Spin-electric coupling and coherent quantum control of molecular nanomagnets

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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.

Dissimilarities:

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

Example: $\text{Mn}_12$, $S=10$

Quantum-to-classical transition regime!
Structure of molecular nanomagnets:

- Ni$_{12}$  $S = 12$
- Mn$_{84}$  $S = 6$
- Fe$_8$  $S = 10$
- Mn$_{12}$  $S = 10$

Images: Christou, 2004; Winpenny, 1999; Lis, 1980; Wiegart, 1984
Bits vs. qubits

- bit 0/1 → qubit \(|\Psi\rangle = c_0|0\rangle + c_1|1\rangle\)

- visualization: spin \(\frac{1}{2}\) on Bloch sphere

- registers \(\underbrace{00100 \ldots 101}_{N \text{ bits}}\) → \(|\Psi\rangle = \sum c_{b_1,\ldots,b_N} |b_1,\ldots, b_N\rangle\)

- 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

\[ H_{\text{ex}}(t) = J(t) s_L \cdot s_R \]

Loss & DiVincenzo (1997)

\[ \sqrt{\text{SWAP}} = T \exp \left[ \frac{i}{\hbar} \int_0^{\tau_{\text{gate}}} dt J(t) s_L \cdot s_R \right] \]

\[ \frac{1}{\hbar} \int_0^{\tau_{\text{gate}}} dt J(t) = \frac{\pi}{2} \mod 2\pi \]

- implemented for two qubits (Petta et al., Science 2005)
Quantum computing via control of exchange interaction

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

Semiconductor quantum dots

Molecular magnets?

Quantum computing with spins localized in QDs

Loss & DiVincenzo (1997)

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

\[ H_{ex}(t) = J(t)\mathbf{s}_L \cdot \mathbf{s}_R \]
Molecular nanomagnets as qubit Candidates:

Electrical contacting:

Electron spin resonance and decoherence:

Qubit Proposals based on molecular nanomagnets:
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: $\text{Cu}_3$ - molecule

- $\text{Cu}_3$ - triangle with spin $s=1/2$ on each Cu-site

- Effective spin-Hamiltonian (no fields):

$$H_s = \sum_{j}^{3} J_{jj+1} s_j \cdot s_{j+1} + \sum_{j}^{3} D_{jj+1} \cdot (s_j \times s_{j+1})$$

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 $S=3/2$: $\Delta \sim 8 \text{ K}$ ($J_{ii+1}\sim 5 \text{ K}$) and $|D_{ii+1}|\sim 0.5 \text{ K}$

\textbf{Cu}_3 \text{ molecule in electric fields}

\textbf{Electric field} $E$ changes bond-strengths $\Rightarrow$ exchange coupling $J \rightarrow J + \delta J_{ij}$

And: broken inversion symmetry $\Rightarrow$ \textit{E}-field couples to spin texture

\[ H_E = \frac{2}{3} d \cdot E \sum_{j}^{3} \sin \left[ \frac{2\pi}{3} (j + 1) + \theta \right] s_j \cdot s_{j+1} \]

\[ d: \text{ electric dipole parameter} \]

\textbullet \ only in-plane \textit{E}-fields couple to spins!
• two-atom molecule (e.g. $D_{2\infty}$) in electric field $E$:

Physics of spin-electric coupling

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

electric dipole matrix-elements:

$$d_{x}^{12} = \int dx dy \phi_1^*(x, y) x \phi_2(x, y) = 0$$

$$d_{y}^{12} = \int dx dy \phi_1^*(x, y) y \phi_2(x, y) = 0$$

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

Note: Inversion symmetry $\Rightarrow$ no linear effects in E-field!
Physics of spin-electric coupling

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

\[ \delta J_{jj+1} \propto d_{jj+1}^{ij} |E_\parallel| = d_0 |E_\parallel| \sin \left[ \frac{2\pi(j-1)}{4} + \varphi \right] \]

**BUT:** Inversion symmetry broken **only** between the ions \( \Rightarrow \) sum over \( d_{jj} \) vanishes \( \Rightarrow \) **no** linear E-field effects!
Physics of spin-electric coupling

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

\[ d_{xj}^{j+1} = \int dx dy \phi_j^*(x, y) x \phi_{j+1}(x, y) =
\]
\[ = -d_0 \sin \frac{2\pi(j - 1)}{3} 
\]
\[ d_{xj}^{j+1} = \int dx dy \phi_j^*(x, y) y \phi_{j+1}(x, y) =
\]
\[ = d_0 \cos \frac{2\pi(j - 1)}{3} 
\]

\( \Rightarrow \delta J_{jj+1} \propto d_{j}^{j+1} \left| E_\parallel \right| = d_0 \left| E_\parallel \right| \sin \left[ \frac{2\pi(j - 1)}{3} + \varphi \right] \)

NB: Inversion symmetry broken **BOTH** in the entire triangle **and** between the ions \( \Rightarrow \) linear E-field effects !
**Cu$_3$-molecule in magnetic and electric fields**

\[ H_s = \sum_{j}^{3} J_{jj+1} \mathbf{s}_j \cdot \mathbf{s}_{j+1} + \sum_{j}^{3} D_{jj+1} \cdot (\mathbf{s}_j \times \mathbf{s}_{j+1}) \]

Add: Zeeman coupling: Spin-electric coupling:

\[ H_Z = \frac{1}{2} g \mu_B \mathbf{B} \cdot \mathbf{S} \quad H_E = \frac{2}{3} d \cdot E \sum_{j}^{3} \sin \left[ \frac{2\pi}{3} (j + 1) + \theta \right] \mathbf{s}_j \cdot \mathbf{s}_{j+1} \]

\[ \Rightarrow \text{effective Hamiltonian (total spin } \mathbf{S} \text{ and chirality } \mathbf{C}) : \]

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

Chirality Operator

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

The chirality operator \( \mathbf{C} \) has the 3 components

\[ C_x = -\frac{2}{3} (s_1 \cdot s_2 - 2s_2 \cdot s_3 + s_3 \cdot s_2) \]
\[ C_y = \frac{2}{3} (s_1 \cdot s_2 - s_2 \cdot s_1) \]
\[ C_z = \frac{4}{\sqrt{3}} s_1 \cdot (s_2 \times s_3) \]

and behaves as pseudo-spin \( \frac{1}{2} \rightarrow \) spin qubit:

\[ [C_a, C_b] = 2i \varepsilon_{abc} C_c \quad [\mathbf{C}, \mathbf{S}] = 0 \]
Chiral Eigenstates

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

**spin texture**

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

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

\[ \varepsilon_\pm = \exp \pm \frac{2\pi i}{3} \]
\[ H_{\text{eff}} = \Delta_{SO} C_z S_z + \frac{1}{2} B \cdot \vec{g} \cdot \vec{S} + dE \cdot C_{||} \]

\( S_z = \frac{1}{2}, \ C_z = 1 \)

\( S_z = \frac{1}{2}, \ C_z = -1 \)

E-field induced transitions

B-field induced transitions (ESR)

\[ C_z = \frac{4}{\sqrt{3}} \vec{s}_1 \cdot (\vec{s}_2 \times \vec{s}_3) \]

\( S_z = -\frac{1}{2}, \ C_z = 1 \)

E-field induced transitions

B-field induced transitions (ESR)

\( S_z = -\frac{1}{2}, \ C_z = -1 \)
Interplay between magnetic and electric fields in Cu₃

\[ H_{\text{eff}} = \Delta_{SO} C_z S_z + \frac{1}{2} B \cdot \vec{g} \cdot S + dE \cdot C_{\parallel} \]

Control of spin

- No mixing of total spin for perpendicular magnetic fields Bₚ!
Interplay between magnetic and electric fields in Cu$_3$

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

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.

$$H_b = \sum_{i,\alpha\beta} \left[ c_{i\alpha}^\dagger \left( t_i \delta_{\alpha\beta} + \frac{i P_i}{2} \cdot \sigma_{\alpha\beta} \right) b_{\beta} + \text{h.c.} \right] + U_1(n_1) + U_2(n_2) + U_b(n_b)$$

Treat hopping as a perturbation.

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

Spin-electric coupling is variation of the spin Hamiltonian in electric field
Coupling constant $d$ - Schrieffer-Wolff transformation

Effective spin Hamiltonian:

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

- isotropic exchange
- Dzyalozhinsky-Moriya symmetric anisotropy

Hubbard superexchange:

$$H_b = \sum_{i,\alpha\beta} \left[ c_{i\alpha}^\dagger \left( t_i \delta_{\alpha\beta} + \frac{\mathbf{P}_i}{2} \cdot \mathbf{\sigma}_{\alpha\beta} \right) b_\beta + \text{h.c.} \right] + U_1(n_1) + U_2(n_2) + U_b(n_b)$$

Symmetry constraints:

$$t_1 = t_2 = t \quad P_{1,y} = -P_{2,y} = p_{xy} \sin \phi$$
$$P_{1,y} = -P_{2,y} = p_{xy} \sin \phi$$
$$P_{1,z} = -P_{2,z} = p_z$$

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

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

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

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

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

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

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

$U$ is an effective on-site repulsion
Coupling constant $d$ - spin electric coupling

Field-dependence of spin Hamiltonian

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

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

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

In a pentagon, the contributions of $\delta J$ cancel out, and the coupling is through $\delta D$.

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$^*$:

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

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

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

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

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

Estimates

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)