# Spin-electric coupling and coherent quantum control of molecular nanomagnets

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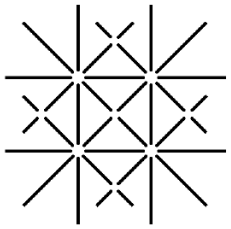
February 15. 2010

Funding: EU MolSpinQIP, Swiss national funds, Swiss Nanoscience Institute




**Collaborators:**

Filippo Troiani (Modena)
Mircea Trif (Basel)
Daniel Loss (Basel)

# Quantum computing with molecular nanomagnets

- Molecular nanomagnets as spin qubits
- Spin-electric effects in $Cu_3$ – triangle

  - chirality of spin texture

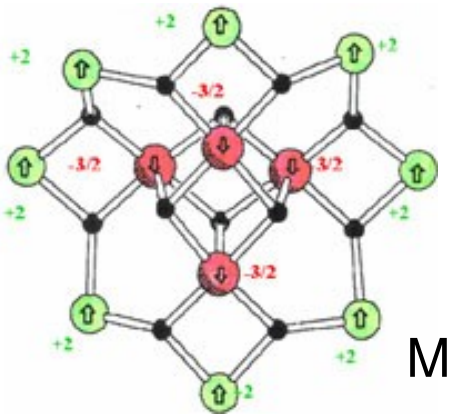
  - coupling to electric field

  - molecular nanomagnets in microwave cavity: spin-photon coupling
- Scalable quantum computer based on spin-electric coupling

# What are molecular nanomagnets ?

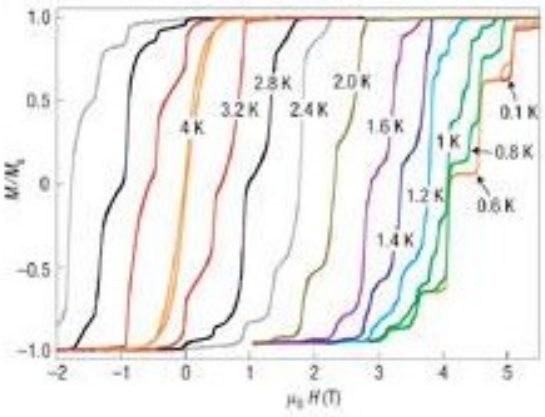
Molecular nanomagnets are large molecules which show magnetic properties similar to bulk magnetic materials

**Example:**




$Mn_{12}$

S=10

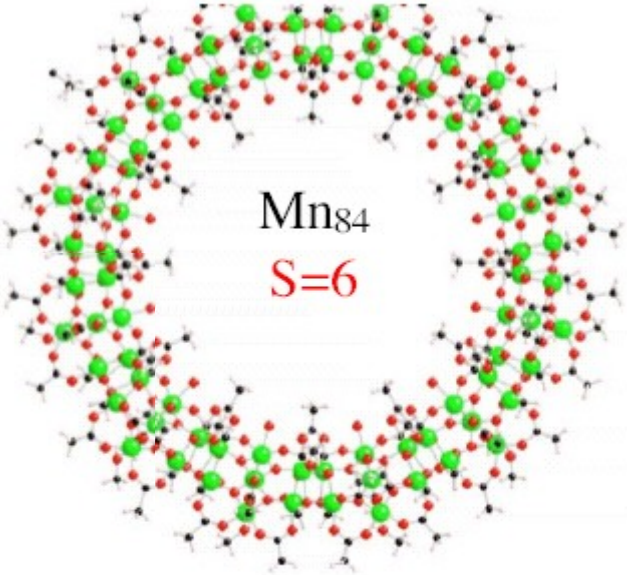



Dissimilarities:

- steps of magnetization
- almost no interaction between molecules
- quantum tunneling of magnetization
- long spin relaxation times
- quantum interference

quantum-to-classical transition regime!

# Structure of molecular nanomagnets:

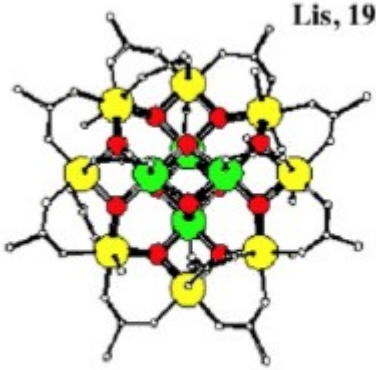



Christou, 2004

$Ni_{12}$ S = 12

Winpenny, 1999

Lis, 1980



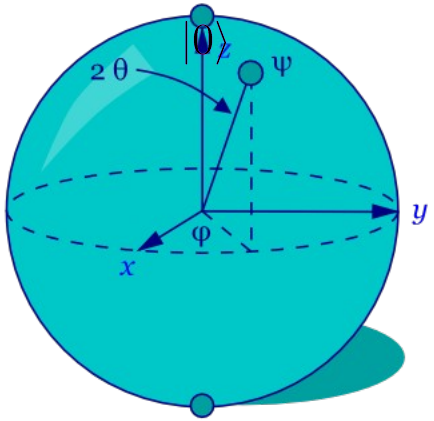
$Mn_{12}$ S = 10

$Fe_8$ S = 10

Wiegart, 1984

# Bits vs. qubits

- bit 0/1 ⟶ **qubit** $\boxed{|\Psi\rangle = c_0|0\rangle + c_1|1\rangle}$




- visualization: **spin ½** on Bloch sphere

- registers $\underbrace{00100\ldots101}_{N \text{ bits}} \longrightarrow |\Psi\rangle = \sum c_{b_1,\ldots,b_N}|b_1,\ldots,b_N\rangle$

  $2^N$ coefficients

- **Efficient factorization of integers** (Shor,1994)

# Bits vs. qubits

DiVincenzo criteria:
Five criteria that any implementation of a quantum computer must satisfy.

1. Well defined qubits

2. Initialization to a pure state

3. Universal set of quantum gates

4. Qubit specific measurement

5. Long coherence times

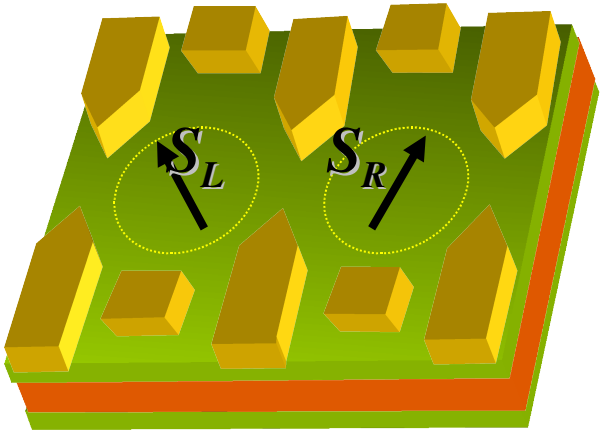
Can a quantum computer be implemented in molecular nanomagnets ?

# Spin qubits in semiconductor quantum dots

**electrical** control of **Heisenberg exchange interaction** between spins in quantum dots

$$H_{\rm ex}(t) = J(t)\mathbf{s}_{\rm L}\cdot\mathbf{s}_{\rm R}$$

Loss & DiVincenzo (1997)




$$\sqrt{\rm SWAP} = {\rm T}\exp\left[\frac{i}{\hbar}\int_0^{\tau_{\rm gate}} {\rm d}t J(t)\mathbf{s}_{\rm L}\cdot\mathbf{s}_{\rm R}\right]$$

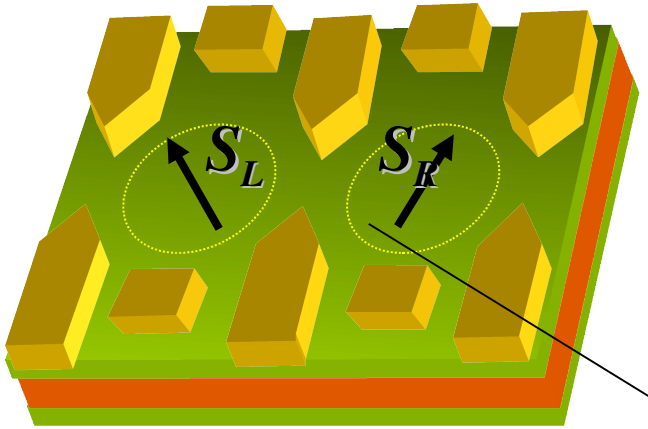
$$\frac{1}{\hbar}\int_0^{\tau_{\rm gate}} {\rm d}t J(t) = \frac{\pi}{2} \quad ({\rm mod} 2\pi)$$

- **implemented** for two qubits (Petta et al., Science 2005)

# Quantum computing via control of exchange interaction

- **electrical** control of **exchange interaction**

semiconductor quantum dots

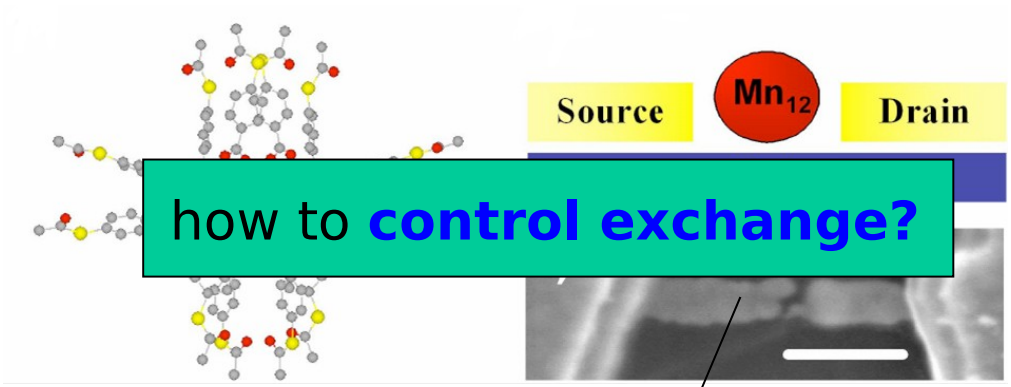



**Quantum computing with spins localized in QDs**

Loss & DiVincenzo (1997)

✓ for two electrons (Delft, Tokyo, Harvard, Princeton, …)

**molecular magnets?**




$Mn_{12}$

✓

?

$$H_{\mathrm{ex}}(t) = J(t)\mathbf{s}_{\mathrm{L}} \cdot \mathbf{s}_{\mathrm{R}}$$

# Molecular nanomagnets as qubit Candidates:

Electrical contacting:

- C. F. Hirjibehedin, C. P. Lutz, and A. J. Heinrich, Science 312, 1021 (2006).
- H. B. Heersche et al., Phys. Rev. Lett. 96, 206801 (2006).

Electron spin resonance and decoherence:

- A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, A.G. A. Timco, and R. E. P. Winpenny, Phys. Rev. Lett., 2007, 98, 057201. [perdeuterated Cr7Ni, 3 µs ]
- S. Bertaina, S. Gambarelli, T. Mitra, B. Tsukerblat, A. Müller & B. Barbara, Nature 453, 203-206 (2008) [V15 cluster, 15 µs]

Qubit Proposals based on molecular nanomagnets:

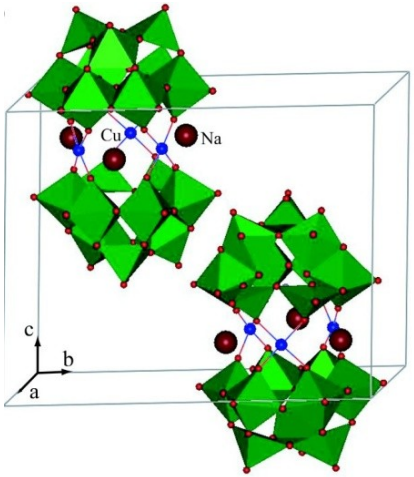
- M. N. Leuenberger and D. Loss, *Nature, 2001, 410, 789.*
- F. Meier, J. Levy and D. Loss, *Phys. Rev. Lett., 2003, 90,* 047901.
- F. Troiani, M. Affronte, S. Carretta, P. Santini, and G. Amoretti, *Phys. Rev. Lett., 2005, 94, 190501*
- J. Lehmann, A. Gaita-Ariño, E. Coronado, and Daniel Loss, Nature Nanotech. **2**, 312 (2007)

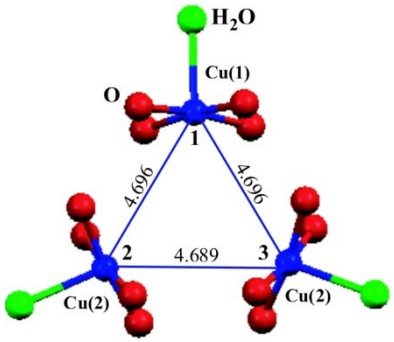
# Electric fields vs. Magnetic fields

- Strong electric fields are easy to obtain (gates, STM-tips, etc)
- Fast switching of electric fields (~ps)
- Easy to apply electric fields locally and on nanoscale

- Strong magnetic (ac) fields are hard to obtain
- Slow switching of magnetic fields (~ns)
- Very hard to apply local magnetic fields on the nanoscale

# Molecular nanomagnets in electric fields: $Cu_3$ - molecule




Choi et al., PRL (2006).

- $Cu_3$ - triangle with spin s=1/2 on each Cu-site

- Effective spin-Hamiltonian (no fields):

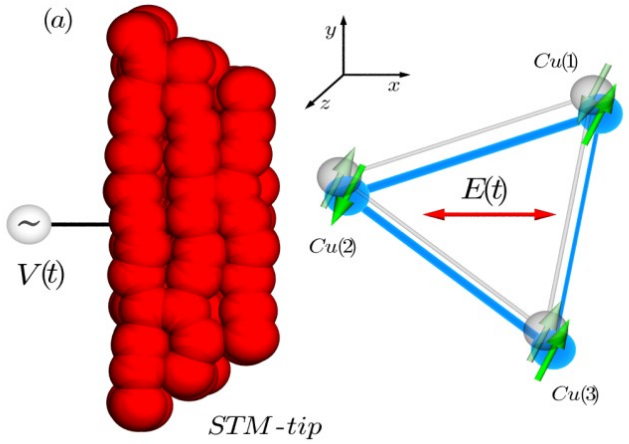
$$H_{\rm s} = \sum_j^3 J_{jj+1}\mathbf{s}_j \cdot \mathbf{s}_{j+1} + \sum_j^3 \mathbf{D}_{jj+1} \cdot (\mathbf{s}_j \times \mathbf{s}_{j+1})$$

Heisenberg exchange + Dzyaloshinski-Moryia

- Antiferromagnetically coupled spins ($J_{ii+1}$<0):
**chiral** ground state with S=1/2 and 1st excited state with S=3/2

- energy splitting between S=1/2 and S=3/2: $\Delta$ ~ 8 K ($J_{ii+1}$~5 K) and $|\mathbf{D}_{ii+1}|$~0.5 K

# $Cu_3$ molecule in **electric fields**




**Electric field *E*** changes bond-strengths
➔ exchange coupling J → J +$\delta J_{ij}$
**And: broken inversion symmetry**
➔***E*-field couples to spin texture**

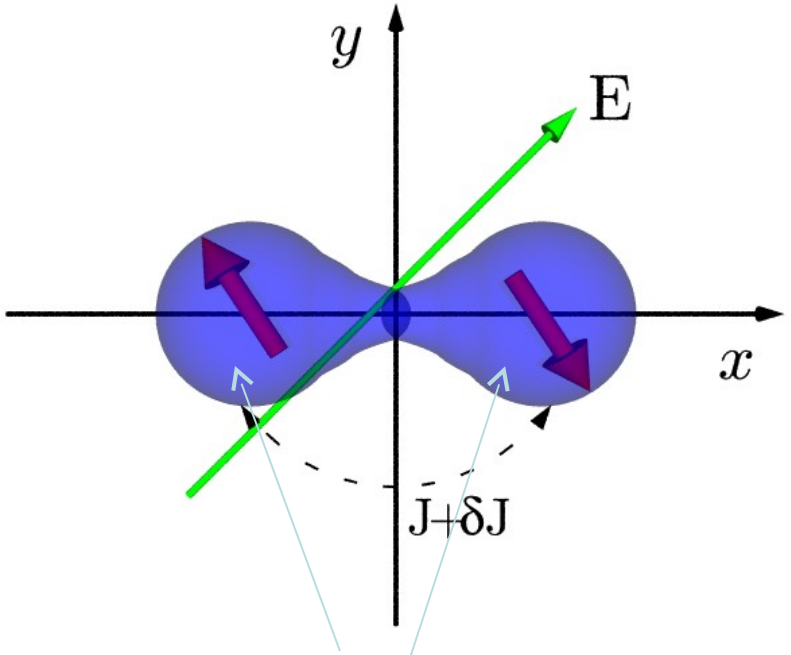
$$H_{\mathrm{E}} = \frac{2}{3} d \cdot E \sum_{j}^{3} \sin\left[\frac{2\pi}{3}(j+1) + \theta\right] \mathbf{s}_j \cdot \mathbf{s}_{j+1}$$

d: electric dipole parameter

- only in-plane E- fields couple to spins!

# Physics of spin-electric coupling

• two-atom molecule (e.g. $D_{2\infty}$) in electric field ***E*** :




Wannier orbitals $\varphi_i(x, y)$ with overlap

exchange splitting: $\delta J \propto d^{12} \cdot E$

electric dipole matrix-elements:

$$d_x^{12} = \int \mathrm{d}x\mathrm{d}y \phi_1^*(x,y) x \phi_2(x,y) = 0$$

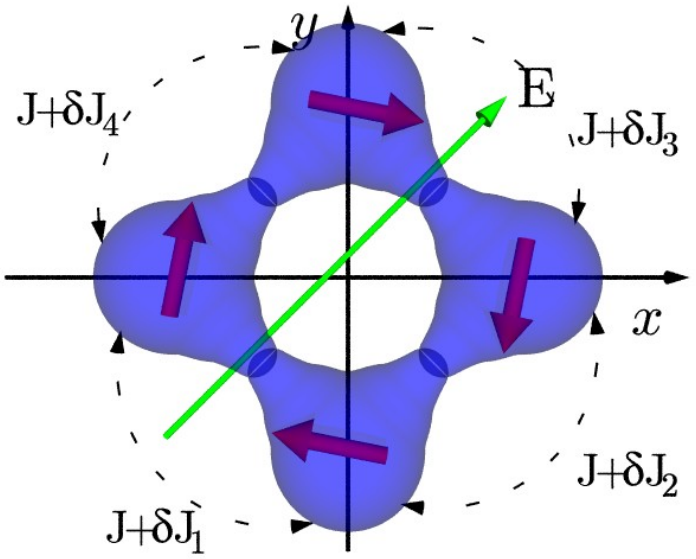
$$d_y^{12} = \int \mathrm{d}x\mathrm{d}y \phi_1^*(x,y) y \phi_2(x,y) = 0$$

➔ $\delta J \propto d^{12} \cdot E = 0$

**Note: Inversion symmetry ➔ no linear effects in E-field!**

# Physics of spin-electric coupling

- square molecule (e.g. $D_{4h}$) in electric field ***E*** :




electric dipole matrix elements:

$$d_x^{jj+1} = \int \mathrm{d}x\mathrm{d}y\phi_j^*(x,y)x\phi_{j+1}(x,y) = = -d_0 \sin\frac{2\pi(j-1)}{4}$$

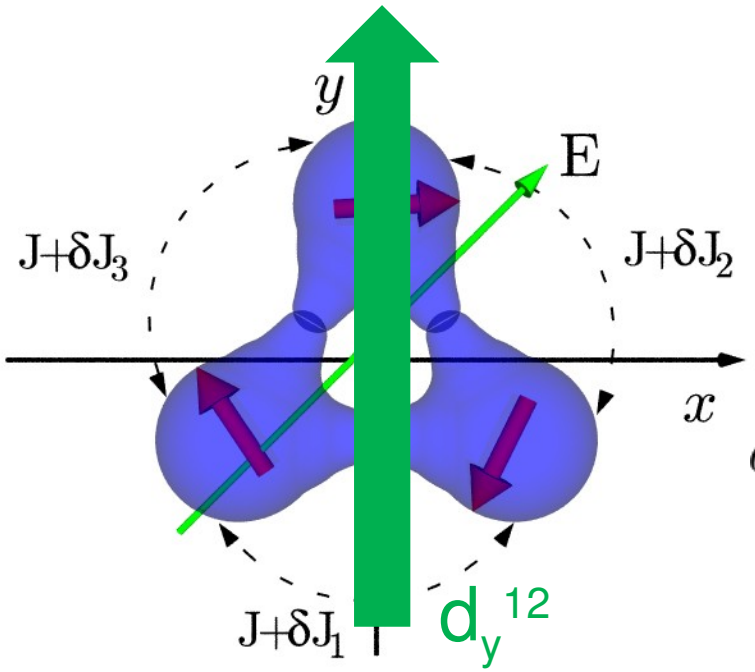
$$d_x^{jj+1} = \int \mathrm{d}x\mathrm{d}y\phi_j^*(x,y)y\phi_{j+1}(x,y) = = d_0 \cos\frac{2\pi(j-1)}{4}$$

➔ $$\delta J_{jj+1} \propto d^{jj+1}\left|\mathbf{E}_\parallel\right| = d_0\left|\mathbf{E}_\parallel\right|\sin\left[\frac{2\pi(j-1)}{4}+\varphi\right]$$

BUT: Inversion symmetry broken **only** between the ions ➔ sum over $d^j$ vanishes ➔ **no** linear E-field effects !

# Physics of spin-electric coupling

• triangular molecule (e.g. $D_{3h}$) in electric field ***E*** :




electric dipole matrix elements:

$$d_x^{jj+1} = \int \mathrm{d}x\mathrm{d}y\phi_j^*(x,y)x\phi_{j+1}(x,y) = -d_0 \sin\frac{2\pi(j-1)}{3}$$

$$d_x^{jj+1} = \int \mathrm{d}x\mathrm{d}y\phi_j^*(x,y)y\phi_{j+1}(x,y) = d_0 \cos\frac{2\pi(j-1)}{3}$$

➔ $$\delta J_{jj+1} \propto d^{jj+1}\left|\mathbf{E}_\parallel\right| = d_0\left|\mathbf{E}_\parallel\right| \sin\left[\frac{2\pi(j-1)}{3} + \varphi\right]$$

NB: Inversion symmetry broken **BOTH** in the entire triangle **and** between the ions ➔ linear E-field effects !

# $Cu_3$-molecule in magnetic and **electric** fields

$$H_{\rm s} = \sum_j^3 J_{jj+1}\mathbf{s}_j \cdot \mathbf{s}_{j+1} + \sum_j^3 \mathbf{D}_{jj+1} \cdot (\mathbf{s}_j \times \mathbf{s}_{j+1})$$

Add: Zeeman coupling:

$$H_{\rm Z} = \frac{1}{2} g\mu_{\rm B}\mathbf{B}\cdot\mathbf{S}$$

Spin-electric coupling:

$$H_{\rm E} = \frac{2}{3} d \cdot E \sum_j^3 \sin\left[\frac{2\pi}{3}(j+1) + \theta\right] \mathbf{s}_j \cdot \mathbf{s}_{j+1}$$

➔ effective Hamiltonian (total spin ***S*** and chirality ***C***):

$$H_{\rm eff} = \Delta_{\rm SO} C_z S_z + \frac{1}{2}\mathbf{B}\cdot\bar{\bar{g}}\cdot\mathbf{S} + d\mathbf{E}\cdot\mathbf{C}_{\|}$$

Trif, Troiani, Stepanenko, Loss, Phys. Rev. Lett. 101, 217201 (2008)

# Chirality Operator

$$H_{\text{eff}} = \Delta_{\text{SO}} C_z S_z + \frac{1}{2}\mathbf{B}\cdot\bar{\bar{g}}\cdot\mathbf{S} + d\mathbf{E}\cdot\mathbf{C}_{\|}$$

The chirality operator **C** has the 3 components

$$C_x = -\frac{2}{3}\left(\mathbf{s}_1\cdot\mathbf{s}_2 - 2\mathbf{s}_2\cdot\mathbf{s}_3 + \mathbf{s}_3\cdot\mathbf{s}_2\right)$$

$$C_y = \frac{2}{3}\left(\mathbf{s}_1\cdot\mathbf{s}_2 - \mathbf{s}_2\cdot\mathbf{s}_1\right)$$

$$C_z = \frac{4}{\sqrt{3}}\mathbf{s}_1\cdot\left(\mathbf{s}_2\times\mathbf{s}_3\right)$$

and behaves as pseudo-spin ½ ➔ spin qubit:

$$[C_a, C_b] = 2i\varepsilon_{abc}C_c \qquad\qquad [\mathbf{C},\mathbf{S}] = 0$$

# Chiral Eigenstates

$$C_z|\pm 1; S = 1/2, S_z\rangle = \pm|\pm 1; S = 1/2, S_z\rangle$$

**spin texture**

$$|C_z = \pm 1, S_z = -1/2\rangle = \frac{1}{\sqrt{3}}\left(|\uparrow\downarrow\downarrow\rangle + \varepsilon_{\pm}|\downarrow\uparrow\downarrow\rangle + \varepsilon_{\mp}|\downarrow\downarrow\uparrow\rangle\right)$$

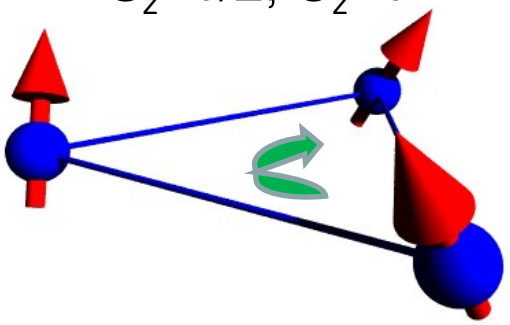
$$|C_z = \pm 1, S_z = 1/2\rangle = \frac{1}{\sqrt{3}}\left(|\downarrow\uparrow\uparrow\rangle + \varepsilon_{\pm}|\uparrow\downarrow\uparrow\rangle + \varepsilon_{\mp}|\uparrow\uparrow\downarrow\rangle\right)$$

$$\varepsilon_{\pm} = \exp \pm\frac{2\pi i}{3}$$

# $Cu_3$-molecule in magnetic and **electric** fields

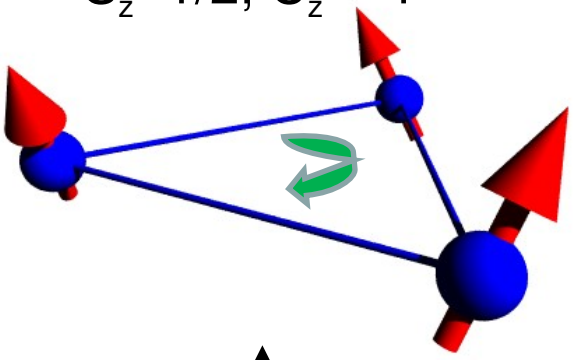
$$H_{\text{eff}} = \Delta_{\text{SO}} C_z S_z + \frac{1}{2}\mathbf{B}\cdot\bar{\bar{g}}\cdot\mathbf{S} + d\mathbf{E}\cdot\mathbf{C}_{\parallel}$$

$S_z$=1/2, $C_z$=1



**E**-field induced transitions

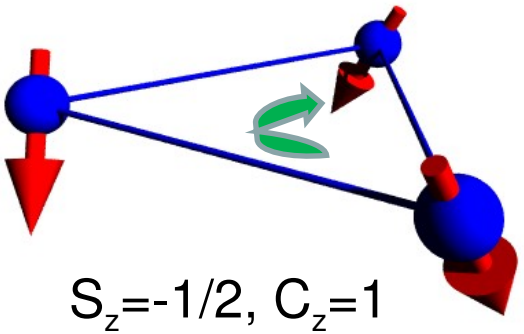
$S_z$=1/2, $C_z$= -1



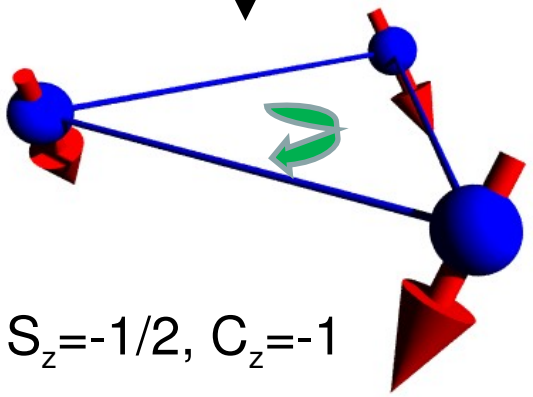
**B**-field induced transitions (ESR)

$$C_z = \frac{4}{\sqrt{3}}\mathbf{s}_1\cdot(\mathbf{s}_2\times\mathbf{s}_3)$$

**B**-field induced transitions (ESR)



**E**-field induced transitions



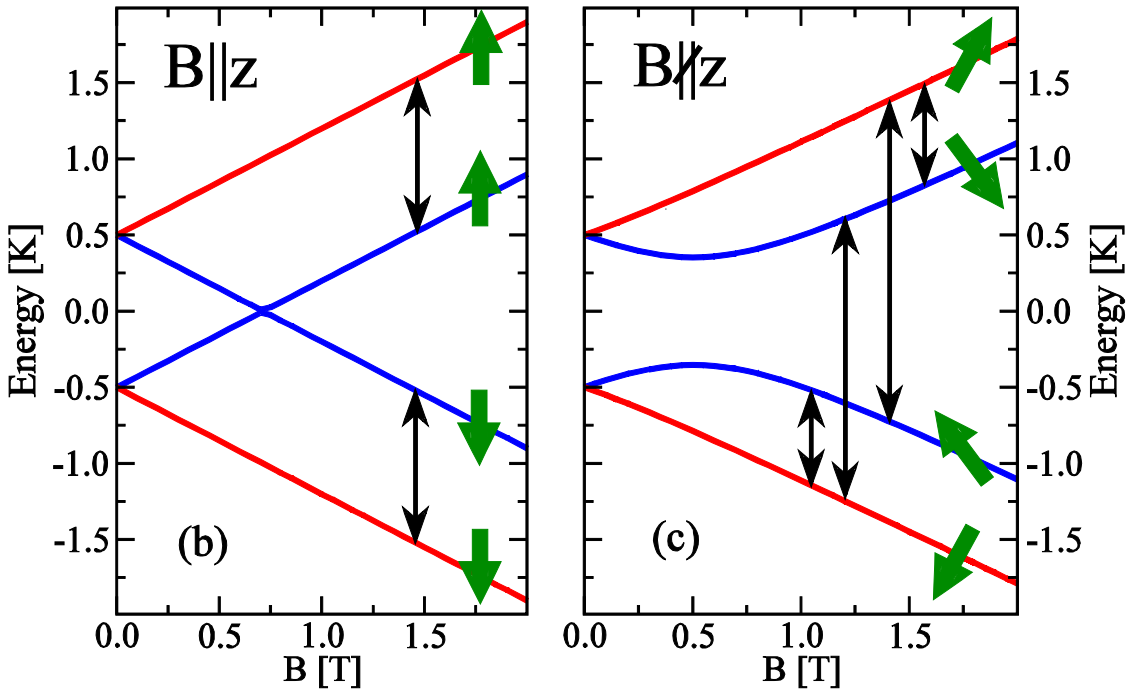
$S_z$=-1/2, $C_z$=1

$S_z$=-1/2, $C_z$=-1

# Interplay between magnetic and electric fields in $Cu_3$

$$H_{\text{eff}} = \Delta_{\text{SO}} C_z S_z + \frac{1}{2}\mathbf{B}\cdot\bar{\bar{g}}\cdot\mathbf{S} + d\mathbf{E}\cdot\mathbf{C}_{\parallel}$$

Control of spin

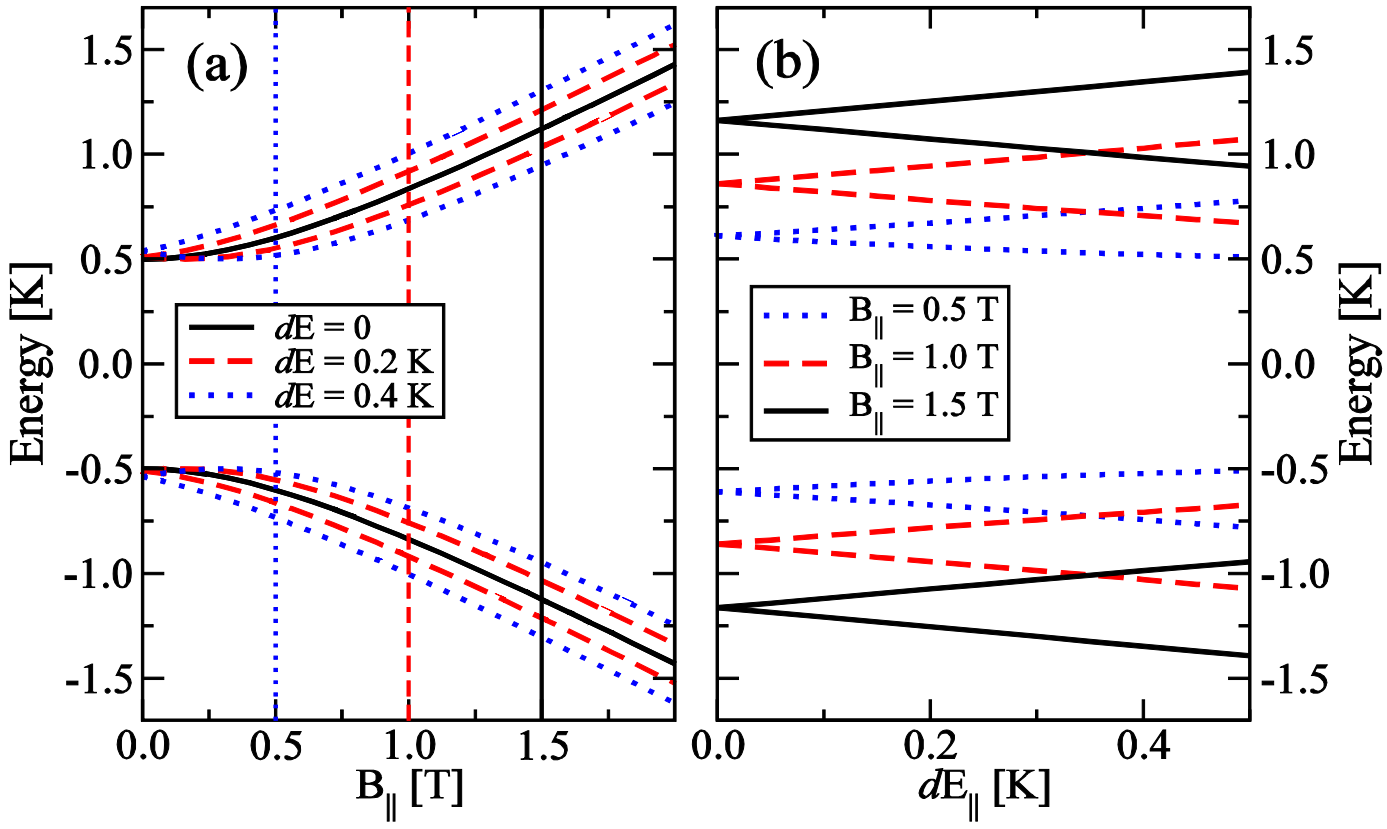



- No mixing of total spin for perpendicular magnetic fields $B_z$!

# Interplay between magnetic and electric fields in $Cu_3$

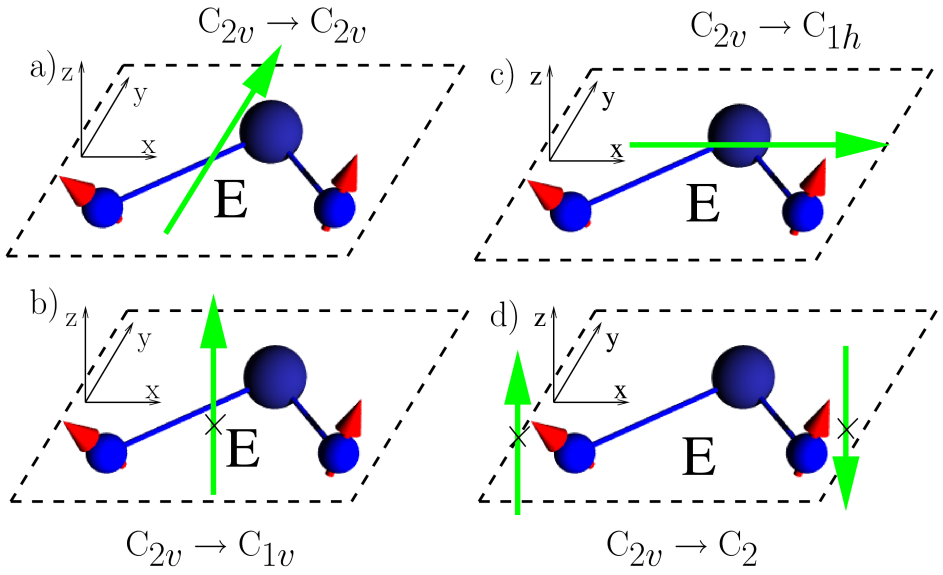
$$H_{\text{eff}} = \Delta_{\text{SO}} C_z S_z + \frac{1}{2}\mathbf{B}\cdot\bar{\bar{g}}\cdot\mathbf{S} + d\mathbf{E}\cdot\mathbf{C}_{\parallel}$$

All-important d!




- standard ESR measurements in static electric fields give direct access to the electric dipole parameter *d* (via slope in (b))

# Coupling constant d - superexchange in molecular bonds




Hopping between magnetic sites and the bridge site.

Electric fields in various directions (a)-(d) reduce the symmetry of the bond.

$$H_{\mathrm{b}} = \sum_{i,\alpha\beta} \left[ c^{\dagger}_{i\alpha} \left( t_i \delta_{\alpha\beta} + \frac{i\mathbf{P}_i}{2} \cdot \boldsymbol{\sigma}_{\alpha\beta} \right) b_{\beta} + \mathrm{h.c.} \right] + U_1(n_1) + U_2(n_2) + U_{\mathrm{b}}(n_{\mathrm{b}})$$

Treat hopping as a perturbation.

Derive the spin Hamiltonian via a Schrieffer-Wolff transformation ($4^{th}$ order).

Spin-electric coupling is variation of the spin Hamiltonian in electric field

# Coupling constant d - Schrieffer-Wolff transformation

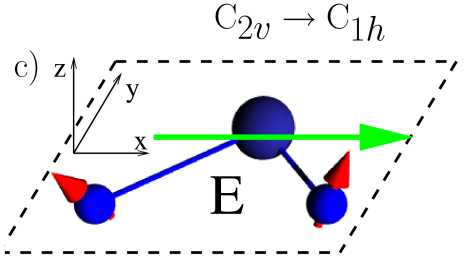
Effective spin Hamiltonian: $$H_{12} = J\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2) + \mathbf{S}_1 \cdot \mathbf{\Gamma} \mathbf{S}_2$$

isotropic exchange — Dzyalozhinsky-Moriya — symmetric anisotropy

Hubbard superexchange: $$H_{\mathrm{b}} = \sum_{i,\alpha\beta} \left[ c_{i\alpha}^{\dagger} \left( t_i \delta_{\alpha\beta} + \frac{i\mathbf{P}_i}{2} \cdot \boldsymbol{\sigma}_{\alpha\beta} \right) b_{\beta} + \mathrm{h.c.} \right] + U_1(n_1) + U_2(n_2) + U_{\mathrm{b}}(n_{\mathrm{b}})$$

Symmetry constraints: $t_1 = t_2 = t$

$$P_{1,y} = -P_{2,y} = p_{xy} \sin\phi$$
$$P_{1,y} = -P_{2,y} = p_{xy} \sin\phi$$
$$P_{1,z} = -P_{2,z} = p_z$$




In a field along y-axis, the spin interaction is:

$$J = \frac{1}{12U^3} \left[ p_{xy}^4 - 2p_{xy}^2 p_z^2 + 3p_z^4 - 8t^2 \left( p_{xy}^2 + 5p_z^2 \right) + 48t^4 - 8p_{xy}^2 \left( p_z^2 - 4t^2 \right) \cos 2\phi + 2p_{xy}^4 \cos 4\phi \right]$$

$$D_y = -\frac{p_{xy}}{U^3} \left( p_z \cos\phi + 2t \sin\phi \right) \left( -p_z^2 + 4t^2 + p_{xy}^2 \cos 2\phi \right)$$

$$D_z = -\frac{1}{2U^3} \left( 4tp_z - p_{xy}^2 \sin 2\phi \right) \left( p_z^2 - 4t^2 - p_{xy}^2 \cos 2\phi \right)$$

U is an effective on-site repulsion

$$\Gamma_{xx} = -\frac{1}{6U^3} \left[ p_{xy}^2 \left( 1 - \cos 2\phi \right) + 2p_z^2 \right] \left[ 8t^2 + p_{xy}^2 \left( 1 + \cos 2\phi \right) \right]$$

$$\Gamma_{yy} = \frac{1}{12U^3} \left\{ -p_{xy}^4 + 8p_{xy}^2 p_z^2 + 32t^2 \left( p_{xy}^2 - p_z^2 \right) + p_{xy}^2 \left[ 8 \left( p_z^2 - 4t^2 \right) \cos 2\phi + p_{xy}^2 \cos 4\phi + 48tp_z \sin 2\phi \right] \right\}$$

$$\Gamma_{yz} = \frac{p_{xy}}{U^3} \left( p_z \cos\phi + 2t \sin\phi \right) \left( -4tp_z + p_{xy}^2 \sin 2\phi \right)$$

# Coupling constant d - spin electric coupling

Field-dependence of spin Hamiltonian → Spin-electric coupling

$$\delta J = \frac{1}{3U^3}\left[\left(48t^3 - 20tp_z^2\right)\delta t + \left(-20t^2 p_z + 3p_z^3\right)\delta p_z\right]$$

Contributions from all the bonds in a triangle give the coupling constant

$$d = \frac{4E_y}{U^3}\left[\left(48t^3 - 20tp_z^2\right)\left(\frac{\partial t}{\partial E_y}\right) + \left(-20t^2 p_z + 3p_z^3\right)\left(\frac{\partial p_z}{\partial E_y}\right)\right]$$

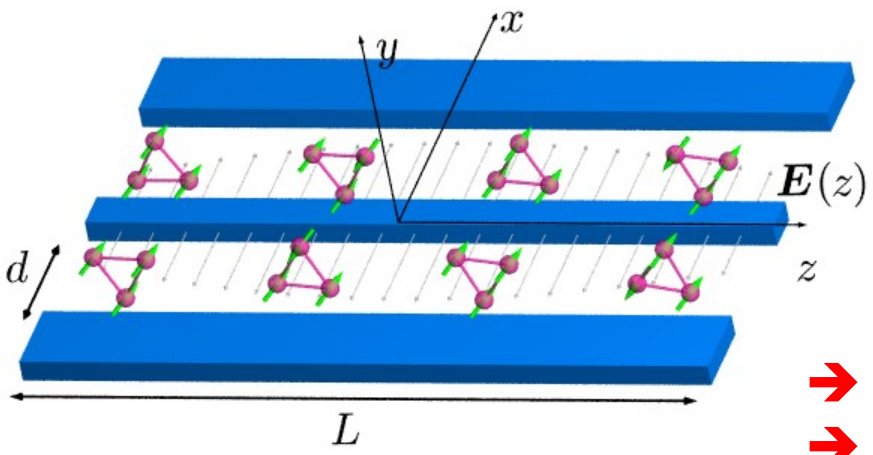
In a pentagon, the contributions of δJ cancel out, and the coupling is through δ**D**.

Ab-initio calculations of the variations of Hubbard parameters would predict the strength of spin-electric coupling.

# $Cu_3$-molecule coupled to a microwave cavity

- N $Cu_3$ molecules placed inside a one-dimensional microwave cavity*):

$$H_N = \sum_{j=1}^{N} \left[ \Delta_{\mathrm{SO}} C_z^j S_z^j + \frac{1}{2} \mathbf{B} \cdot \bar{\bar{g}} \cdot \mathbf{S}^j + d\mathbf{E} \cdot \mathbf{C}_{\parallel}^j \right] + \hbar\omega a^\dagger a$$




$$\mathbf{E} = \mathbf{E}_0 \sin\left(\frac{\pi z}{L}\right)\left(a^\dagger + a\right)$$

$$|\mathbf{E}| \sim \sqrt{\frac{\hbar\omega}{Ld}}$$

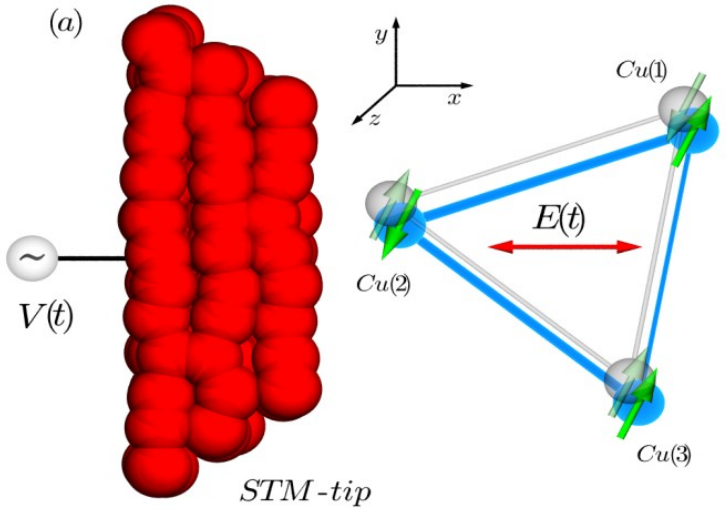
➔ spin-photon coupling

➔ spin-spin coupling between distant molecules (via virtual photon exchange)

- Conditional dynamics of distant molecule's spin chiralities and total spins!

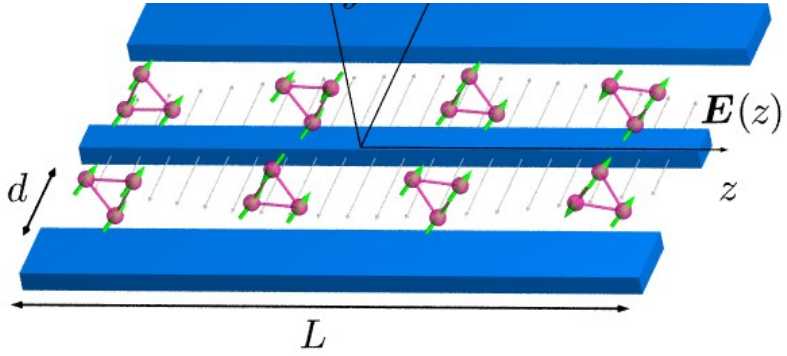
*) Wallraff et al., Nature 431,162 (2004) (superconducting qubits)

# Estimates




$$d \in \left(10^{-4}, 1\right) eR_{12} \qquad |\mathbf{E}| \sim 10^{7}\mathrm{V/m}$$

$$\tau_{\mathrm{Rabi}} \sim 0.1 - 10^{3}\mathrm{ps}$$




$$d \in \left(10^{-4}, 1\right) eR_{12} \qquad |\mathbf{E}| \sim 10\mathrm{V/m}$$

$$\tau_{Rabi} \sim 0.01 - 10\mu\mathrm{s}$$

**Note: Electric field in cavity increases with decreasing volume**

# Summary

- Spin-electric coupling exists in molecular nanomagnets with no inversion symmetry: $Cu_3$ is an example.

- Cavity coupling of molecular magnets enables long-distance controllable coupling and scalable spin-qubits!

- Possibility of new hybrid qubits (e.g. molecular qubits + qdot spins or superconducting qubits)

Trif, Troiani, Stepanenko, Loss, Phys. Rev. Lett. 101, 217201 (2008)