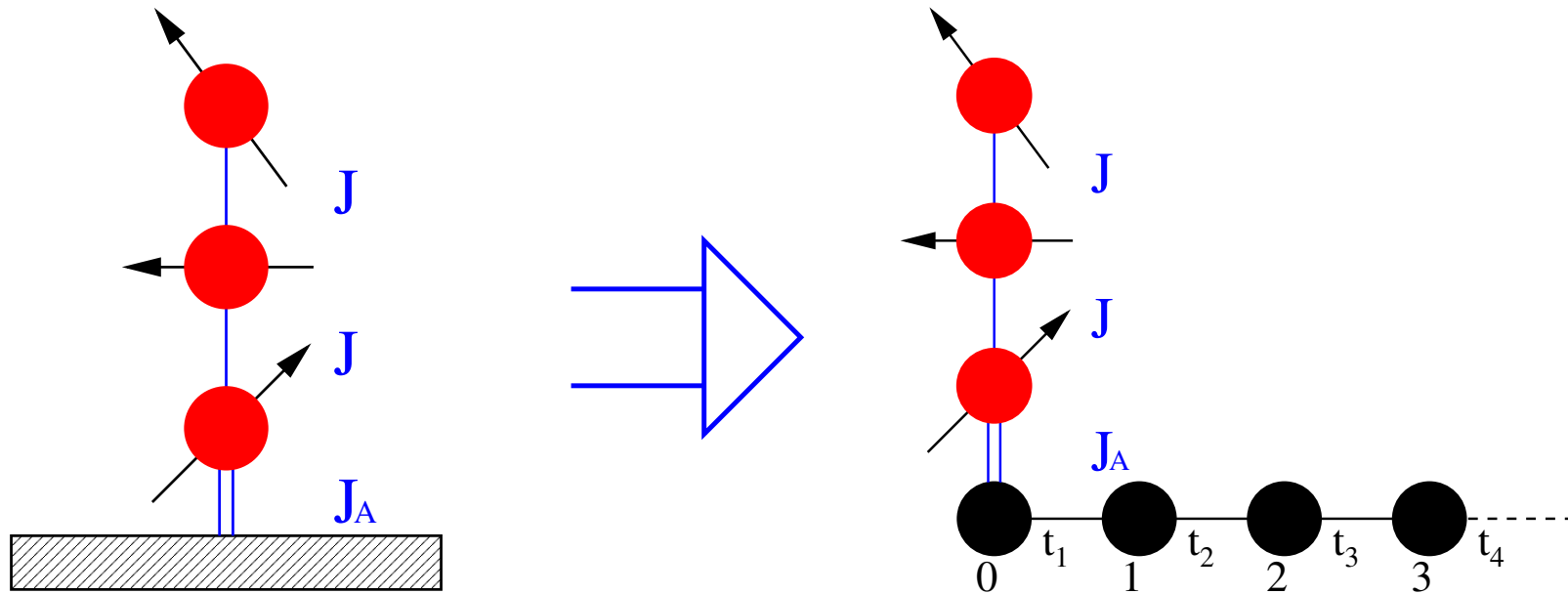
- $\tilde{H} = \tilde{H}_{\text{electrons}} + \tilde{H}_{\text{coupling}} + \tilde{H}_{\text{impurity}}$

$$\tilde{H}_{\text{electrons}} = \sum_{i \neq j, \sigma} t_{ij} d_{i\sigma}^\dagger d_{j\sigma} + g_e \mu_B B \mathcal{S}^z$$

$$\tilde{H}_{\text{coupling}} = -2J_A \mathcal{S} \cdot \mathfrak{s}_0 \quad , \quad \mathfrak{s}_0 - \text{spin density at contact}$$
- $\tilde{H}_{\text{impurity}} = \text{Hamiltonian of your molecule!}$
- **NRG \equiv construction of a small (!) effective model in order to evaluate properties of the deposited cluster, the impurity (3).**

(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
 (2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
 (3) *Impurity* is a technical term in this context and not an insult to chemists.

NRG in a cartoon



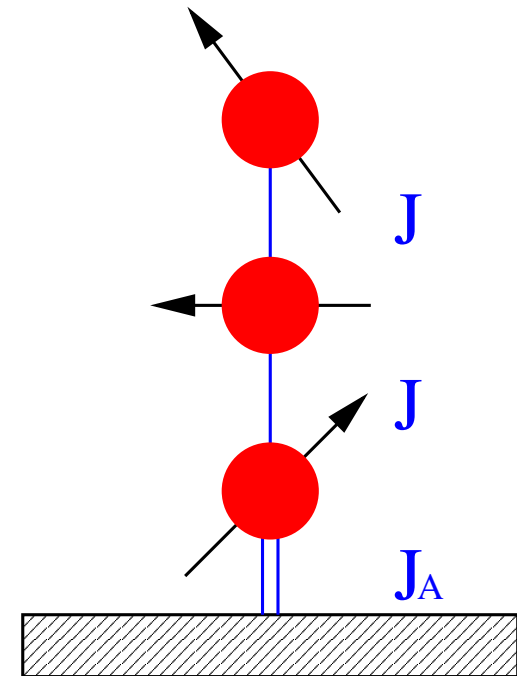
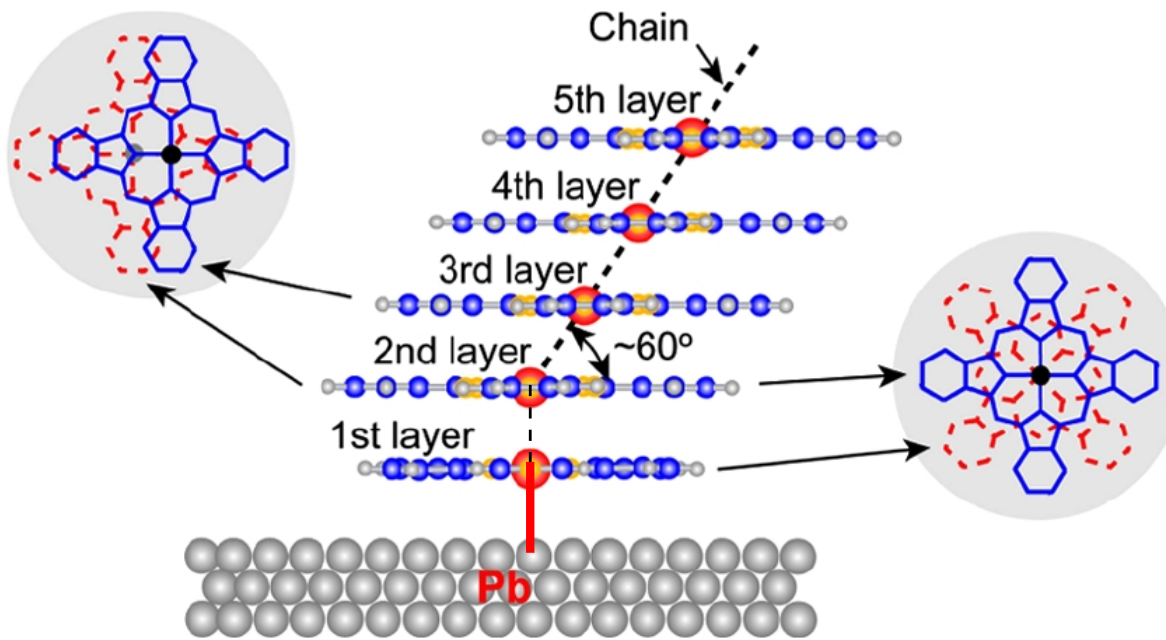
Metallic surface is replaced by semi-infinite Hubbard chain;

Parameters of the chain: hopping matrix elements and on-site energies;

Stepwise enlargement of the chain ($t_1 > t_2 > t_3 \dots$);

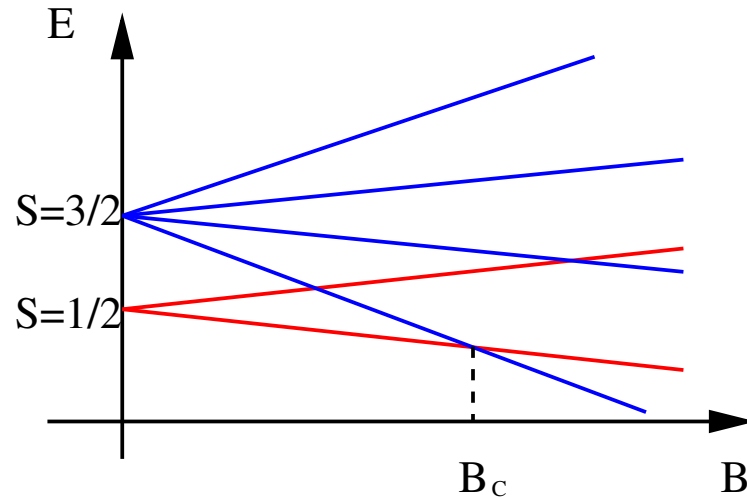
Truncation of basis set when matrices grow too big.

Once more: deposited chain

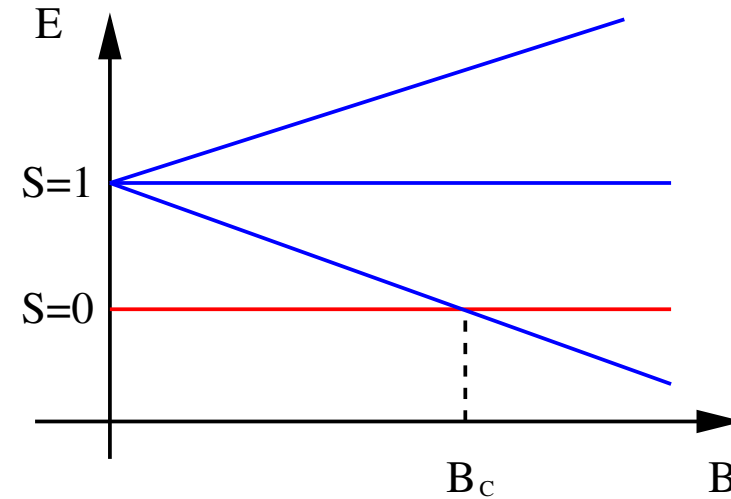


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



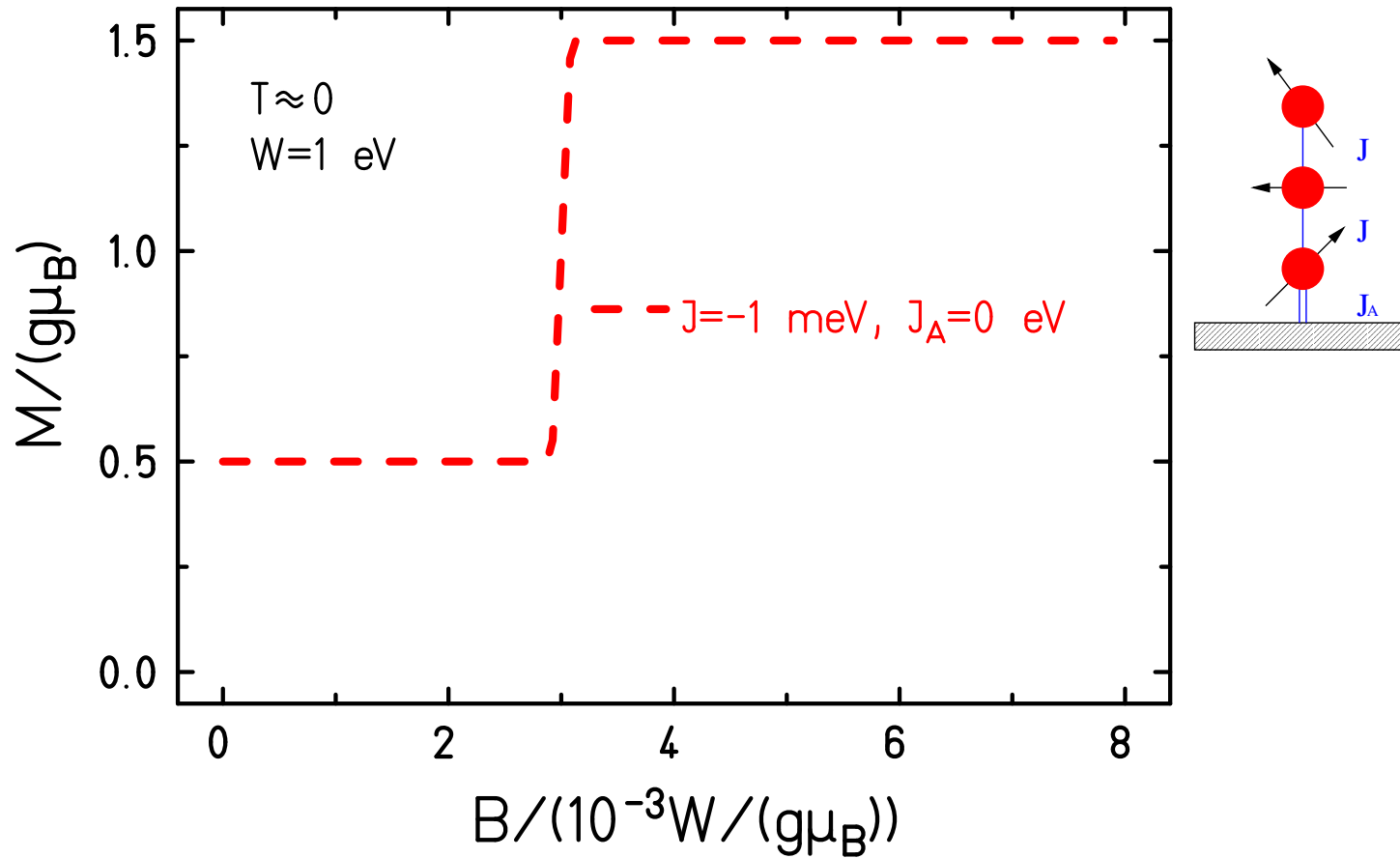
• energy levels of a trimer



• energy levels of a dimer

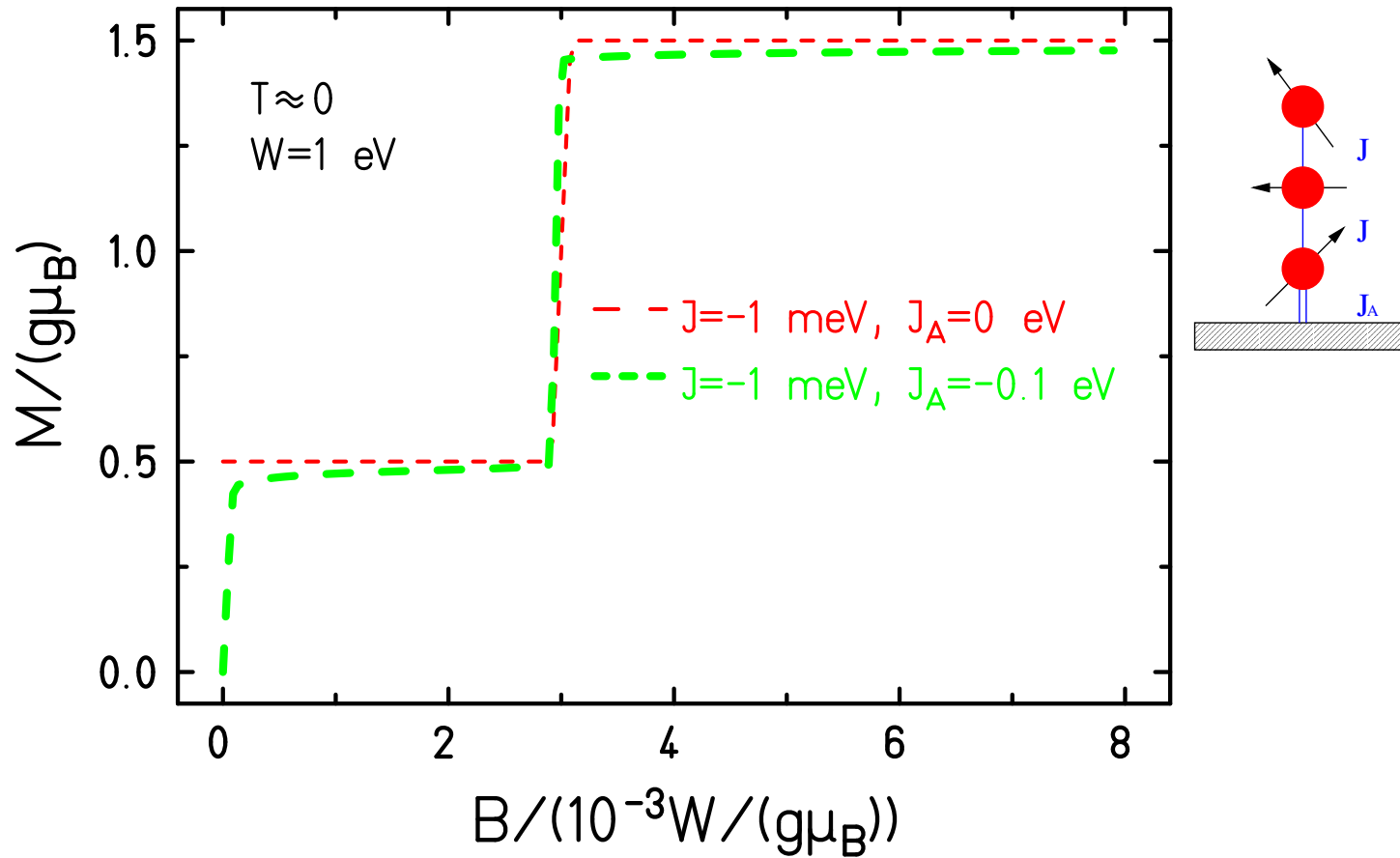
Magnetization curves different; could be seen in XMCD.
 NRG calculates observables also between limiting cases
 and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



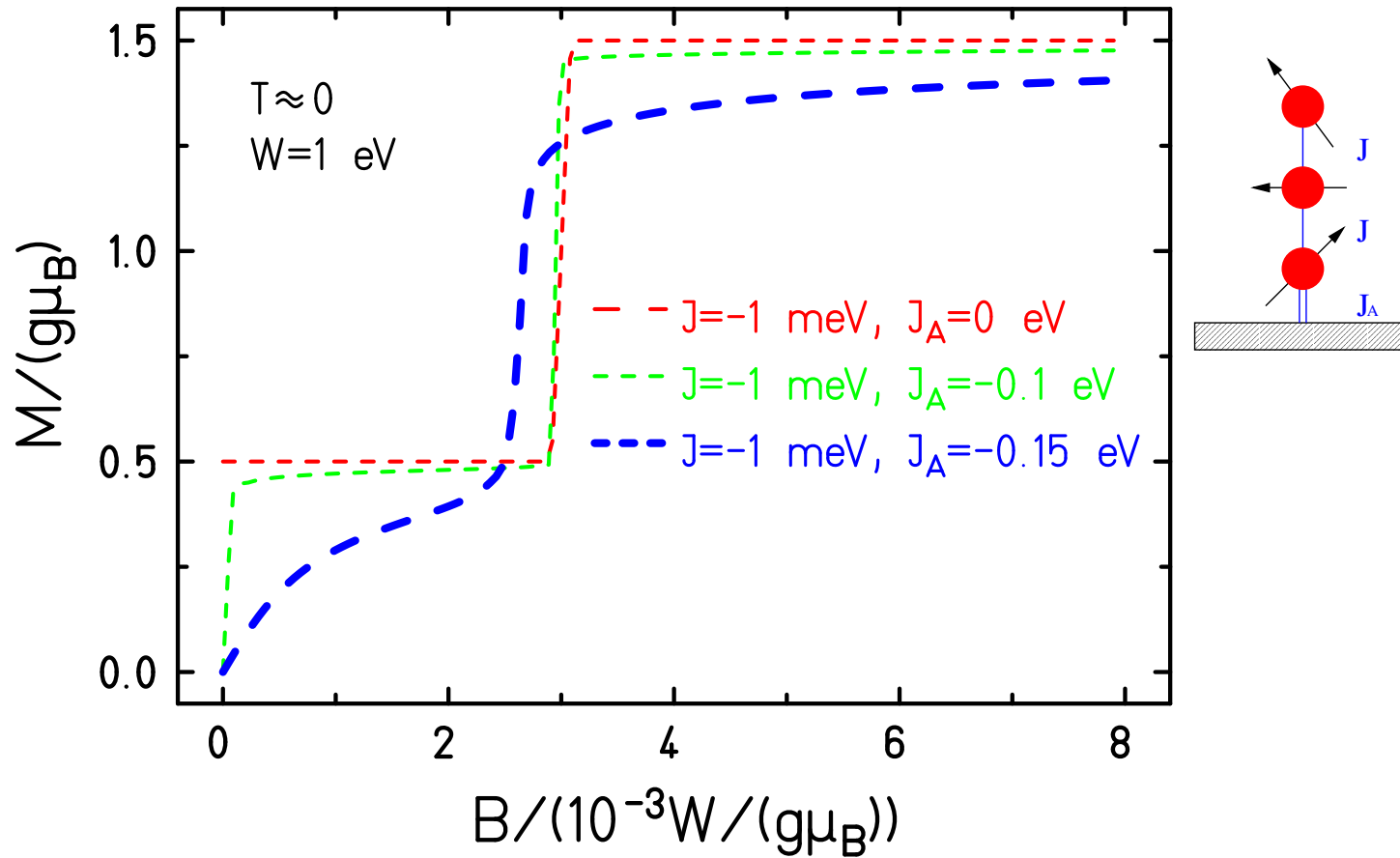
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



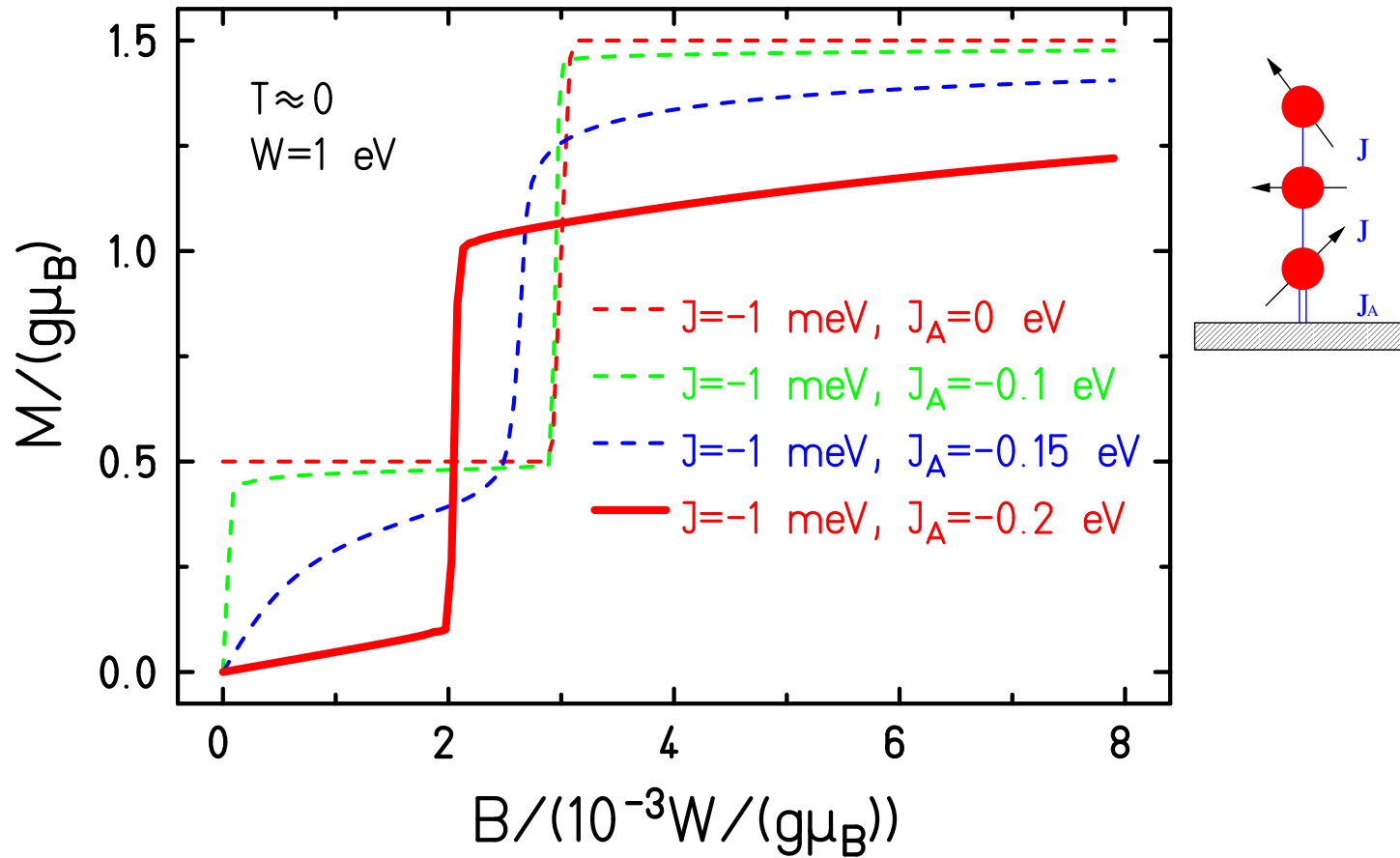
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



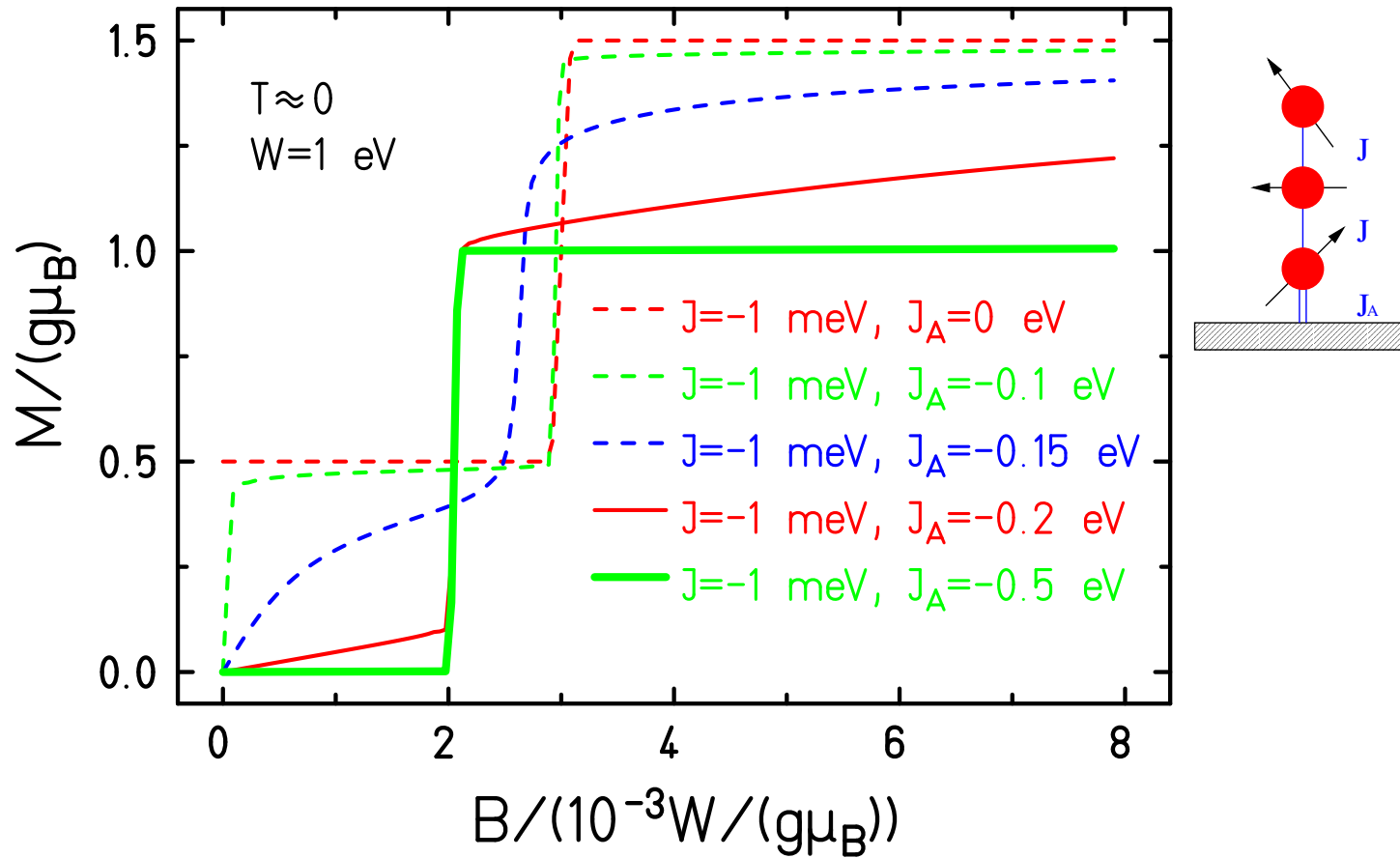
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



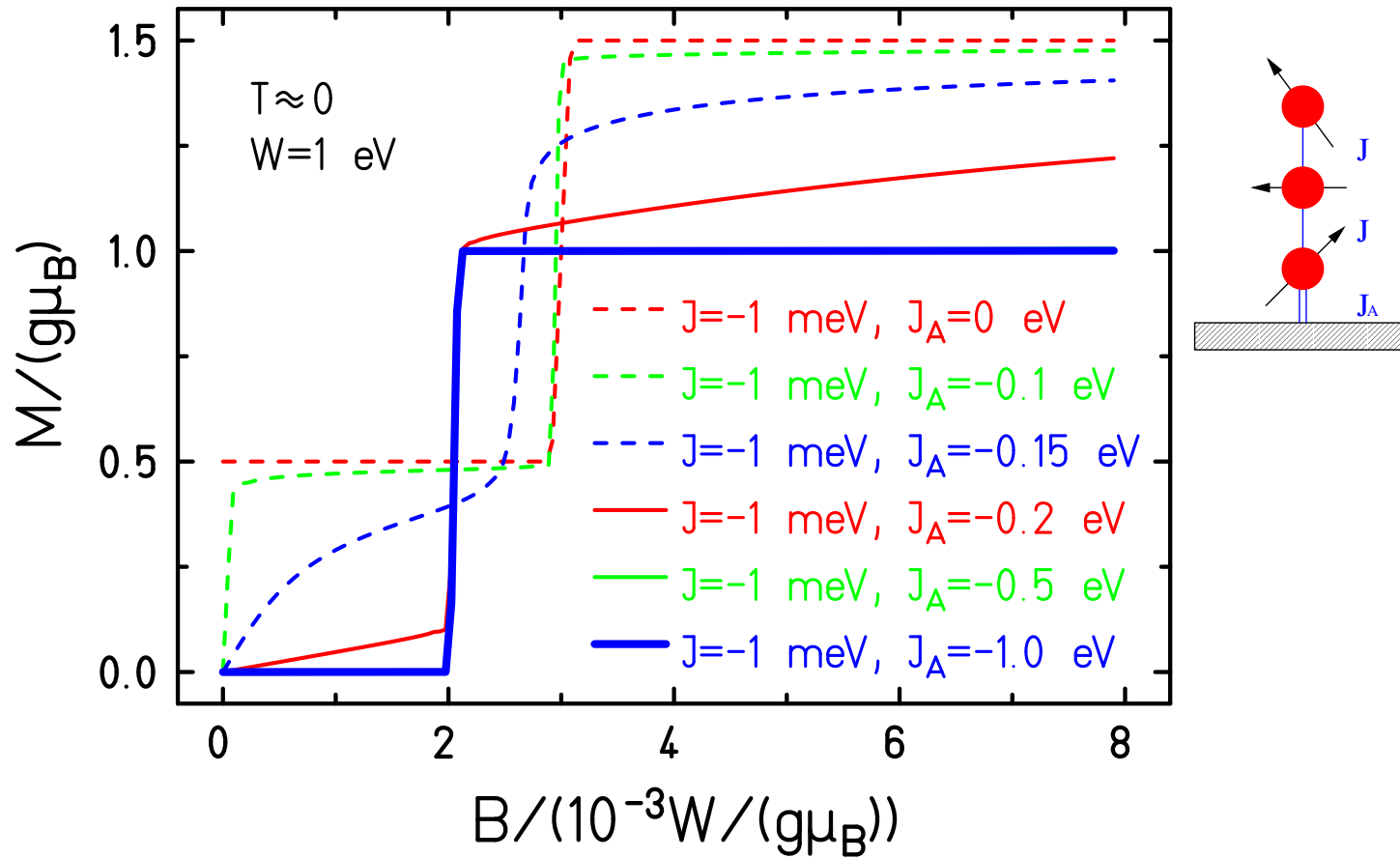
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



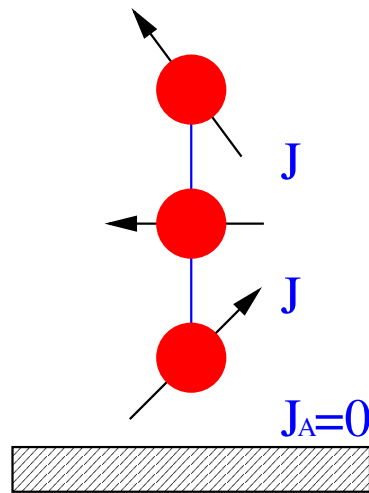
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Increasing coupling to the substrate



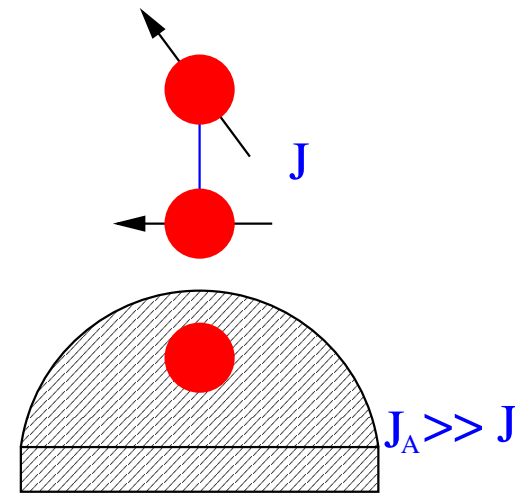
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Weak vs. strong coupling



- weak coupling limit:
unperturbed molecule (trimer)

- $|J_A| \lesssim 0.1W$

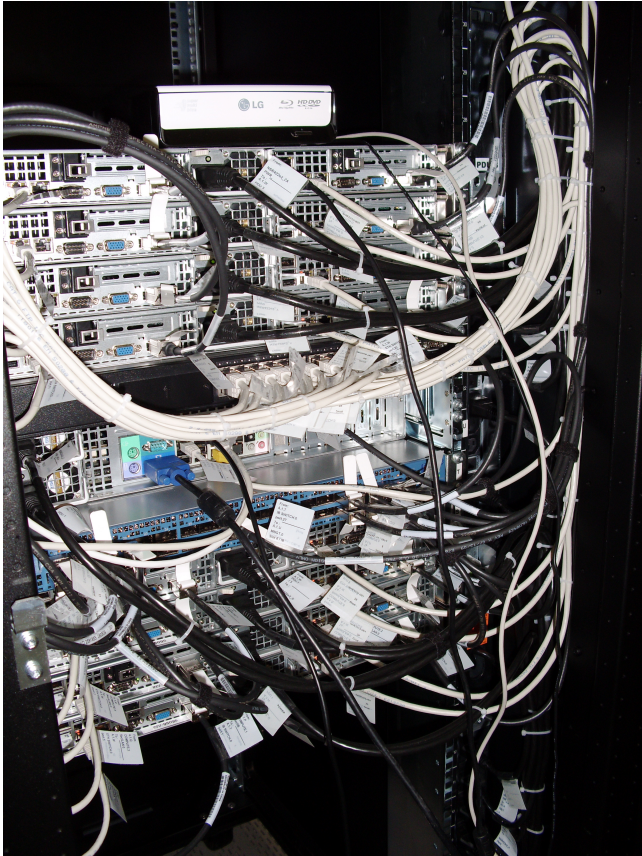


- strong coupling limit:
effective remainder (dimer)

- $|J_A| \gtrsim 0.5W$

Inbetween: no simple characterization + further sequential screening possible

Summary



- There are many interesting problems without the complications of the dark horse.
- Interaction with the environment important, but hard to model. Realistic interactions preferred.
- We should simulate a small quantum computer on a classical one.
- What about the anisotropic terms in the Hamiltonian?

Many thanks to my collaborators worldwide

- T. Glaser, Chr. Heesing, M. Höck, N.B. Ivanov, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum, O. Wendland (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); R.E.P. Wimpenny, E.J.L. McInnes (Man U, UK); L. Cronin, M. Murrie (Glasgow, UK); E. Brechin (Edinburgh, UK); H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France); M. Evangelisti (Zaragosa, Spain)
- J. Richter, J. Schulenburg (Magdeburg); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your
attention.

The end.

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