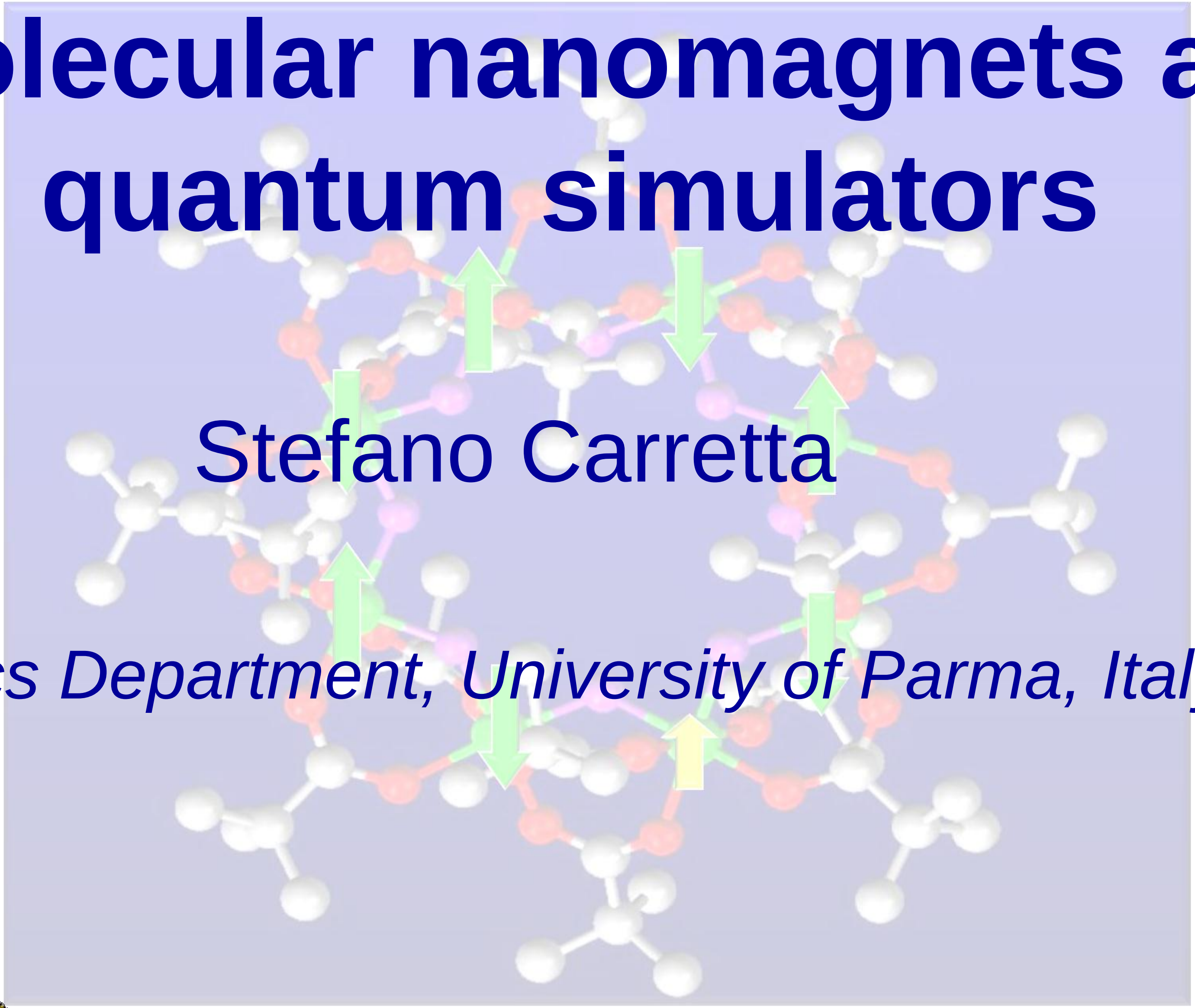
Molecular nanomagnets as quantum simulators



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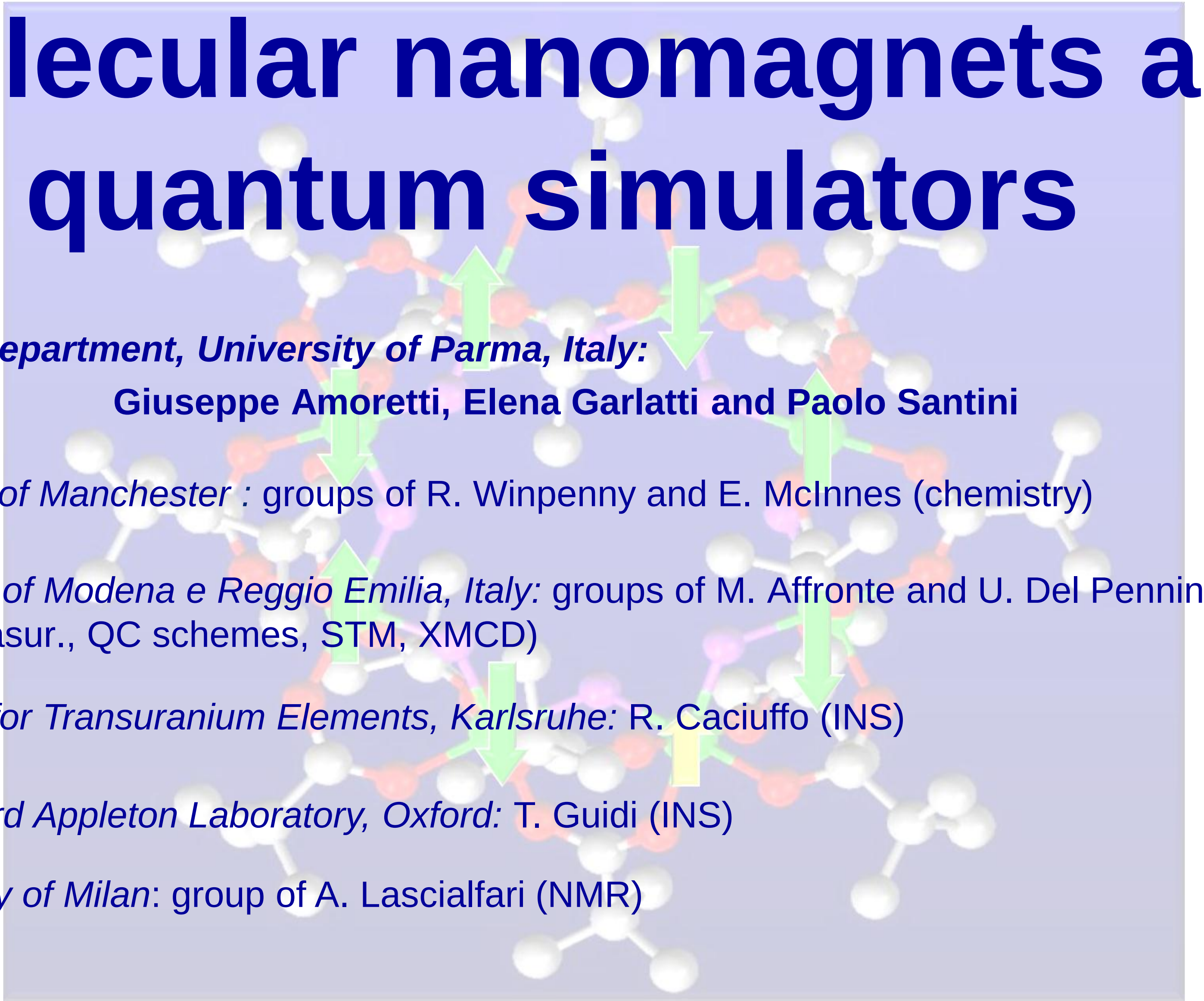
Molecular nanomagnets as quantum simulators



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-*University of Manchester :* groups of R. Winpenny and E. McInnes (chemistry)

-*University of Modena e Reggio Emilia, Italy:* groups of M. Affronte and U. Del Pennino (macr. measur., QC schemes, STM, XMCD)

-*Institute for Transuranium Elements, Karlsruhe:* R. Caciuffo (INS)

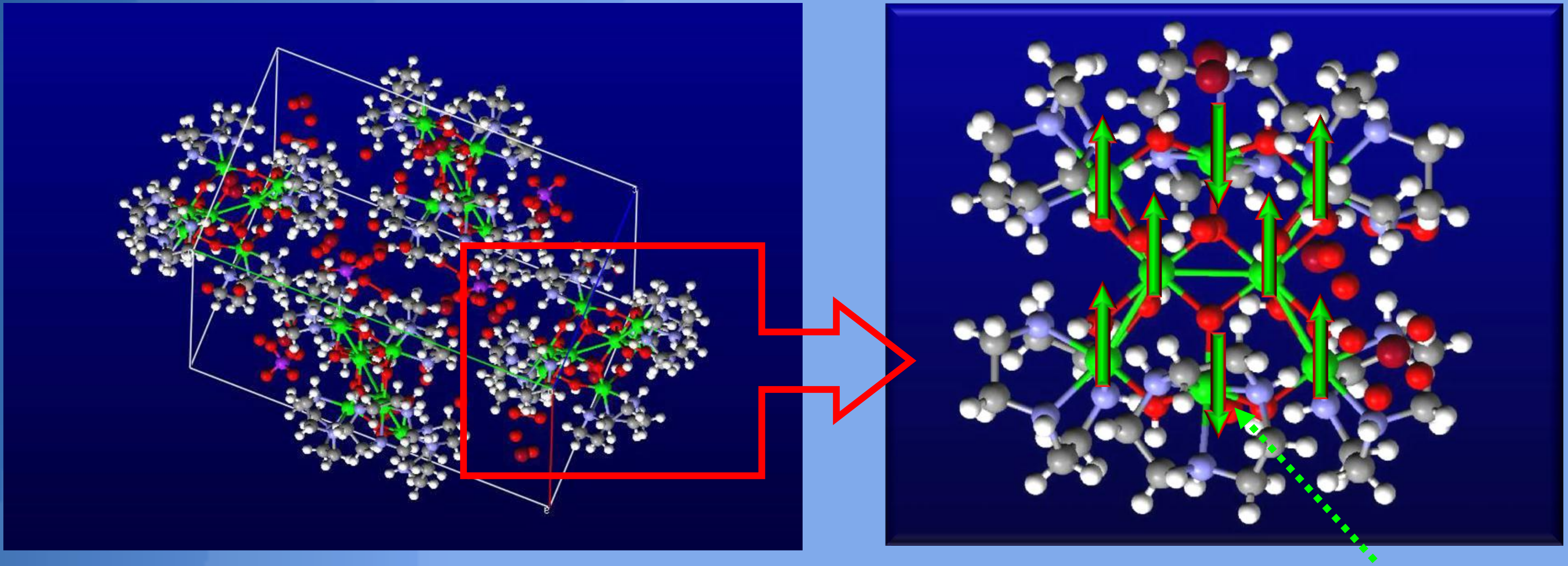
-*Rutherford Appleton Laboratory, Oxford:* T. Guidi (INS)

-*University of Milan*: group of A. Lascialfari (NMR)

Molecular Nanomagnets

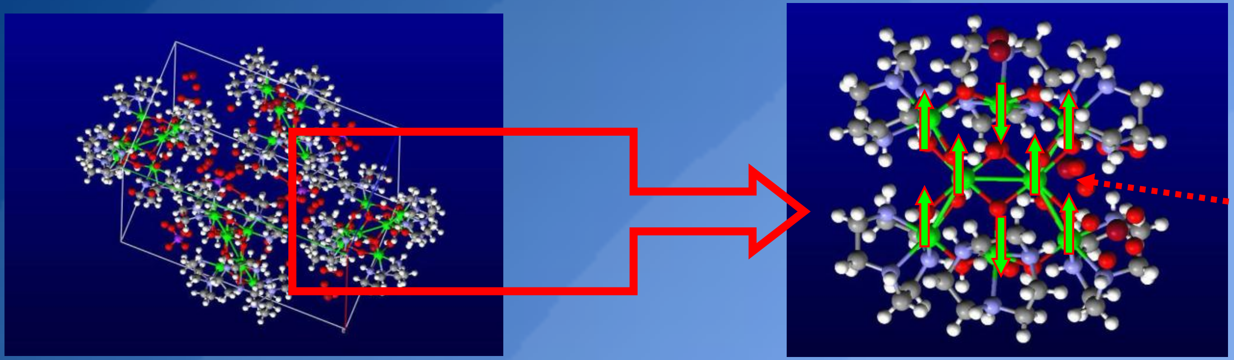
Organometallic molecules, in which the magnetic core is constituted by a small number of strongly exchange-coupled transition metal ions (3d) ions.

Molecules are arranged on a crystal lattice *(see, e.g., D. Gatteschi, R. Sessoli and J. Villain, Molecular Nanomagnets, Oxford University Press (2006))*.



$Fe_8O_2(OH)_{12}(tacn)_6]Br_8$

Fe^{3+} S=5/2

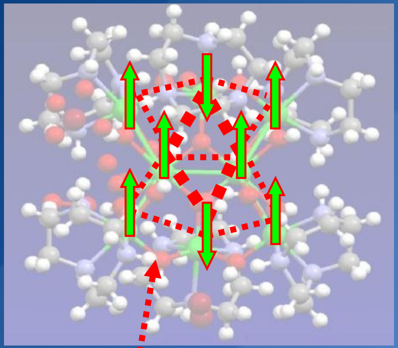


$H_{eff}(\mathbf{S}_1,\ldots\mathbf{S}_N)$

The main difference with respect to a typical magnetic compound is that here shells of organic ligands provide an effective **magnetic separation** between neighboring molecules. Hence, the crystal approximately behaves as a collection of **identical and non-interacting magnetic particles.** Single-molecule properties can be probed by bulk measurements.

Theoretical modeling : A magnetic molecule can modeled as a set of N spins interacting through an appropriate effective spin hamiltonian **$H_{eff}(S_1,\ldots S_N)$,** in which often the dominant term is the isotropic exchange interaction.

Microscopic description : spin Hamiltonian



$H_{eff}(\mathbf{S}_1,\ldots\mathbf{S}_N)$

$$H_{Heis} = \sum_{ij} J_{ij}\mathbf{s}_i \cdot \mathbf{s}_j$$

Isotropic exchange

Anisotropic terms

$$H_{CF} = \sum_i \sum_{\substack{k=2,4\\ q}} b_q^k(i) O_q^k(\mathbf{s}_i)$$

Crystal-field

$$H_{an} = \sum_{ij} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j$$

Anisotropic exchange and dipole-dipole interactions

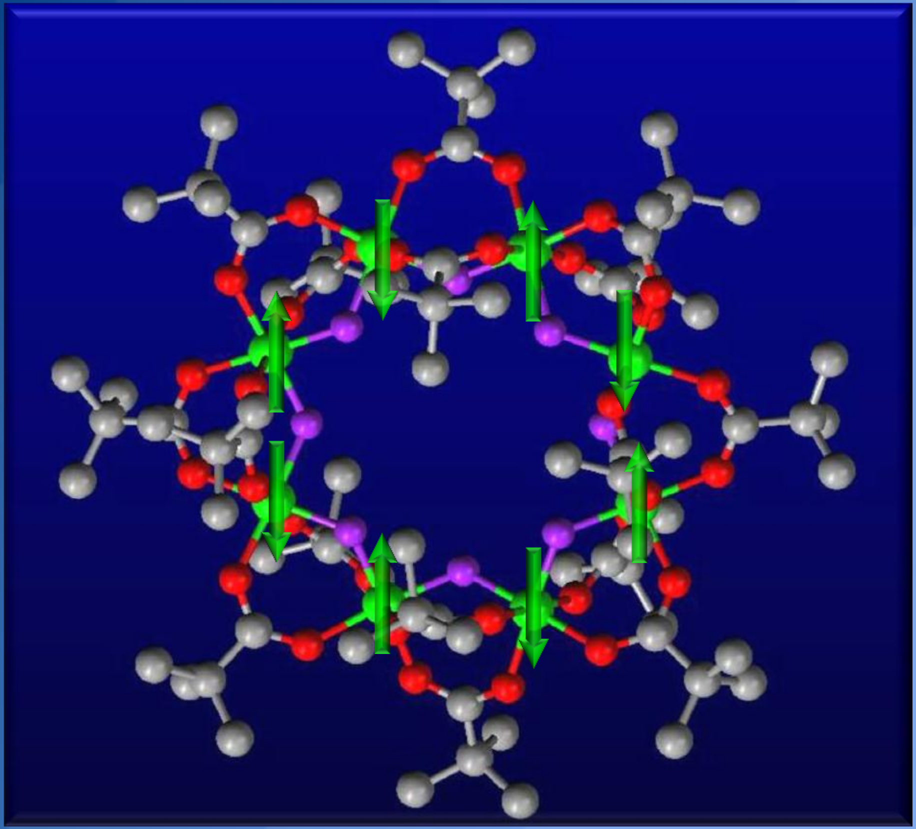
$$H_{DM} = \sum_{ij} \mathbf{G_{ij}} \cdot \left[\mathbf{s}_i \times \mathbf{s}_j\right]$$

Antisymmetric (DM) exchange

$$H_{Zeeman} = \mu_B \boldsymbol{B} \cdot \sum_i \underline{\underline{\boldsymbol{g}}}_i \cdot \mathbf{s}_i$$

Zeeman

Antiferromagnetic Rings (e.g., Cr_8)



-AF n.n. exchange interaction.

-Nonmagnetic S=0 ground state.

-Interesting for fundamental physics (e.g. Néel-vector tunnelling, quantum oscillations of the total spin.).

NVT: A.Chiolero and D. Loss, PRL 80, 169 (1998), S.C. + al. PRB 71, 184405 (2005), O. Waldmann et al., PRL 102, 157202 (2009).

QOTS: S. C.,et al., PRL 98, 167401 (2007), PRB 72, 060403(R).

-One ion can be replaced by a different ion (→ground state with S>0).

-Ni-substituted Cr_8 : S=1/2, a good candidate qubit.

Interest of molecular nanomagnets

Fundamental issues

- Tunable model systems for quantum phenomena (quantum tunneling, coherence, etc.), and to study microscopic magnetic interactions. Exact calculations are often possible.

Main potential applications

- High-density information storage

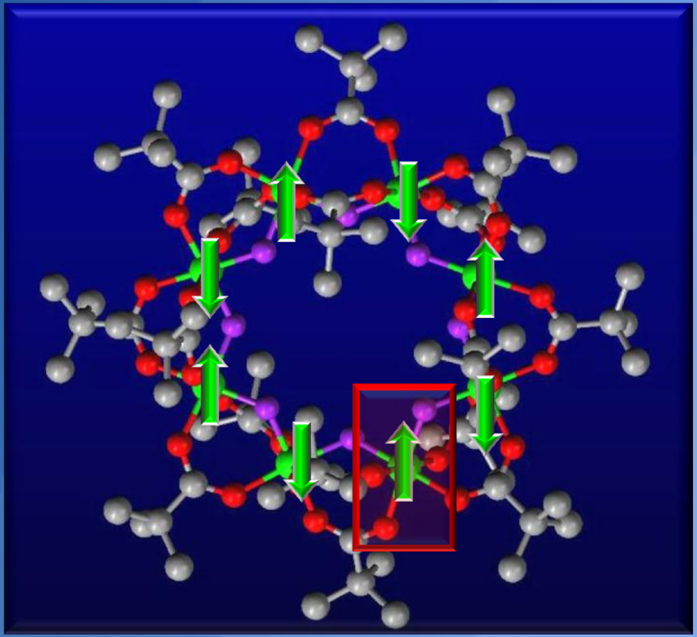
- Quantum computation and quantum information

- Magnetocaloric refrigerants

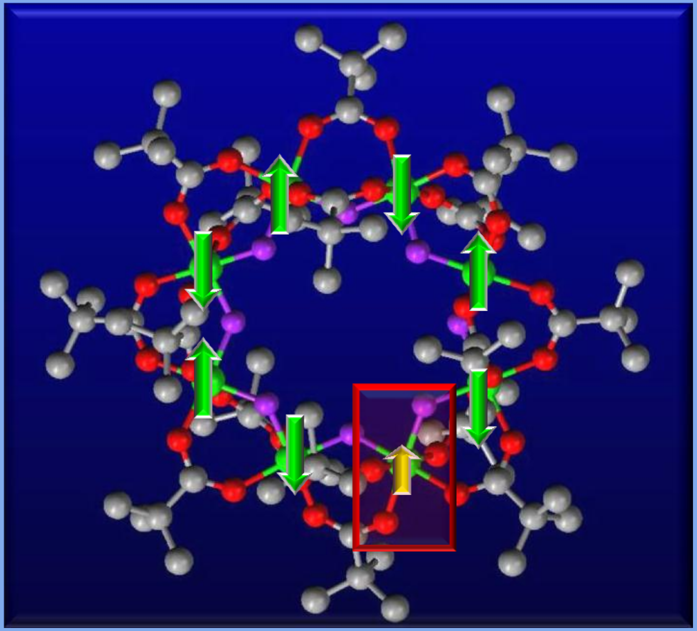
Magnetic molecules as qubits : Cr_7Ni

Magnetic molecules with a **(pseudo)-spin ½ ground manifold** are possible candidates as qubits. In particular, we have targeted **the heterometallic Cr_7Ni antiferro-magnetic ring** which appears to be an excellent candidate:

The idea of using magnetic molecules for quantum information processing has been initially proposed by D. Loss and coworkers, e.g. Nature 410, 789 (2001).



Cr_8



Cr_7Ni

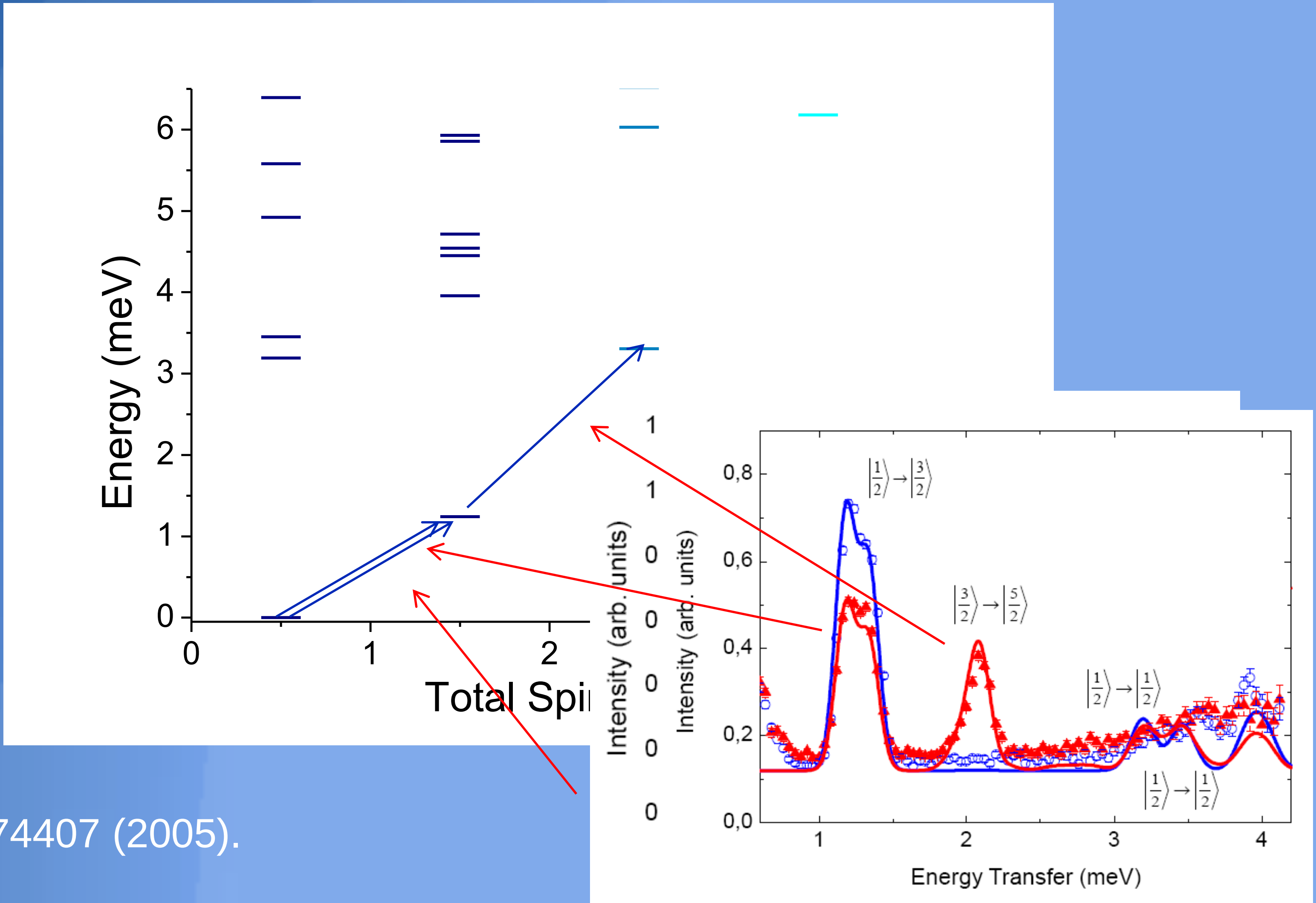
F. K. Larsen, et al., Angew. Chem. 42,1 (2003)

Singlet ground state, total spin S=0

Doublet ground state, total spin S=1/2

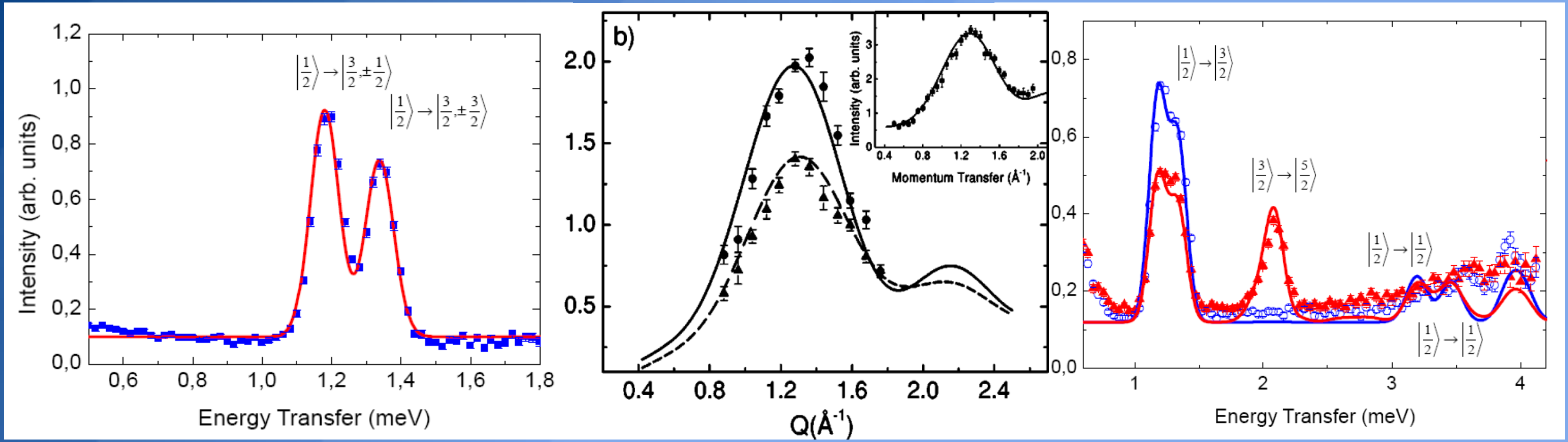
Heterometallic wheel Cr_7Ni

Isotropic exchange is the dominant interaction → The spectrum is composed of total-spin multiplets split by magnetic anisotropy



PRB **71**, 174407 (2005).

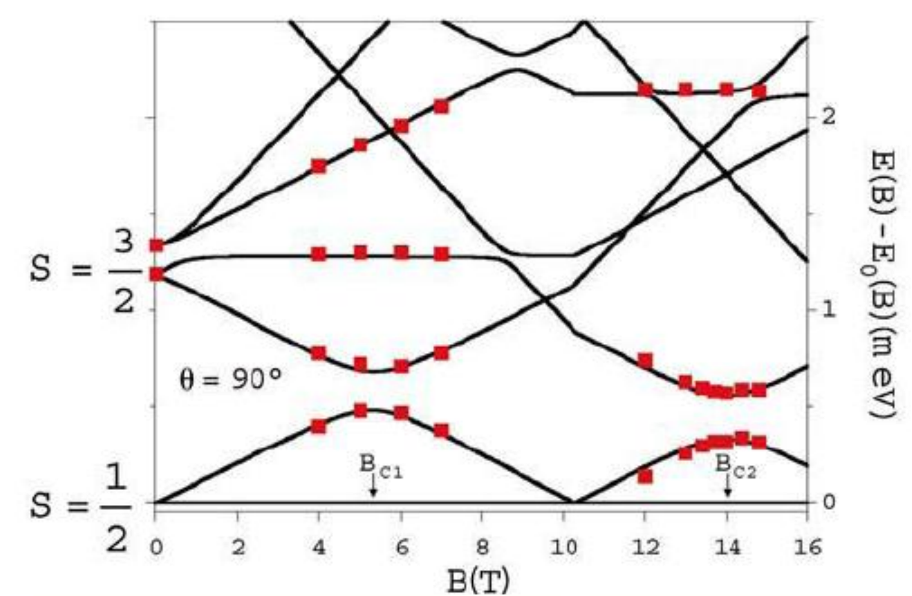
Heterometallic wheel Cr_7Ni

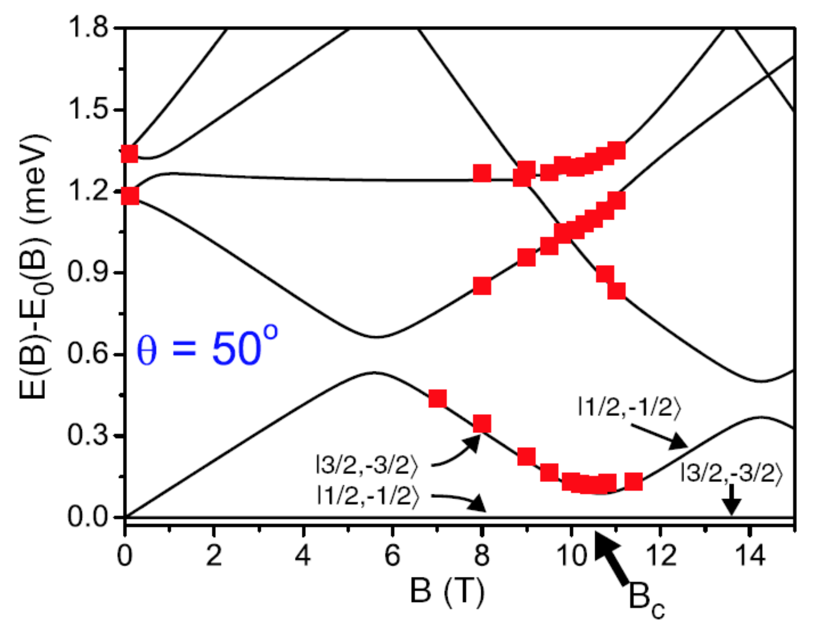


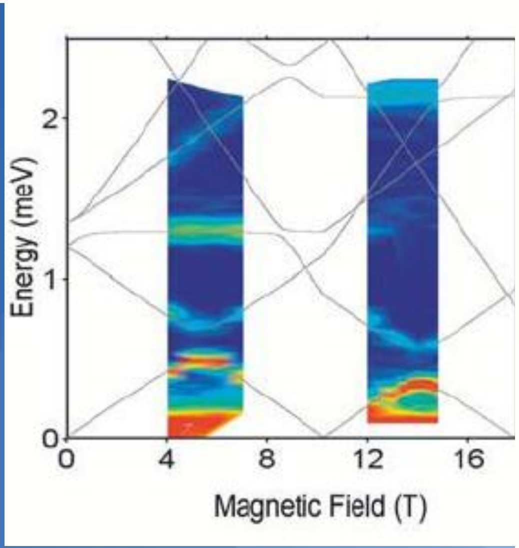
J(Cr-Cr)/meV	J(Cr-Ni)/meV	D(Cr)/meV	D(Ni)/meV
1.46	1.69	-0.03	-0.35

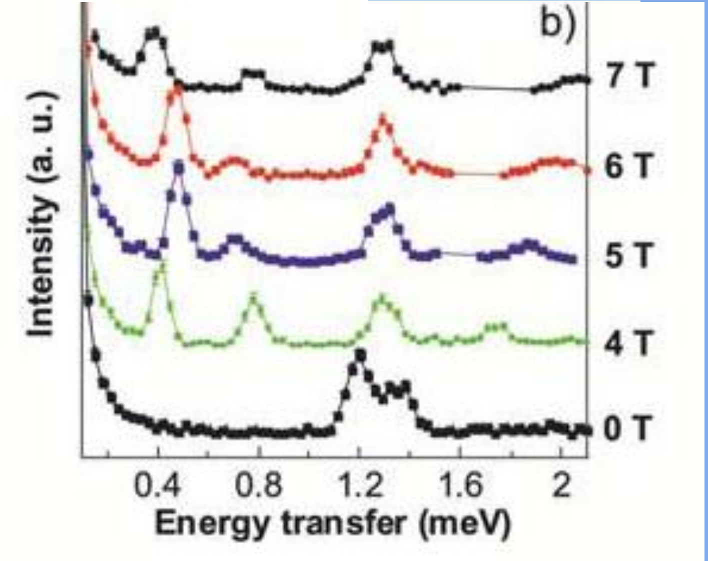
PRB **71**, 174407 (2005).

Inelastic neutron scattering studies of Cr_7Ni under magnetic field









PRL98, 167401 (2007)

Macroscopic measurements on Cr_7Ni

Magnetometry and specific heat measurements are very well reproduced too.

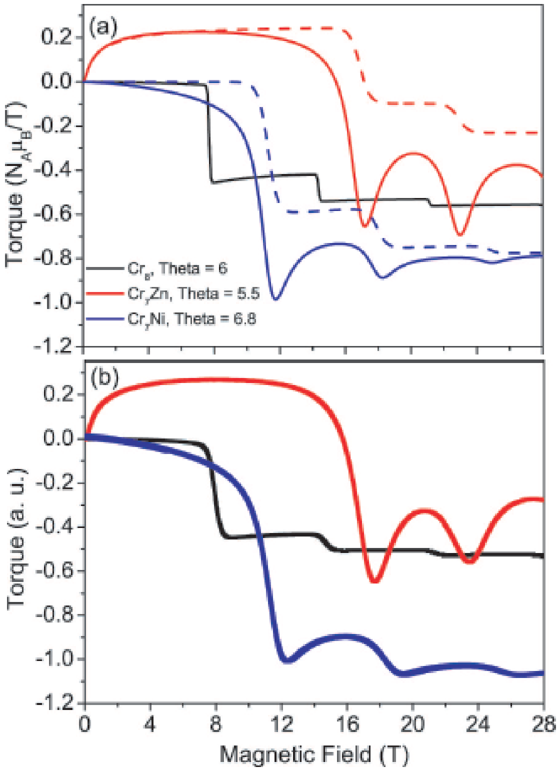
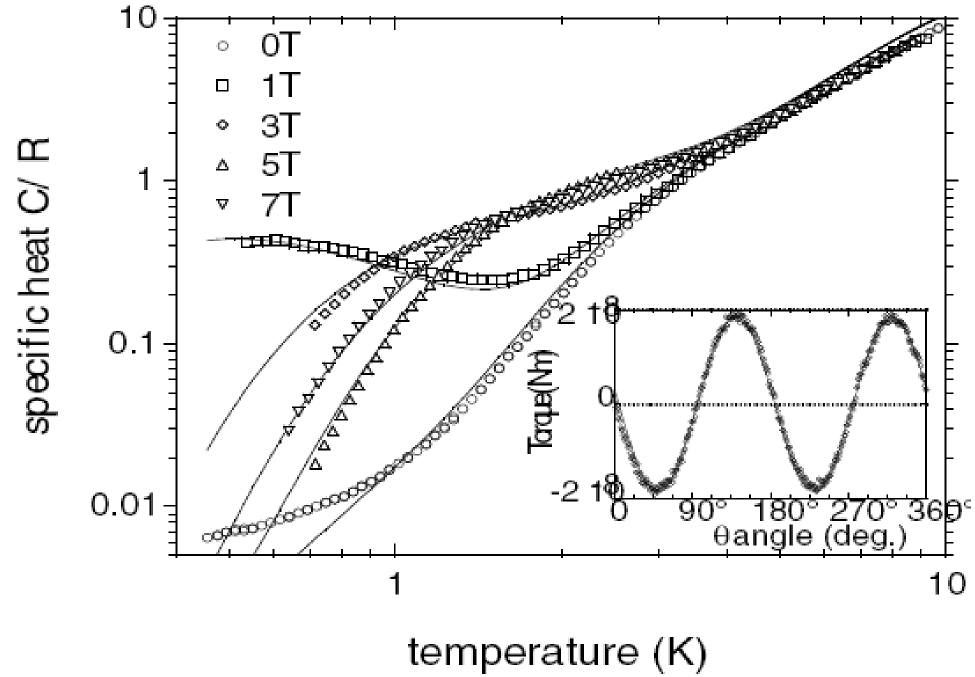


FIG. 2: (a): solid lines : calculated torque *vs* the applied field intensity B for Cr_8 ($T = 50$ mK), Cr_7Zn and Cr_7Ni ($T = 400$ mK). Dashed lines : the same for Cr_7Zn and Cr_7Ni with S-mixing forced to zero. (b): Experimental results for the same conditions as in (a).

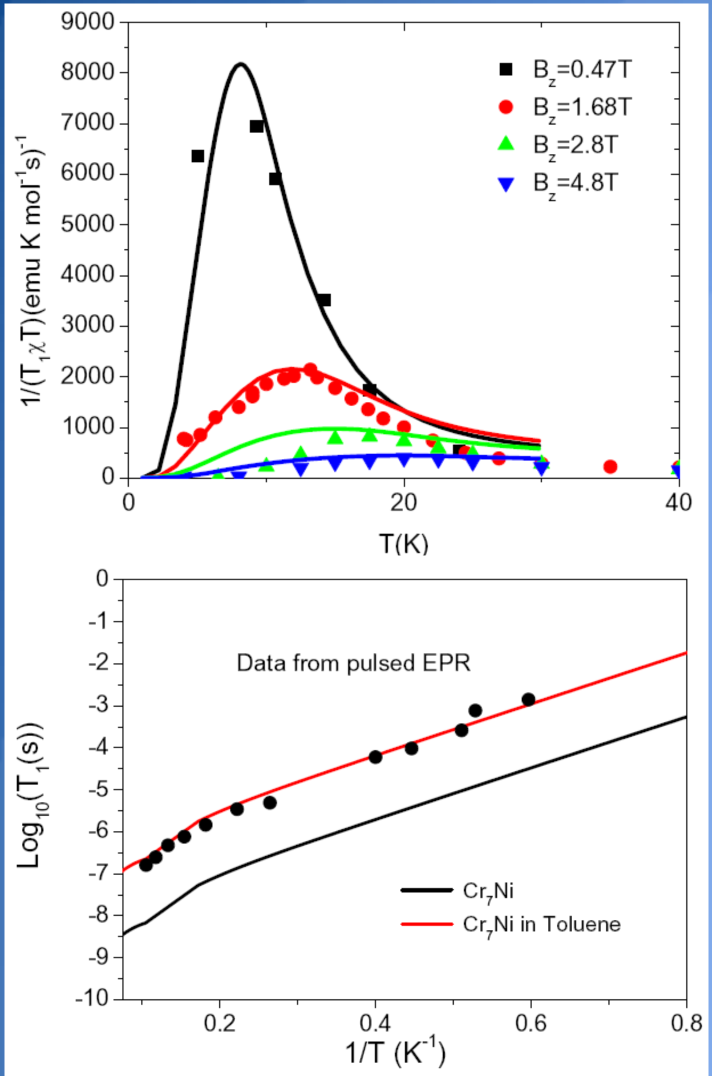
Torque, *PRB* ***72, 060403(R) (2005)***



Specific heat, *PRL* **94, 207208 (2005)**

Relaxation dynamics of Cr_7Ni: ^1H NMR

We have investigated phonon-induced relaxation of Cr_7Ni by modelling $1/T_1$ NMR and EPR measurements.



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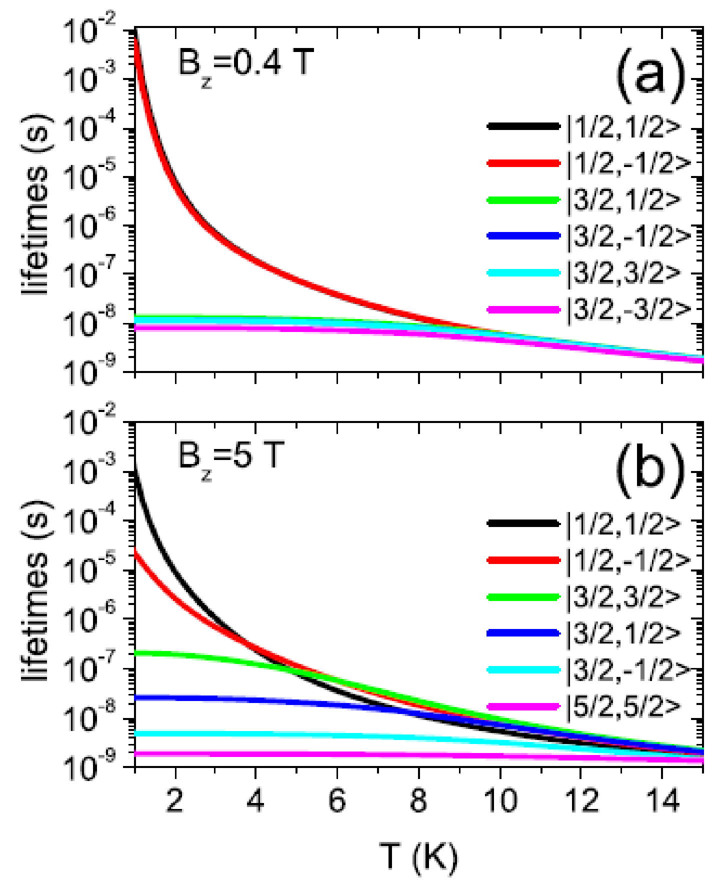


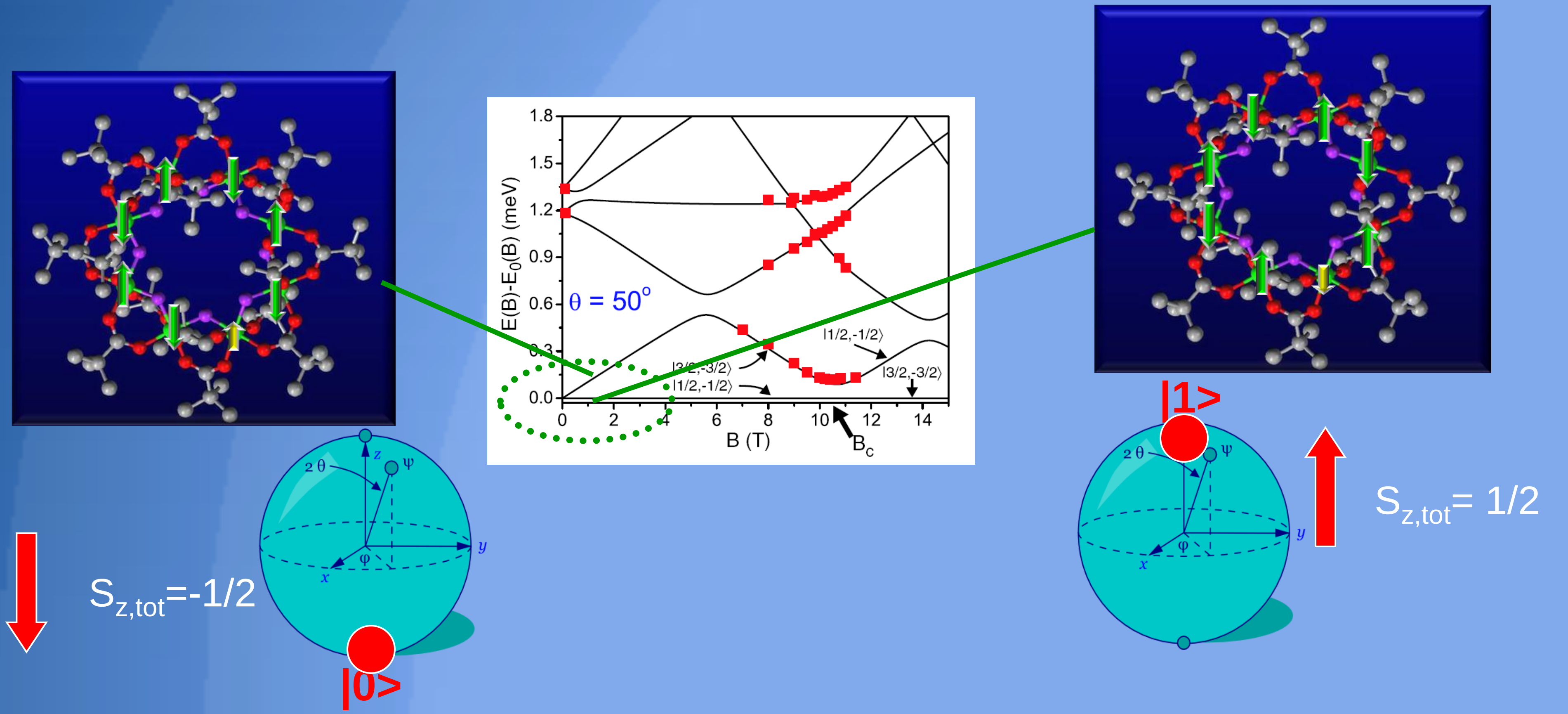
PRB **82**, 134403 (2010)

EPR from A. Ardavan et al., PRL 98, 057201 (2007)

Magnetic molecules as qubits : Cr_7Ni

The ground doublet is well separated from excited multiplets and practically behaves as a S=1/2 spin

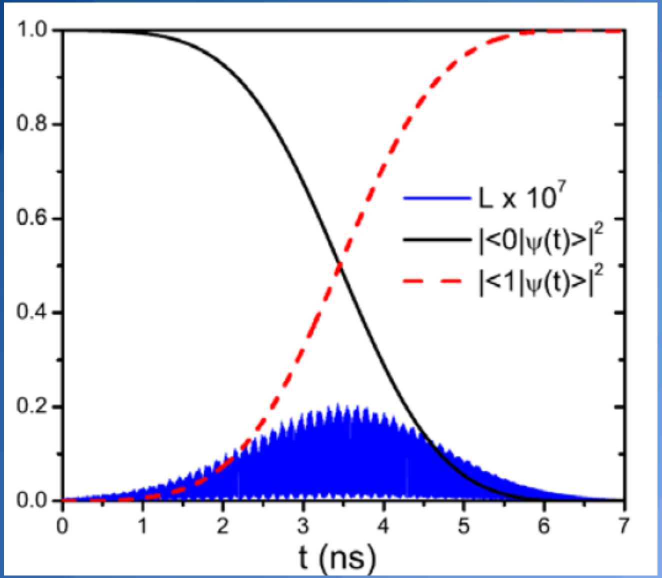
The two qubit states |0> and |1> are the two lowest-lying states (corresponding to a total spin along z of +1/2 or -1/2).
Any other qubit-state on the Bloch sphere (i.e., any possible superposition of |0> and |1>) can be produced by applying resonant em pulses of appropriate duration and polarization.



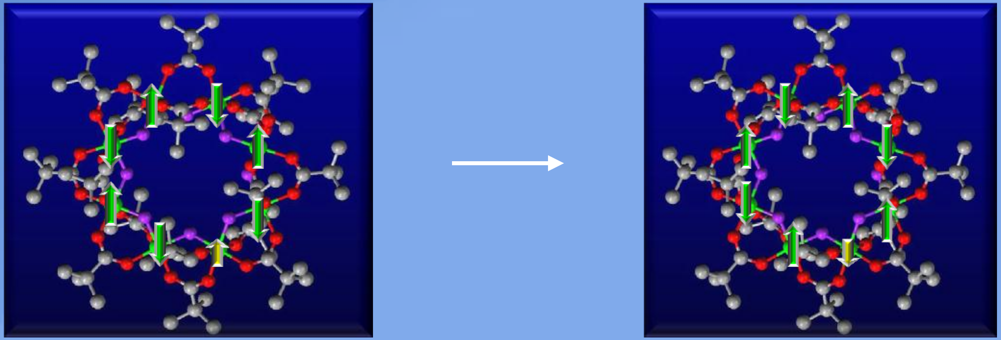
$S_{z,tot}$= 1/2

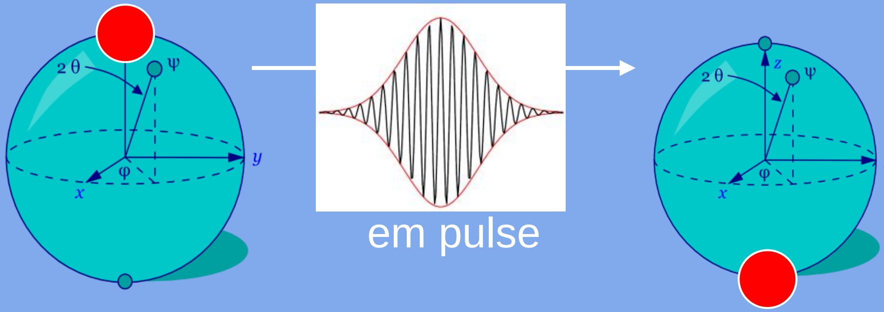
$S_{z,tot}$=-1/2

Numerical simulations of quantum gates



ONE-QUBIT GATE ("NOT" gate): *Simulated time evolution of the spin state of a single Cr_7Ni molecule, initially prepared in |0>, under the effect of a transverse magnetic field with a Gaussian temporal profile. The black, red, and blue lines correspond to $|c_0|^2$, $|c_1|^2$ and the "leakage" L (multiplied by a factor 10^7). The static field is B = 2 T.*





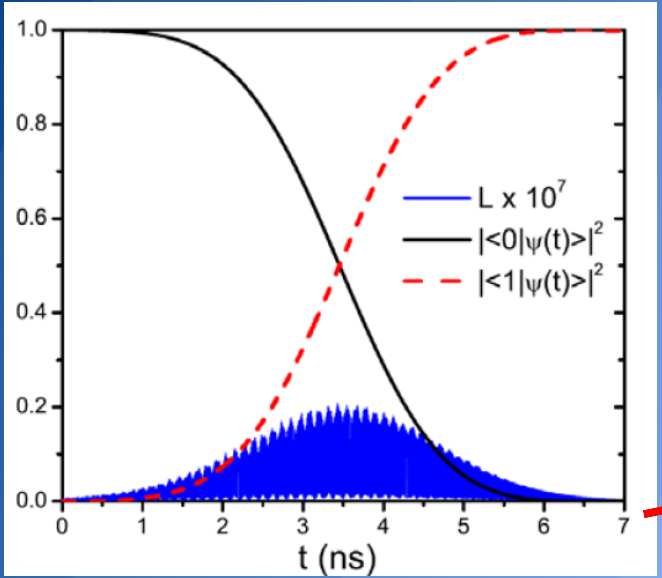
PRL 94, 207208 (2005).
PRL 94, 190501 (2005).
PRB 76 024408 (2007).

Single-qubit gates can be performed by e.m. pulses with negligible leakage L

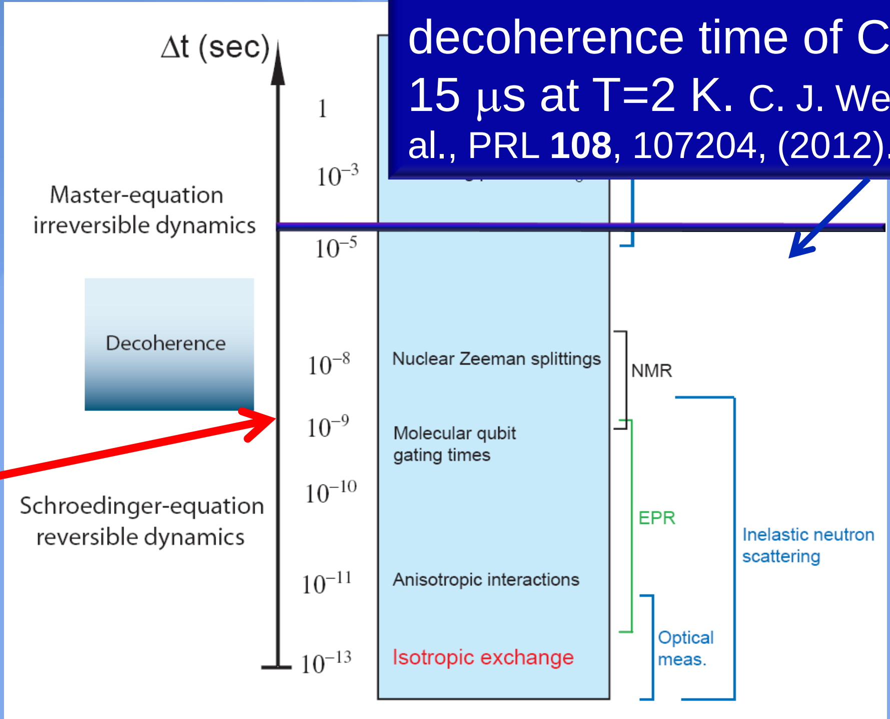
Excited states are not detrimental and represent a potential resource if deliberately populated

Numerical simulations of quantum gates

Actual measured decoherence time of Cr_7Ni: 15 μs at T=2 K. C. J. Wedge et al., PRL **108**, 107204, (2012).

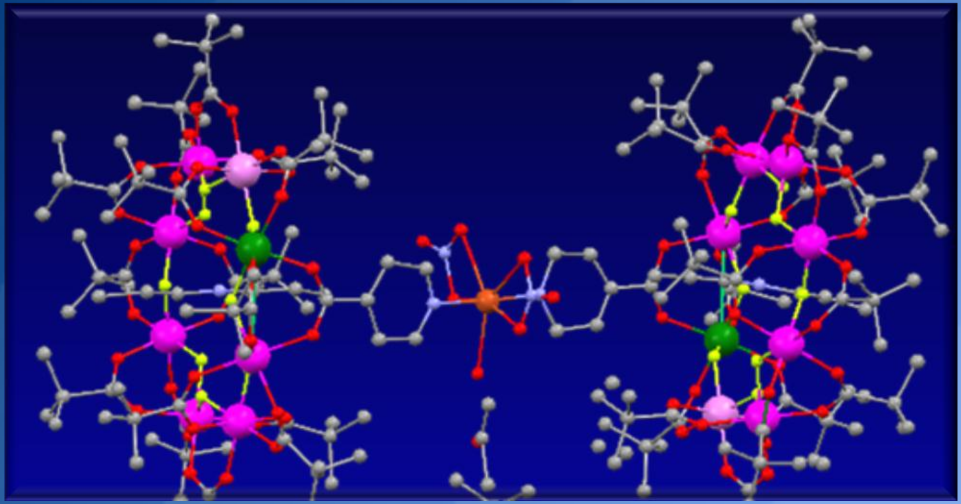


ONE-QUBIT GATE ("NOT" gate): Simulated time evolution of the spin state of a single Cr_7Ni molecule, initially prepared in |0>, under the effect of a transverse magnetic field with a Gaussian temporal profile. The black, red, and blue lines correspond to $|c_0|^2$, $|c_1|^2$ and the "leakage" L (multiplied by a factor 10^7). The static field is B = 2 T.

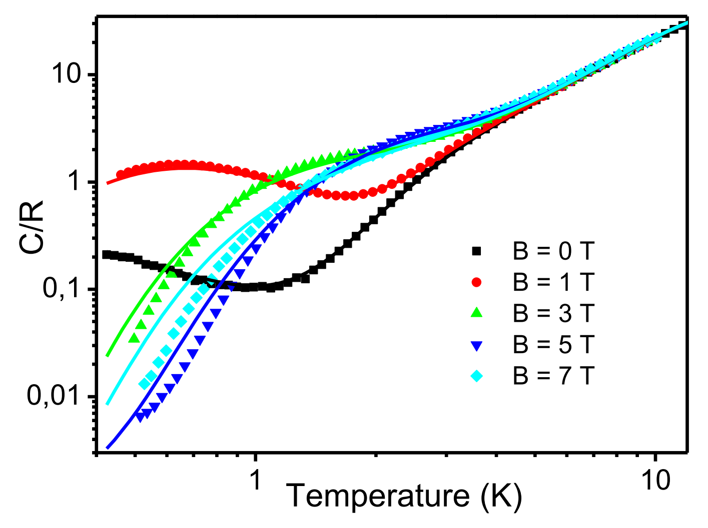


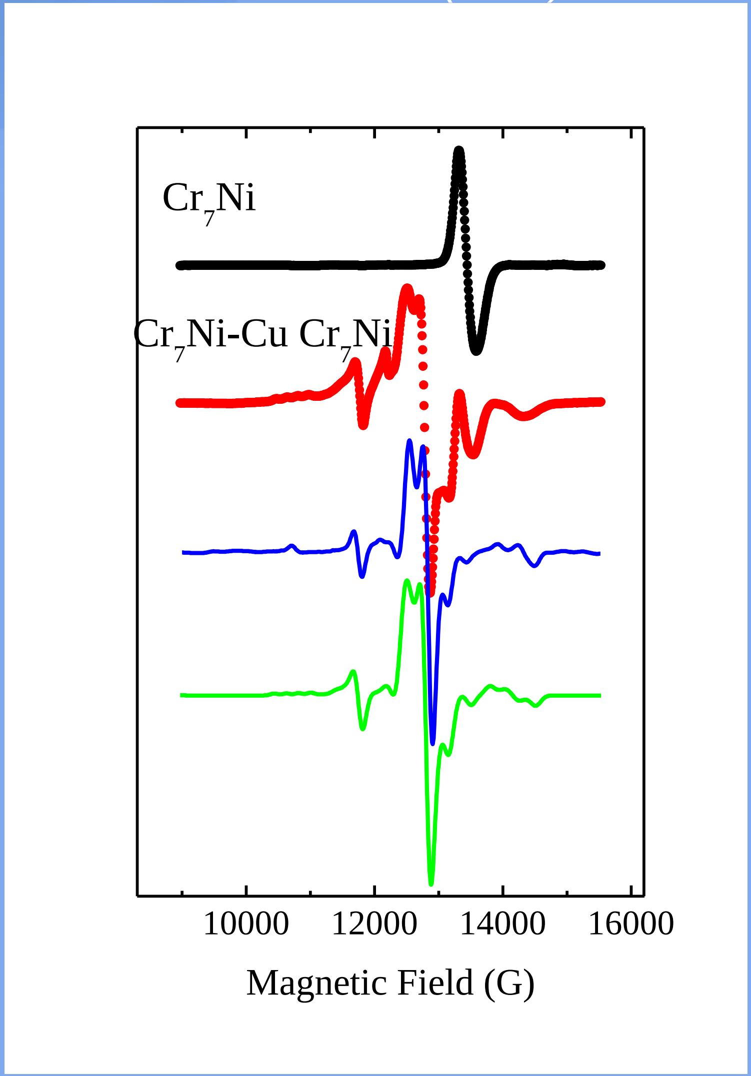
PRL 94, 207208 (2005).
PRL 94, 190501 (2005).
PRB 76 024408 (2007).

Gating times (a few ns) are much shorter than the measured decoherence time!



Nature Nanotech. 4, 173 (2009)

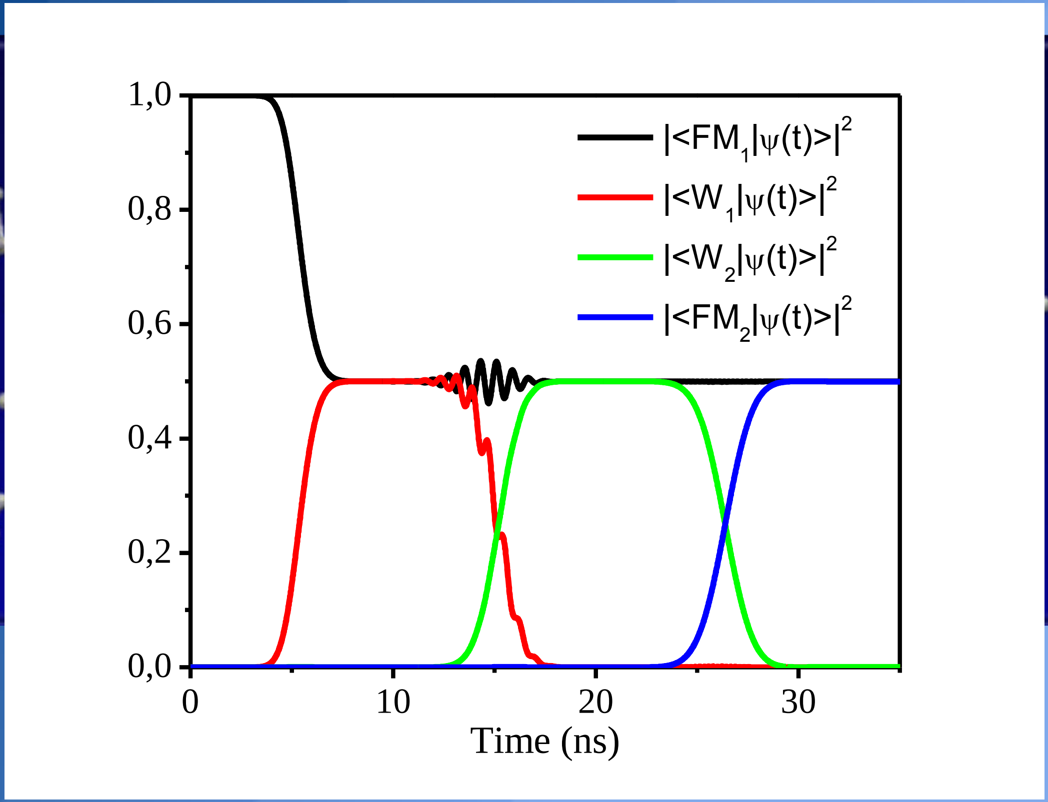


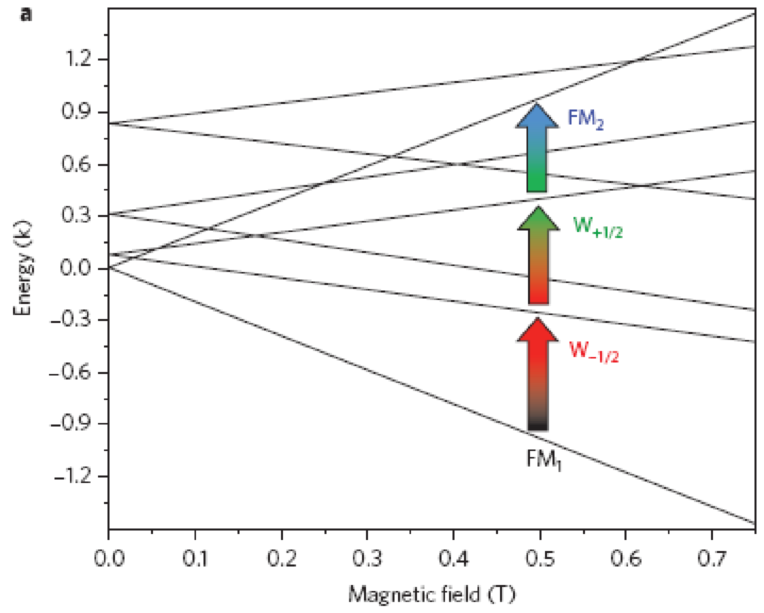


The analysis of specific heat and EPR data demonstrate the presence of a sizeable ferromagnetic ring-Cu exchange coupling.

Controlled multipartite entanglement

By a sequence of e.m. pulses it is possible to bring the trimer from its factorized (FM) ground state to a maximally-entangled **Greenberger–Horne–Zeilinger (GHZ) state**.





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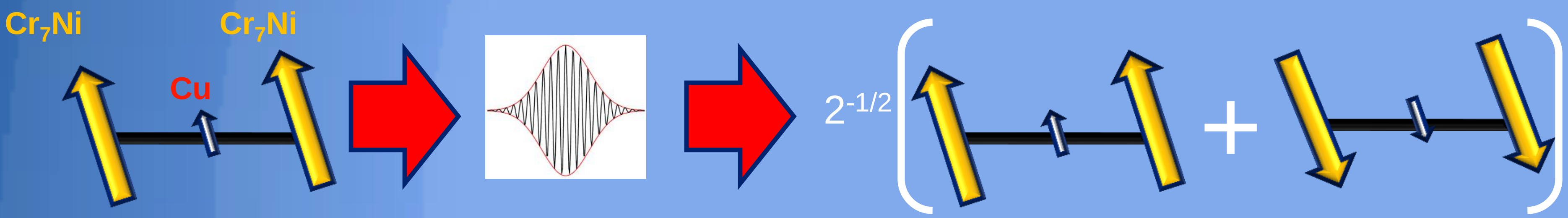
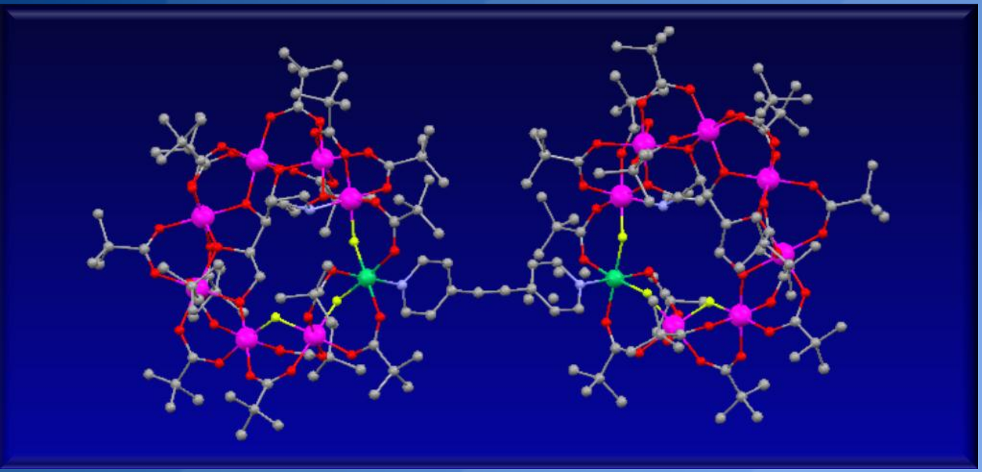
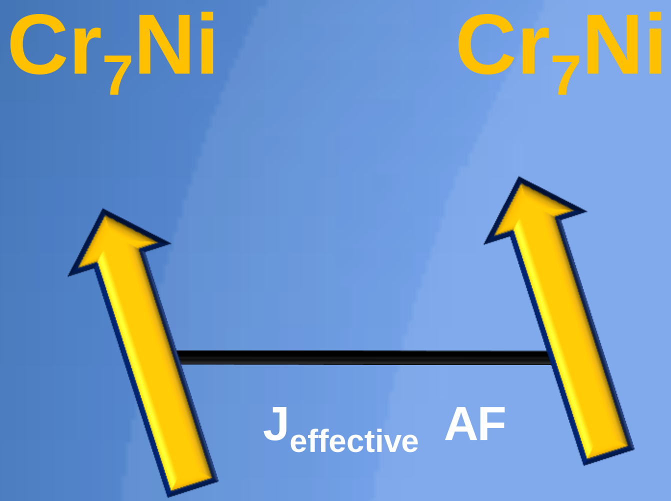


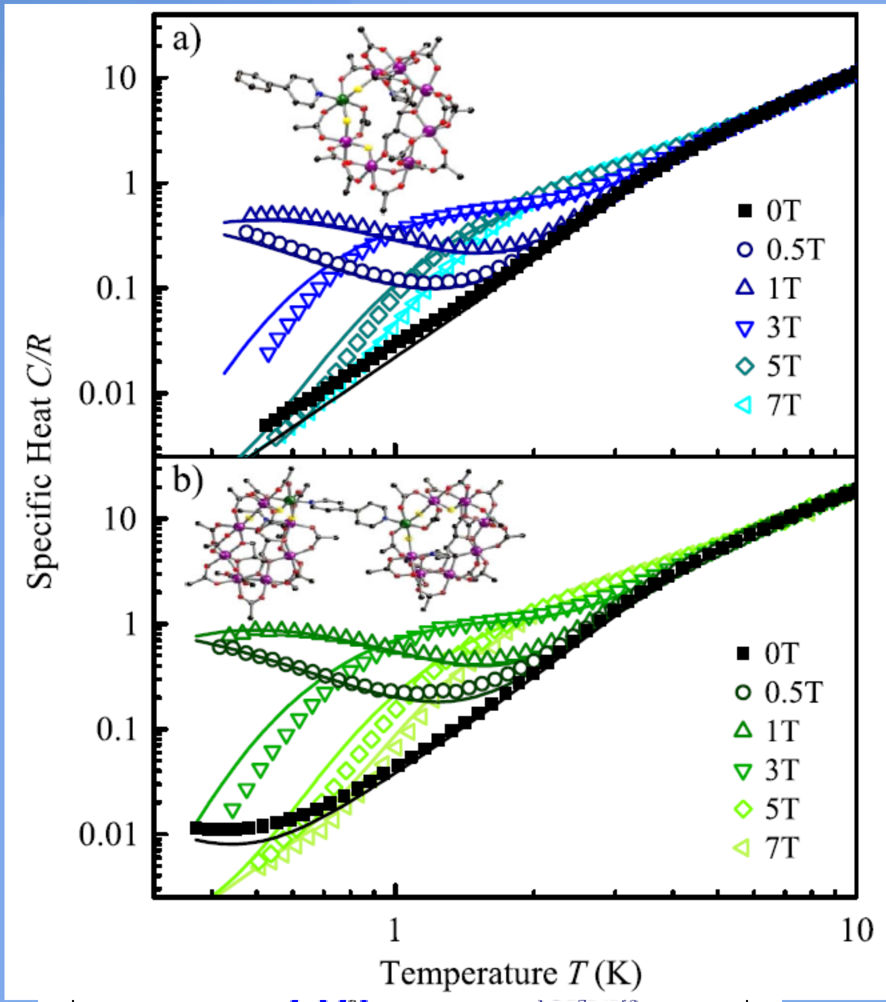
Entanglement in coupled antiferromagnetic Cr7Ni rings

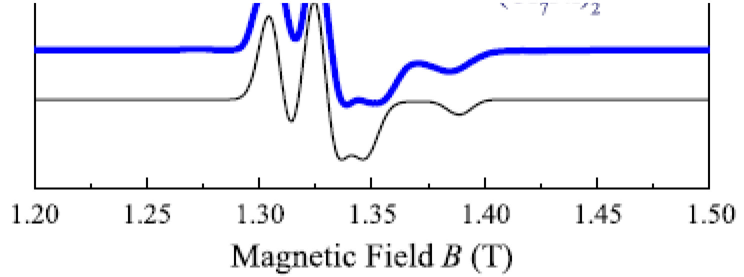




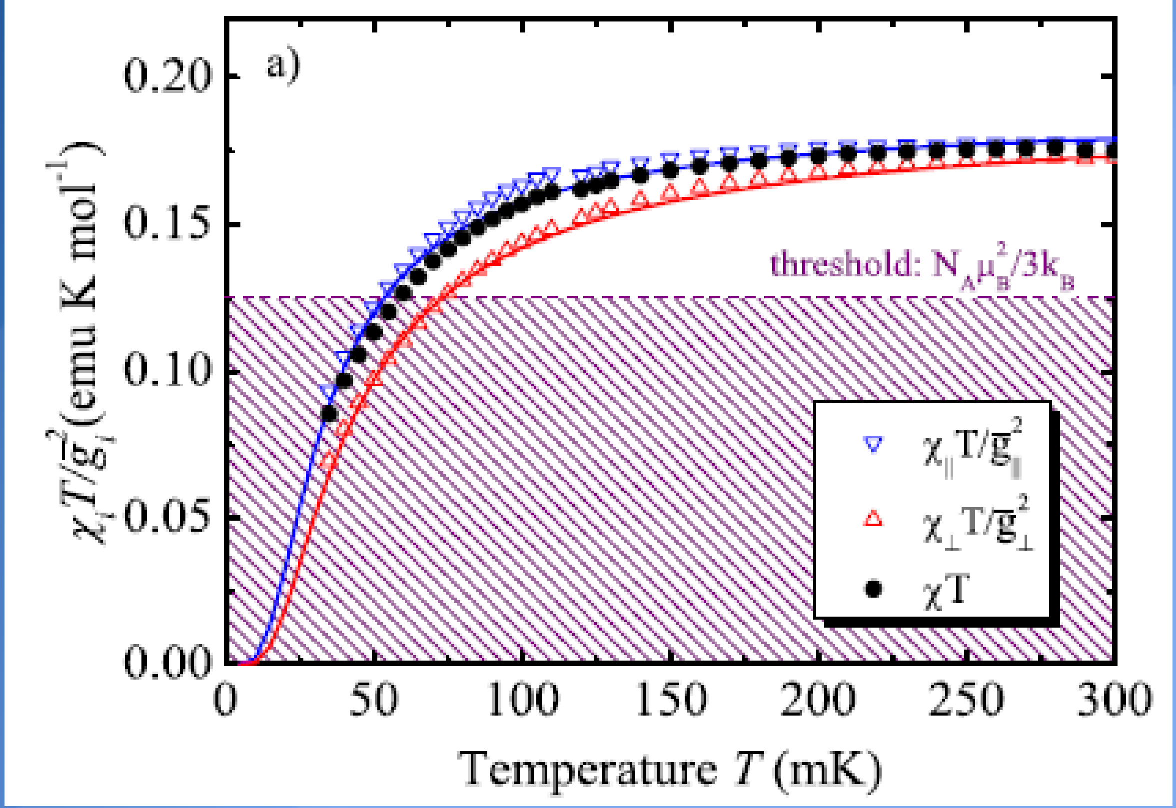
Cr_7Ni **Cr_7Ni**

$J_{effective}$ AF





PRL 104, 037203 (2010)



For a system of exchange-coupled spins the value of the magnetic susceptibility, averaged over three orthogonal directions, represents an entanglement witness:

$$\sum_\beta \chi_\beta T/\bar{g}_\beta^2 < N_A \mu_B^2/k_B$$

For T< 50 mK the density matrix of the two effective spins S=1/2 is non-factorizable, there is entanglement between the two rings.

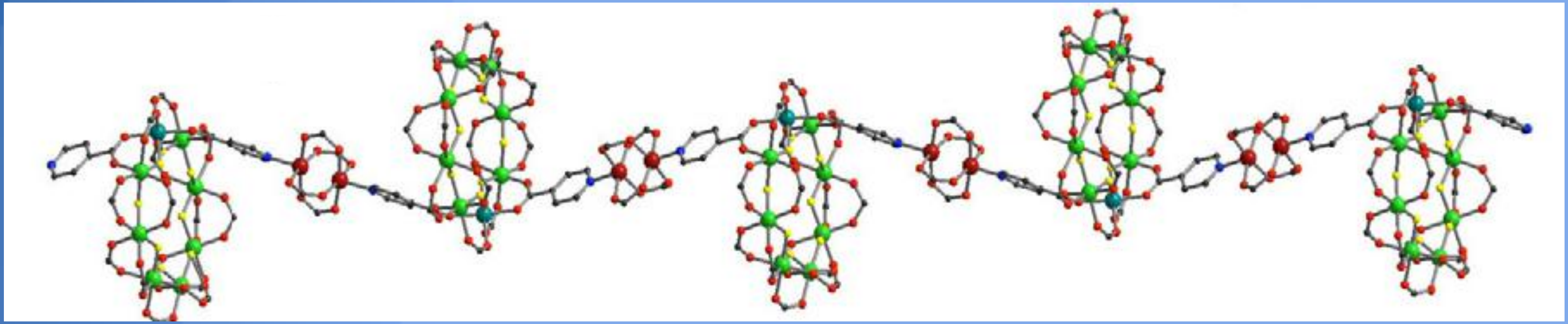
PRL 104, 037203 (2010)

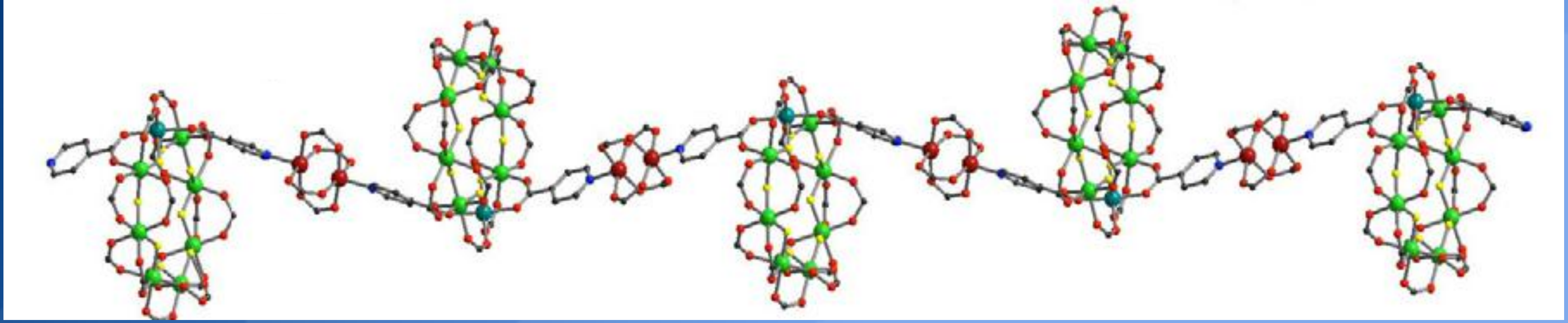
Molecular nanomagnets as quantum simulators

The simulation of quantum systems by a classical computer is intrinsically inefficient because the required number of bits grows exponentially with the system size.

QUANTUM SIMULATORS: encode the information in a hardware which operates according to quantum mechanics and whose dynamics can be controlled to mimic the evolution of the target system.

IDEA: using a chain of molecular qubits as a quantum simulator





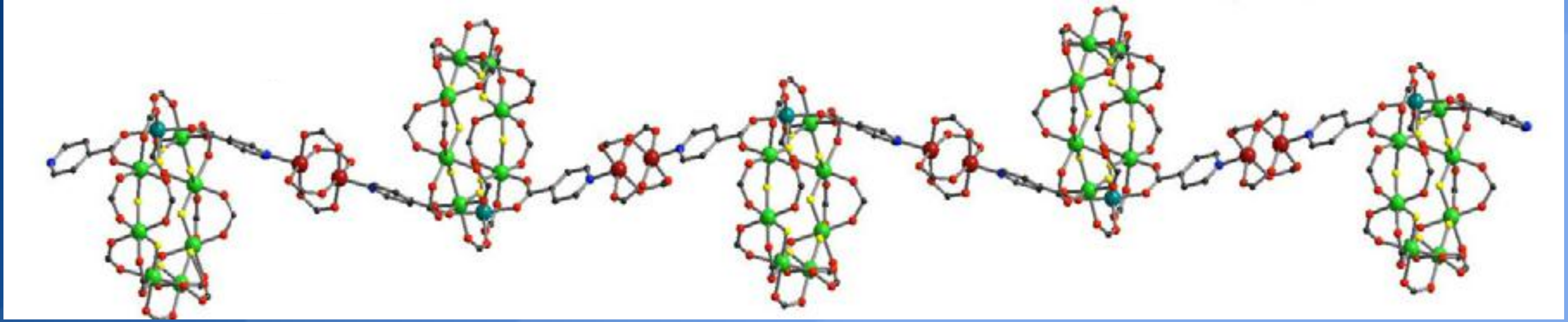
Use a sequence of uniform em pulses to simulate the time evolution of **s = ½ or s = 1 chains and fermionic systems**.

Three-step procedure:

1) The target Hamiltonian is mapped onto a one-dimensional hamiltonian describing interacting spin ½.

2) The states of each ½ spin are mapped onto the states of a qubit

3) The time evolution is simulated by exploiting a suitable sequence of uniform em pulses.



Quantum simulation of a spin-1/2 chain

(e.g., Transverse Field Ising Model)

$$H = \lambda \sum_i s_{iz}\, s_{(i+1)z} + b\sum_i s_{ix} = H^{(2)}{}_{even} + H^{(2)}{}_{odd} + H^{(1)}$$

Here the two states of each qubit directly encode the two states of each spin, and we would like the wavefunction of our chain of qubits to evolve as that of the TIM.

The hardware Hamiltonian is very different from the Transverse Field Ising Model. How we can exploit our qubits to perform the simulation?

We approximate the time-evolution operator of the TIM by the Trotter-Suzuki formula

$$U(t) = e^{-iHt} \simeq \left[e^{-iH^{(2)}_{\mathrm{odd}}\tau} e^{-iH^{(2)}_{\mathrm{even}}\tau} e^{-iH^{(1)}\tau} \right]^n$$

For very small τ the Zeeman (H_1) time evolution occurs independently of the Ising evolution (H_2), which in turn can be factored in even- and odd-bond contributions.

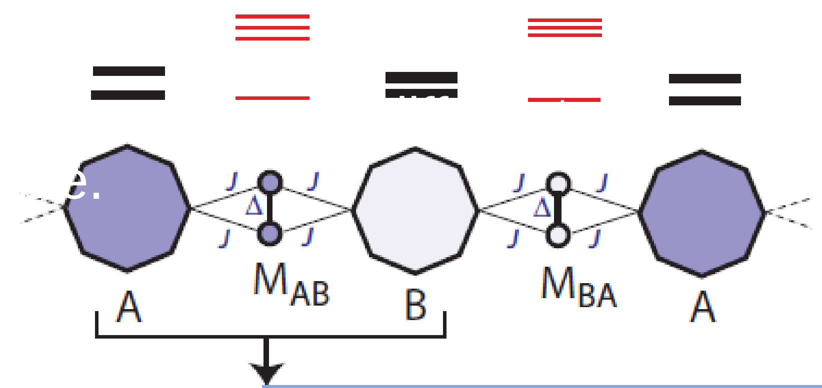
- During the Zeeman evolution qubits behave as noninteracting units evolving in the same way and in parallel.
- The Ising terms requires a two-body evolution, in which each pair of qubits evolves in the same way, and independently of all the others.

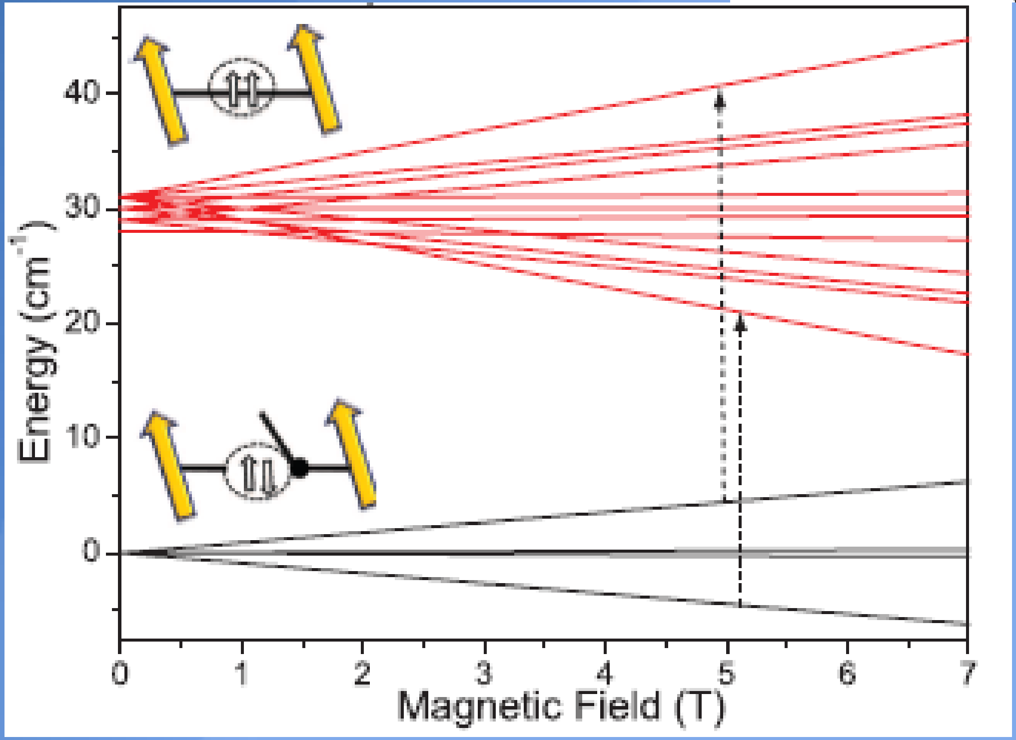
⇒ some kind of switchable interaction between adjacent qubits is needed.

The effect of a switchable coupling can be obtained by inserting an AF dimer between neighboring qubits

Turning on and off a physical exchange inte

molecular qubits on a ns timescale is unfea e.





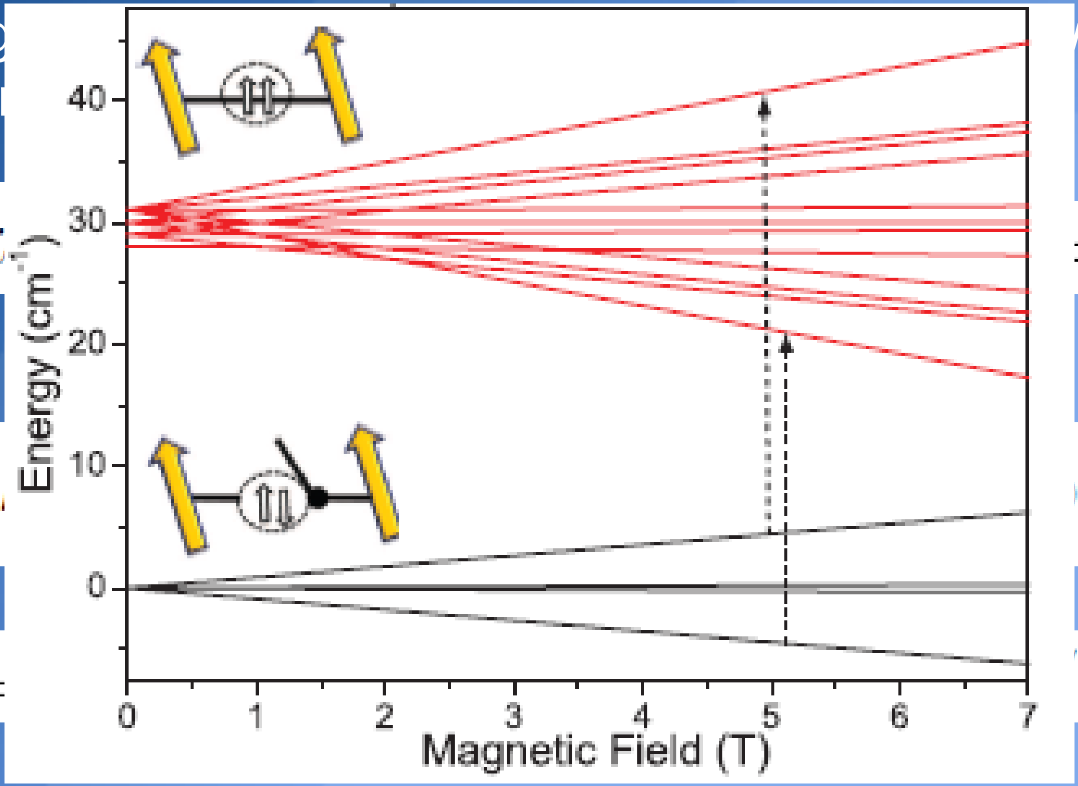
When the dimer is in the *S* = 0 singlet, the qubits behave as non-interacting. In higher-lying levels the dimer is in the *S* = 1 triplet and the levels are split by the non vanishing *J*.

These splitting … o qubits evolve as
that of two spi…

$h^{(2)} = \kappa$ … $= x, y, z.$

$\exp(-i$ … $u_{2\beta}]^{\dagger}$

where $\Lambda =$ … $^{2}, \; u_z = I.$



u_α corresponds to a single-qubit rotation, and can be implemented through an em pulse resonant with the Zeeman gap

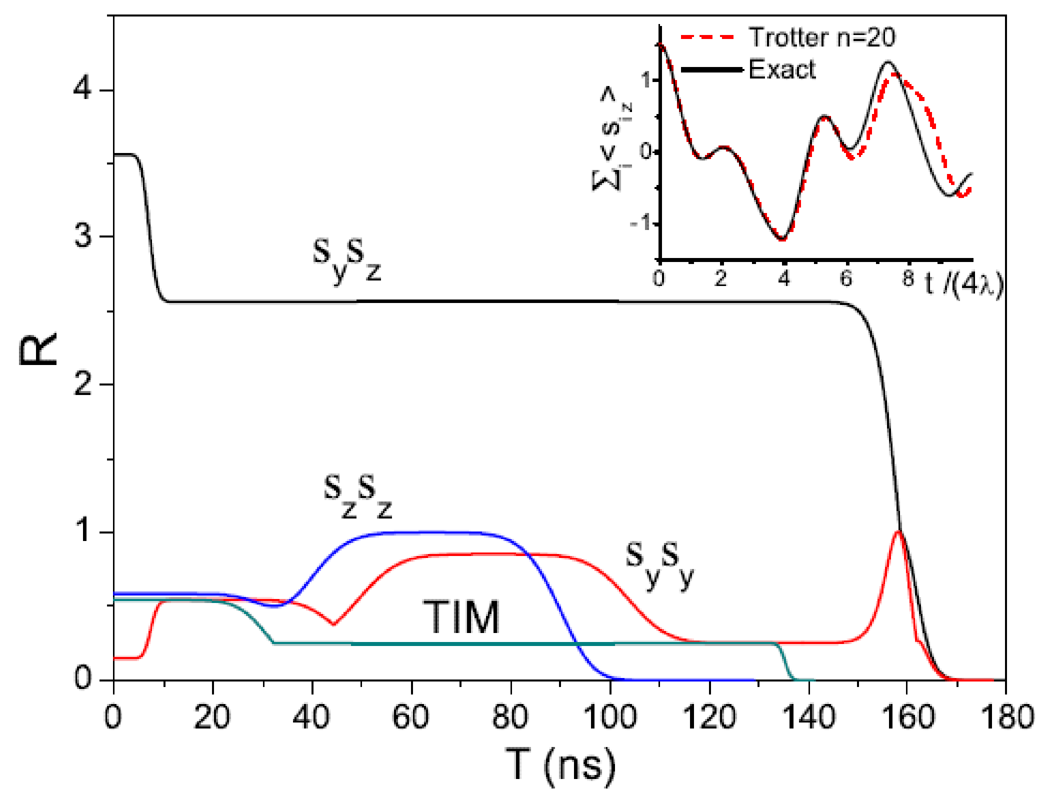
The two-qubit evolution $e^{-i\Lambda\tau}$ can be implemented through two simultaneous π pulses, resonant with the gaps indicated by arrows, followed by a repetition of the two pulses that bring the dimer back to its singlet ground state.

PRL 107, 230502 (2011)

These splittings can be exploited to make the state of the two qubits evolve as that of two spin ½ experiencing a physical interaction

$$h^{(2)} = \kappa s_{1\alpha} s_{2\beta}$$

$$\alpha, \beta = x, y, z.$$



T is the actual operation time of the hardware

At the end of the pulse sequence R vanishes. The state of our qubits matches the evolved state of the target Hamiltonian

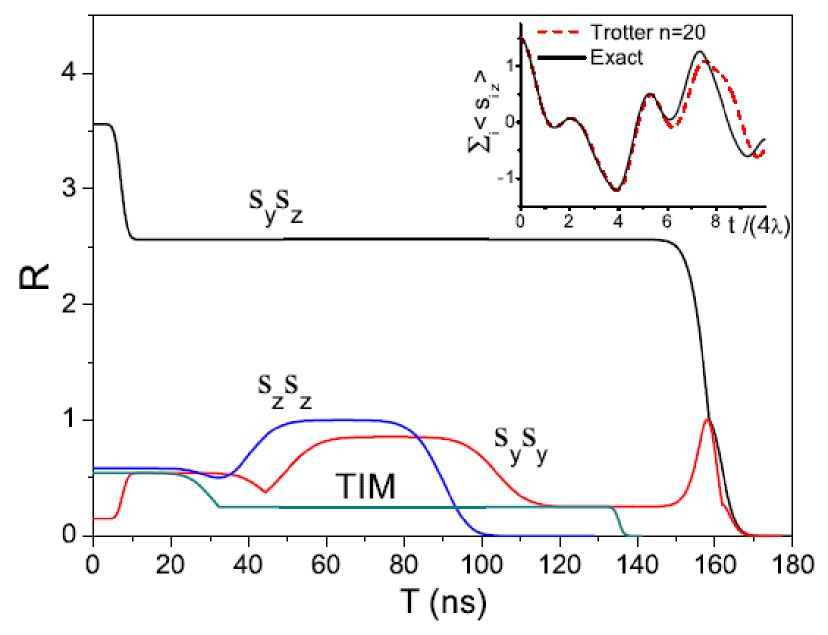
Much shorter than the expected decoherence time

R measures the deviation from the target evolution operator

$$R = max_{i,j} |\tilde{U}_{ji} - U_{ji}(\tau)|^2$$

$$\tilde{U}_{ji}(T) \equiv \langle \psi_j | \psi_i(T) \rangle$$

PRL 107, 230502 (2011)



Exploting ***uniform em pulses*** a NN s=1/2 AB Hamiltonian can be simulated

$$H = H_{odd} + H_{even} = \sum_{\text{odd } i} V^{(2)}_{odd}(i,i+1) + V^{(1)}_{odd}(i) + \sum_{\text{even } i} V^{(2)}_{even}(i,i+1) + V^{(1)}_{even}(i)$$

- The simulation **time does not depend on the lenght** of the chain
- Possible proof-of-principle experiment: simulation of TIM on a trimer

This evolution is witnessed by oscillations of the magnetization whose frequencies are set by the energy gaps of the TIM.

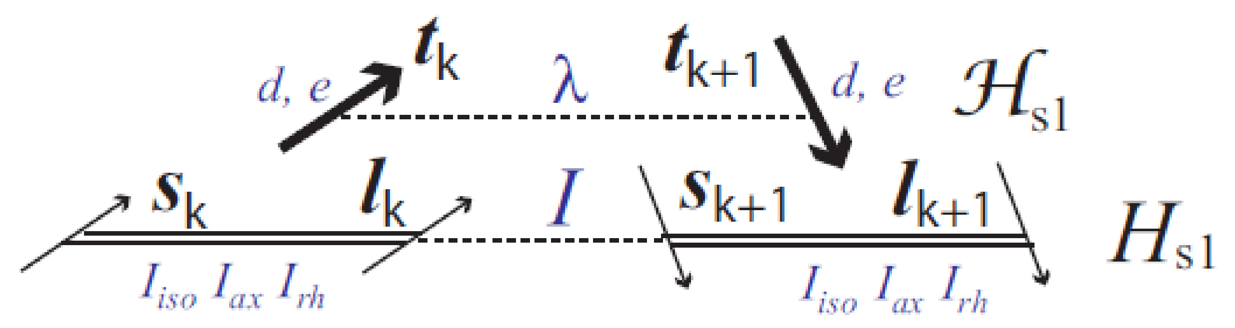
TIM evolution brings the system from a factorized FM initial state to multipartite entangled ones.

Simulating $S = 1$ *spins*

A chain of spins one ($\mathbf{t}_k$) with NN exchange interactions and single-spin crystal-field anisotropy:

$$\mathcal{H}_{\mathrm{s1}} = \lambda \sum_{k=1}^{N} \mathbf{t}_k \cdot \mathbf{t}_{k+1} + \sum_{k=1}^{N} [d\, t_{kz}^2 + e(t_{kx}^2 - t_{ky}^2)]$$

The dynamics of a spin-1 chain is equivalent to that of a dimerized spin-1/2 chain with twice the number of spins, provided one of the two isotropic exchange constant (I_{iso}) is ferromagnetic and dominant.



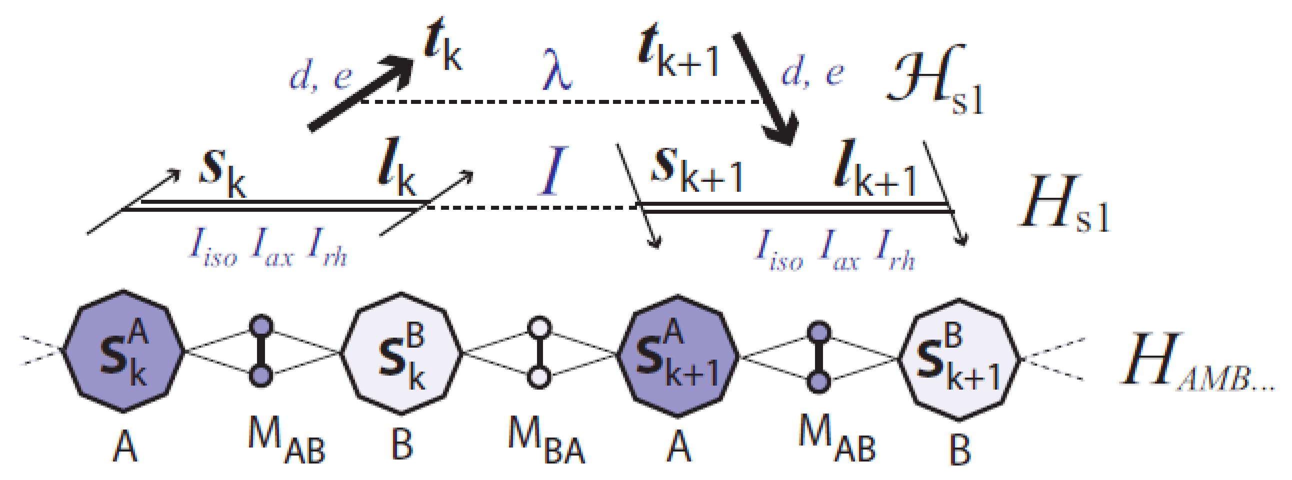
By exploiting the Wigner-Eckart theorem, the crystal-field terms are mapped onto axial (I_{ax}) and rhombic (I_{rh}) exchange terms. I is proportional to λ

Simulating $S = 1$ *spins*

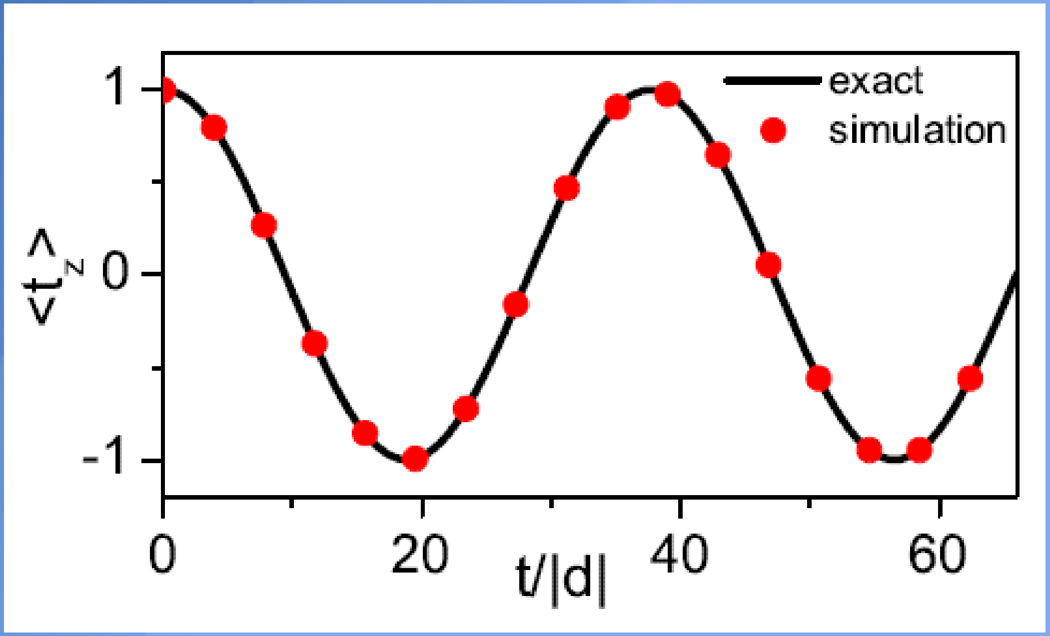
A chain of spins one ($\mathbf{t}_k$) with NN exchange interactions and single-spin crystal-field anisotropy:

$$\mathcal{H}_{\mathrm{s1}} = \lambda \sum_{k=1}^{N} \mathbf{t}_k \cdot \mathbf{t}_{k+1} + \sum_{k=1}^{N} [d\, t_{kz}^2 + e(t_{kx}^2 - t_{ky}^2)]$$

Having mapped H_{s1} onto a chain of spins 1/2 with NN interactions, we can now simulate its dynamics as before.



A simple proof-of-principle experiment: simulation of a S = 1 spin experiencing tunneling of the magnetization (using a crystal of qubit-dimer-qubit units).



The duration T_f of the pulse sequence implementing the simulation is about 480 ns

It can be monitored by measuring the total magnetization *M* of the crystal

PRL 107, 230502 (2011)

Fermions: the one-dimensional Hubbard model

$$\mathcal{H}_{\mathrm{Hub}} = -t \sum_{k\sigma} (c^{\dagger}_{k\sigma} c_{k+1\sigma} + h.c.) + U \sum_{k} n_{k\uparrow} n_{k\downarrow}$$

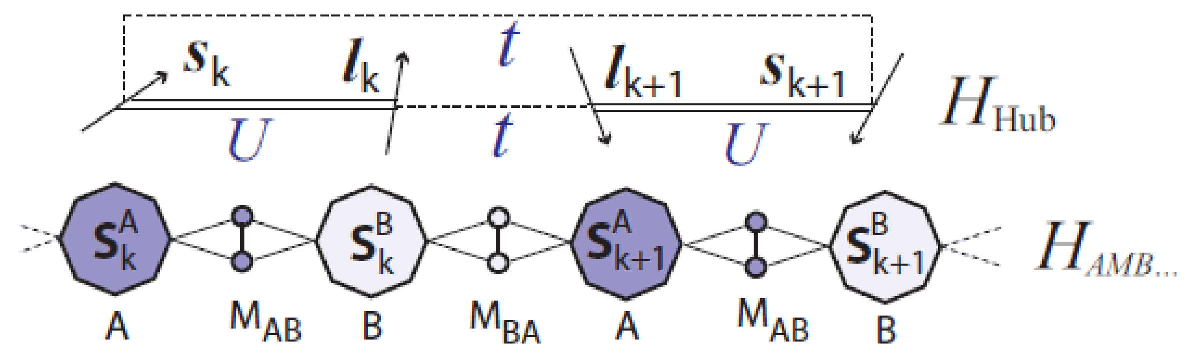
The occupation numbers (0 or 1) of the orbitals is mapped to the states of the qubits.

By exploiting the Jordan-Wigner representation

$$\begin{aligned} H_{\mathrm{Hub}} \; &= \; NU/4 - 2t \sum_{k=1}^{N-1} \sum_{\alpha=x,y} (s_{k\alpha} s_{(k+1)\alpha} + l_{k\alpha} l_{(k+1)\alpha}) \\ &+ \; U \sum_{k=1}^{N} s_{kz} l_{kz} + U/2 \sum_{k=1}^{N} (s_{kz} + l_{kz}) \end{aligned}$$

$$
\begin{aligned}
H_{\mathrm{Hub}} &= NU/4 - 2t\sum_{k=1}^{N-1}\sum_{\alpha=x,y}\left(s_{k\alpha}s_{(k+1)\alpha} + l_{k\alpha}l_{(k+1)\alpha}\right) \\
&+ U\sum_{k=1}^{N} s_{kz}l_{kz} + U/2\sum_{k=1}^{N}\left(s_{kz} + l_{kz}\right) \qquad (6)
\end{aligned}
$$

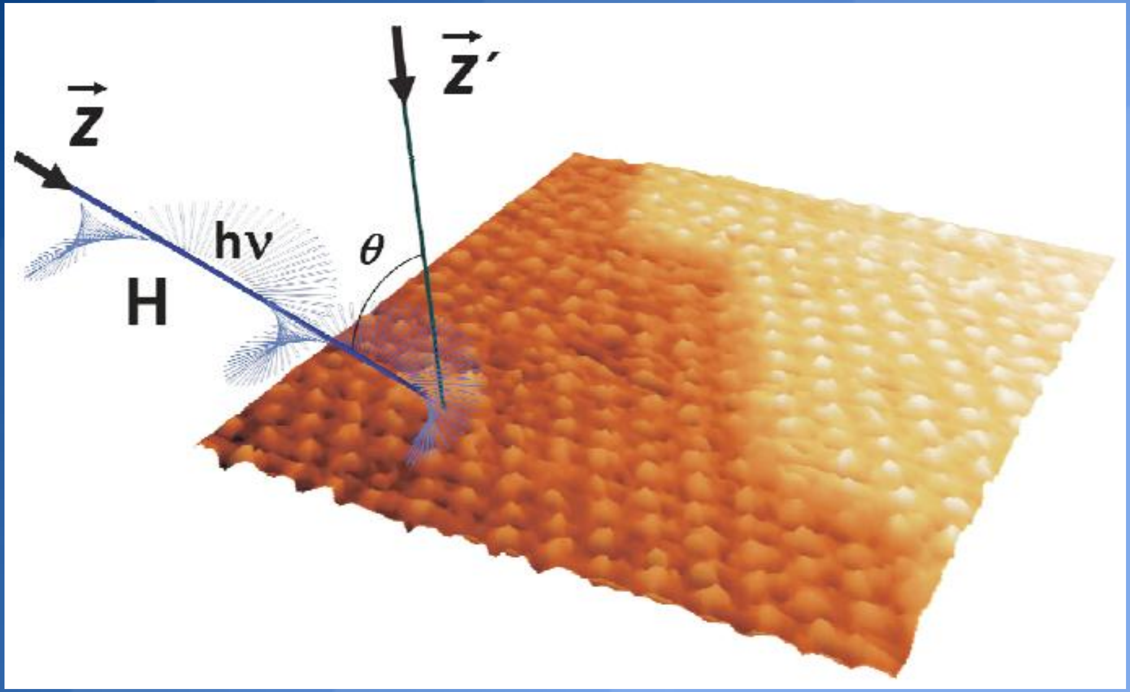
The state of the *s* and *l* spins is encoded in the state of the molecular qubits in an alternating pattern

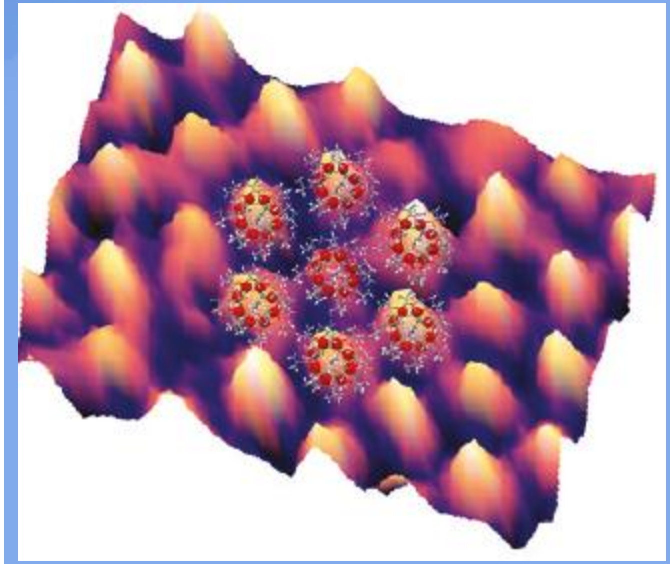


This Hamiltonian can be then simulated with the same method as before by exploiting **uniform em pulses**.

PRL 107, 230502 (2011)

Grafting Cr7Ni on Au surfaces

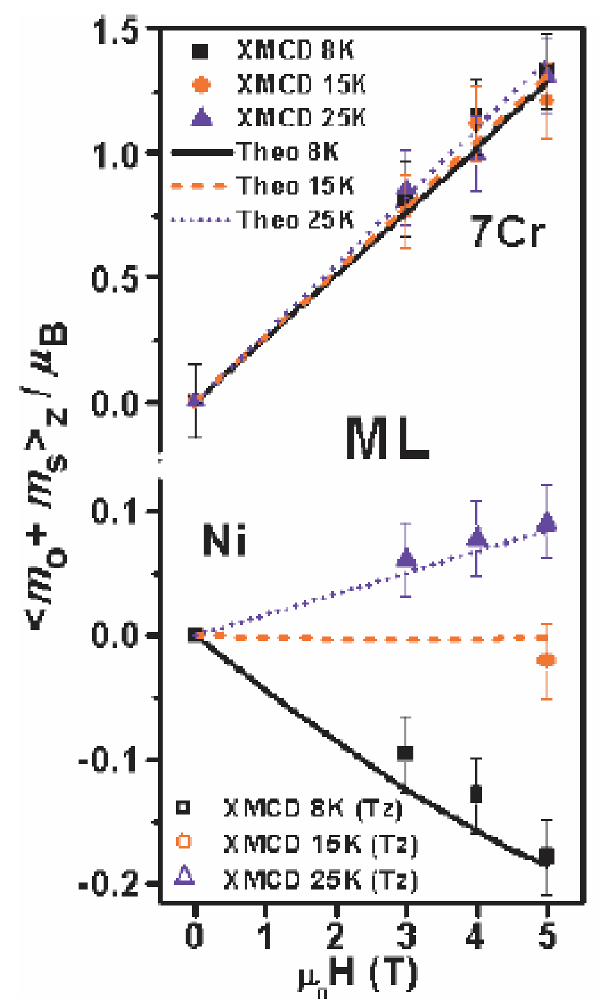


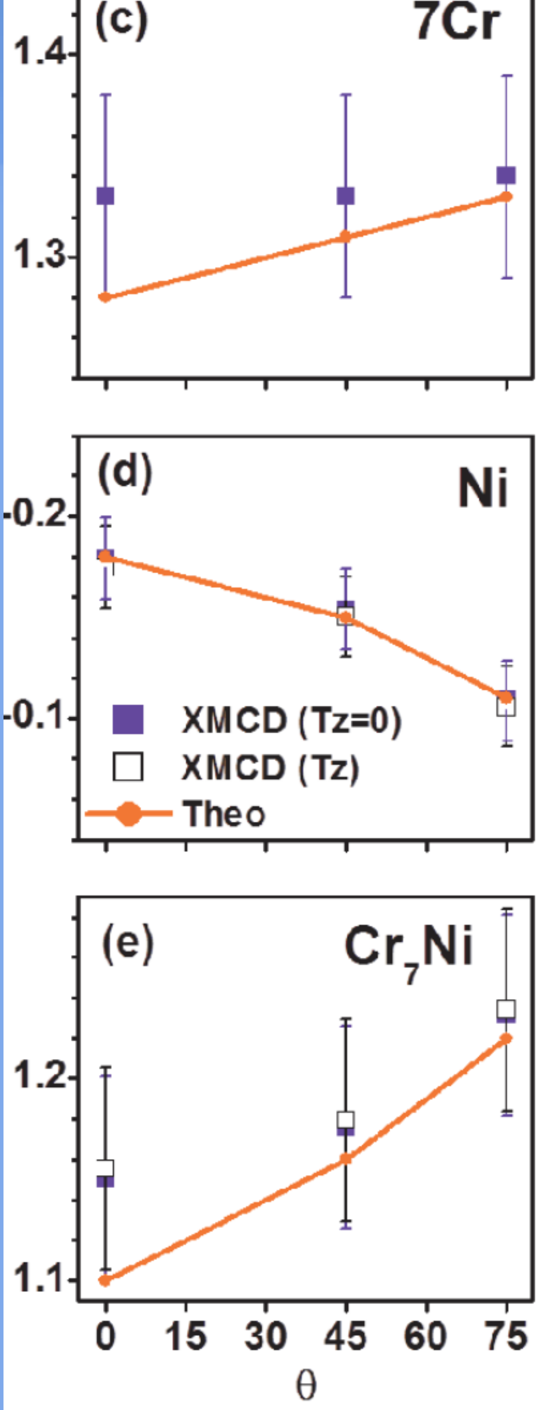


A. Ghirri, et al., *ACS Nano.* **2011**, *5*, 7090*.*

The Cr7Ni-bu derivative on Au(111) forms a highly ordered 2D hexagonal layer.

X-ray absorption spectra measured at the Cr and Ni edges show that the grafting does not affect the oxidation state and the local symmetry of the Cr and Ni sites.

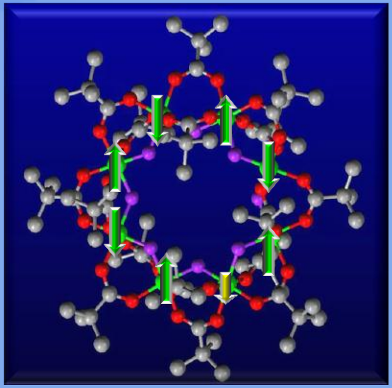




Cr7Ni rings grafted on Au surfaces preserves the structure of their magnetic Hamiltonian

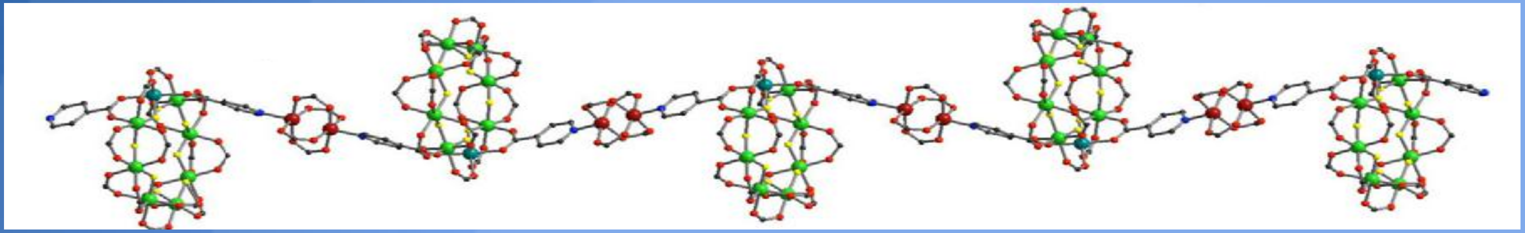
PRB 79, 144419 (2009)
ADVANCED FUNCTIONAL MATERIALS (in press)

Conclusions



- Cr_7Ni antiferromagnetic rings have a level scheme and eigenfunctions suitable for qubit encoding and manipulation.

- Arrays of molecular nanomagnets can be used as quantum simulators of different 1-D model Hamiltonians (including spin 1 and fermionic systems).



- We have proposed proof-of-principle implementations, where the means required for manipulating the system and measuring the relevant observables can be provided by the current technology.

- This approach allows the simulation of a much larger class of Hamiltonians, including higher-dimensional and inhomogeneous ones.