Electron Transport Through Single-Molecule Magnets

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Mesoscopic transport

Molecules Surface

V_{bias}

V_{gate}

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(1) Transport through single molecules
   • Experimental setups
   • Theoretical framework

(2) Spin effects in transport through single molecule magnets (SMM):
   • Magnetic excitations
   • Magnetic & low-lying electronic excitations

Experiment
Experimental approaches

Mechanically-Controlled Break Junction (MCBJ)

- Strong tunnel coupling
- Stable contact: high voltage and current levels
- Controlled contact: stretch, rebond “symmetrize” tunnel coupling
- Good statistics possible

Electro-Migrated Junction (EMJ)

- Gate voltage: identification of resonances
- Weak / moderate tunnel coupling
- Very low temperature T ( ~ 50 mK)

*STM: no gate and asymmetric
Mechanically Controlled Break Junction

J. van Ruitenbeek
M. Reed
J. P. Bourgoin
H. Weber

Symmetry of molecule

Gate-effect by sidegroups

Intramolecular conjugation

Courtesy H. Weber
Electro-Migrated Junction

J. W. Park
P. McEuen
D. Ralph
H. K. Park
H. van der Zant
Theory - setup

electrode L

gate

electrode R
Current spectroscopy

\[ E_0 \quad \Delta_0 \quad E_1 \quad \Delta_1 \]

charge 0 \hspace{1cm} charge \ -e

\[ \text{electrode L} \quad \text{gate} \quad \text{electrode R} \]

\[ (E_1 + \Delta_1) - E_0 \]

\[ E_1 - E_0 + \Delta_1 - \Delta_0 \]

\[ E_1 - E_0 \]

\[ E_1 - (E_0 + \Delta_0) \]

\[ \mu_L \quad \mu_R \]
Current spectroscopy

2 Excitation spectra

Energy conservation
Amplitudes $\sim$ wavefunction
Non-equilibrium occupations

2 Charge states

$\Delta_1$
$E_1$
$E_0$
$\Delta_0$

"irrelevant"
Energy scales

Higher order processes:
\[ \Gamma \sim T \]

Temperature
\[ T \sim 50 \text{ mK} - 5 \text{ K} \]
\[ \sim 0.005 - 0.5 \text{ meV} \]

Excitations
- Vibrational \( \sim 1 - 100 \text{ meV} \)
- Magnetic \( \sim < 5 \text{ meV} \)

Addition energy
\( U \sim \delta > 100 \text{ meV} \)

Tunnel coupling
\( I \sim 0.5 \text{ nA} \)
\[ \Gamma \sim 0.1 \text{ meV} \]

Fingerprint of single-molecule transport

Coulomb effect + Energy quantization

\[ E_1 - E_0 \]
\[ E_0 - E_{-1} \]
Systematic approach

Model-based
Perturbative in tunnel coupling $\Gamma$

Theoretical starting point:
1\textsuperscript{st} order: sequential tunneling
2\textsuperscript{nd} order: co-tunneling

....
Non-perturbative: Kondo-tunneling

“\textbf{Ab-initio} molecular non-equilibrium \textit{transport theory}”

No DFT yet \textit{in principle} for non-equilibrium
Mean-field .... strong interactions effects
Sequential tunneling transport

\[ \frac{dp_a}{dt} = 0 = \sum_b \{ W_{a\rightarrow b} p_b - W_{b\rightarrow a} p_a \} \]

**Probabilities**

**Current**

\[ I^L = \sum_{ab} W_{a\rightarrow b}^L p_b - \sum_{ab} W_{b\rightarrow a}^L p_a \]

**Golden rule rates**

\[ W_{a\rightarrow b} = W_{a\rightarrow b}^L + W_{a\rightarrow b}^R \]

\[ W_{a\rightarrow b}^\alpha = \Gamma_{ab}^\alpha f_\alpha (E_a - E_b) \quad \alpha = L, R \quad \text{for} \quad N_a > N_b \]

\[ W_{a\rightarrow b}^\alpha = \Gamma_{ba}^\alpha (1 - f_\alpha (E_b - E_a)) \quad \text{for} \quad N_a < N_b \]

\[ \Gamma_{ab}^\alpha = 2\pi \sum_{k\sigma} |t_{k\alpha}|^2 \delta (E - \epsilon_{k\alpha}) \times \sum_{i\sigma} \left| \langle a | d_{i\sigma}^{\text{dag}} | b \rangle \right|^2 \]

**Spin-blockade of electron tunneling:**

rate = 0 unless
\[ |S-S'|=1/2 \text{ and } |M-M'| =1/2 \]

**Electron tunneling rate**

- Spin selection rules
- Orbital symmetry
- Nuclear wavefunction overlap (Franck-Condon factors)
Sequential tunneling transport

A. Thielmann, M. H. Hettler, J. König, G. Schön

Conditional-probabilities

\[ 0 = WP \]

Zero-frequency current noise

\[ S(\omega=0) = e^T(W p + WPW p) \]

Schottky term \( \sim V \)
Thermal noise (fluctuation-dissipation)

Golden rule rates

Slow processes:
- Suppressed current
- Enhanced noise
Molecular Magnetism:
Access magnetic excitations in *multiple charge states*
Create *non-equilibrium* magnetic states

- *Hidden resonances*
- "Fake" resonances
- Negative dI/dV
- Current & noise oscillations
- Current suppression

Tunneling transport through single molecule magnets (SMM)

* e.g. Mn12, \( S=10 \)
Single Molecular Magnet (SMM)

Large $S$

Molecular:
- No preferred direction
- Easy-plane anisotropy
  - Discrete molecular symmetry

Quantum Tunneling of Magnetic moment (QTM)

Identifiable transport effects of QTM?
- weak perturbation
- forbidden for $S=n+\frac{1}{2}$

Electronic control of magnetic states?
Experimental motivation

\[ \text{Mn}_{12}\text{O}_{12}\left(\text{O}_2\text{C-} \text{C}_6\text{H}_4\text{-SAc}\right)_{16}\left(\text{H}_2\text{O}\right)_{4} \]

-1

-0.5

0.0

0.5

\( V_{\text{bias}} \) [mV]

0

10

\( V_{\text{gate}} \) [V]

T = 3K

T = 1.5 K

Current suppression up to 5 meV

diamond edge - PDC - NDC @ 2.5 meV

Multiple stable devices

Reproducible features

16 meV

~ 5 meV

Two measurement setups

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Magnetic excitations: Magnetic Anisotropy Barrier (MAB)

\[ H_{\text{MAB}} = -D N S_z^2 \]

Tunneling \( \Rightarrow \) spin selection rule for \( S \) and \( S_z \)


Charge-induced “magnetic distortion”
Sessoli 93, Takeda 97, Aubin 99, Soler 00 & 01
Kuroda-Sowa 01, Coronado 04
Magnetic excitations: (QTM) Quantum Tunneling of Magnetic moment

\[ H_{MAB} = -D_N S_z^2 \]

\[ H_{QTM} = \frac{1}{2} B_2 (S_-^2 + S_+^2) + \frac{1}{2} B_4 (S_-^4 + S_+^4) \]
QTM effect on non-linear transport?

**Numbers: (~ Mn12)**

\[
\begin{align*}
S & \sim 10 \\
D & \sim 5 \times 10^{-2} \text{ meV} \\
B_2 & \sim 1 \times 10^{-4} \text{ meV}
\end{align*}
\]

**Small energy scale but violates selection rule!**

Lifts a strong restriction on non-equilibrium occupations magnetic states

Magnetic anisotropy barrier \(\sim D S^2 \sim 5 \text{ meV}\)

*Electronic* Excitations \(\sim 5 \text{ meV}\)
Magnetic & *electronic* excitations

\[ H_{MAB} = -D_{N\alpha} S_z^2 + \Delta_{N\alpha} \delta_{\alpha 1} \]

\[ H_{QTM} = \frac{1}{2} B_2 (S_-^2 + S_+^2) \]

\( N=0 \)
\( \alpha = 1 \)
\( \alpha = 0 \)
\( B_2 \)
\( \Delta_0 \)

\( N=1 \)
\( S=9\frac{1}{2} \)

Low-symmetry QTM $B_2 \gg B_4$

$N=0$

$S$

$B_2$

$D$

$N=1$

$S-\frac{1}{2}$

$B_2$

$D'$

or $S+\frac{1}{2}$
Hidden lines: $D=D', B_2=0$

Eigenstates: $S$, $S_z$ approximately good quantum numbers

$|S_z|$

Hidden transitions:
initial states cannot be occupied at the transition energy

Inverted parabola + spin selection rules

General result for $D=D'$ and any spin $S$

Only 2 current steps
Others hidden
NDC and “fake” lines: $D = D', B_2 > 0$

QTM:
“fake” resonance lines + negative resonance
Hidden lines: $D > D'$, $B_z = 0$

Charge-induced "magnetic distortion"

Anisotropy barrier different in 2 charge states
⇒ more transition lines appear
NDC and "fake" lines: $D > D', B_2 > 0$

Charge-induced "magnetic distortion"

\[ \left| S_z \right| \]

\[ 0 \]

\[ D \]

\[ T \times 1.5 \]

\[ 1 \]

\[ 3D \]

\[ 2D' \]

\[ 2 \]

\[ 3/2 \]

QTM x 0.01

\[ S=2 \]

\[ S=3/2 \]

QTM: "fake" resonance lines + negative resonance
NDC and “fake” lines: $D > D', \ B_2 \neq 0$

$D$ fixed
$B_2$ varied

“Fake” resonances shift with QTM ....even though addition spectrum is not altered!

Negative Differential Conductance (NDC): associated with “fake” lines (black resonance)
QTM affects populations

\[ \frac{\Gamma_{\text{forbidden}}}{\Gamma_{\text{allowed}}} \sim (\frac{B_2}{D})^2 \]

Excitation depleted already before transition energy reached

\[ \sim \Gamma_{\text{allowed}} e^{(\Delta E-V)/kT} \]

Weak violation of spin selection rule

\[ \Rightarrow \]

Line moves downwards:
- decreasing QTM
- increasing temperature


\[ B_2 = 10^{-5} \]
QTM-induced current oscillations

(1) Negative conductance resonances: map out anisotropy barriers

(2) Positive resonances shift with $T$: extract $B_2$

...even though QTM-splittings cannot be resolved!
Noise identifies “fake” resonances

\[ \frac{dI(V)}{dV} \]

\[ \frac{d \ln F(V)}{dV} \]

\[ \frac{dF}{dV} > 0 \]

\[ \frac{dI}{dV} < 0 \]

N=1: equal occupations

“Fake” lines terminate

Less fast spin-allowed charge transfer

More slow spin-forbidden processes

Noise enhancement ~ Negative differential conductance
High-symmetry QTM $B_4 >> B_2$

2 groups of states with different magnetic symmetry

$N=0$

$B_4 < D$

$N=1$

$B_4 \sim D'$

Level crossing: ground-state changes character
Current blockade: suppressed overlap

$B_4 < D$

$B_4 \sim D'$

$B_4 < D$

$B_4 < D'$
Magnetic & electronic excitations

$\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{C-C}_6\text{H}_4-\text{SAc})_{16}(\text{H}_2\text{O})_4$

Current suppression up to 5 meV

Diamond edge - PDC - NDC @ 2.5 meV

$V_{bias}$ [mV]

$V_{gate}$ [V]

T = 3 K

T = 1.5 K
2 spin-multiplets / charge state

New type of spin-blockade:
electronic excitation ~ anisotropy barrier $DS^2$
Spin blockade due to $S_z$

CCS due to bias driven population inversion between $N=-1$, $S_z = 9\frac{1}{2}$ and $S_z = 8\frac{1}{2}$

Cascade via excited state spin multiplet into blocking state of ground state spin multiplet
“Relay/Estafette” - mechanism

Sequence of blocking states
\( N=-1, S_z = 8\frac{1}{2}...\frac{1}{2} \)

Connection to experiment:
Size of blocked region \( \sim \) MAB
NDC

Cascade into higher excited states $N=1, S_z=6\frac{1}{2}$

$\Delta_1 = 0.6$

Partially consistent with experiment...

Blocking states "active" beyond some threshold
Advances and prospects in molecular magnetism

Transport spectroscopy

Magnetic excitations in multiple charge states
Non-equilibrium magnetic states:
  Detection
  Control

QTM visible in transport
Non-equilibrium shift of “fake” resonances
  Shot-noise identifies “fake” resonances
  High-symmetry $B_4 \gg B_2$
  Blocking in ground-state

Anisotropy barriers + electronic excitations
Magnetic state population inversion
  - blocking in excited states
  Persistent spin($M$) - blockade

Include
  spin-relaxation