Transport through single molecules

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- Molecular electronics
- Transport theory
- Recent experiments
- Theory: Tunneling through magnetic molecules
Molecular electronics

extrapolation: single molecules as transistors?
**Also:** possible self-assembly of components

using chemical or biochemical processes

(bottom-up approach)

**simple example:**
ester synthesis

\[
\text{COOH} + \text{HO} \rightarrow \text{COO}^- + \text{H}_2\text{O}
\]

**E. Braun et al., Nature 391, 775 (1998)**

**not so simple example:**
DNA encoding

[Diagram showing DNA encoding process]

scalability
Molecular electronics

Also: possible self-assembly of components

using chemical or biochemical processes

(bottom-up approach)

simple example:
ester synthesis

\[ \text{ester} \xrightarrow{\text{reaction}} \text{product} + \text{water} \]

not so simple example:
DNA encoding

DNA

scalability

Switches and memory

- deformations, change of conformation
- local magnetic moments

Readout (and writing)

require electronic tunneling through molecules

Mechanical break junction / electromigration

- **break junctions:** bending of substrate
  - **advantage:** “reversible”

- **electromigration:**
  - strong current, “fuse”

*e.g.*, Reed *et al.*, Science **278**, 252 (1997)

Transport theory
Weak coupling, sequential tunneling regime

![Graph showing current vs. bias voltage](image)

**Transport theory**

- **Coulomb blockade** (like in quantum dots)

- **Graph showing current vs. bias voltage**

- **Diagram** showing the sequential tunneling regime with steps indicating current changes at specific bias voltages.
Weak coupling, sequential tunneling regime

Transport theory
Weak coupling, sequential tunneling regime

Transport theory
Weak coupling, cotunneling regime

\[ \frac{dI}{dV} \text{ (small)} \]

Coulomb blockade

Transport theory
Weak coupling, cotunneling regime

- excitation far from chemical potentials (typical if no gate)
- virtual excitation

\[ I \sim \frac{1}{V} \sim \frac{e^2}{h} \]

Transport theory
Weak coupling, cotunneling regime

Transport theory

- inelastic tunneling opens new set of channels
- local excitation
Tunneling through single molecules: Mechanical break junction


- steps in conductance
- symmetric & small \( \ll e^2/h \) conductance

→ cotunneling, no molecular excitations close to chemical potentials

Experiments
Coupling to vibrations: $C_{60}$ contacts: electromigration


Experiments
$dI/dV \sim \omega_{1/4} 35 \text{ meV}$

$C_{60}$

$\sim \omega_{1/4} 5 \text{ meV}$
Coupling to magnetic moment, **Kondo effect**


electromigration

**Experiments**

weak coupling to leads

magnetic mode

strong coupling to leads

peak pinned at zero bias (no shift with $V_g$)

Kondo effect

Experiments
Anisotropic magnetic molecules: \( \text{Mn}_{12} \) acetate

contacts: electromigration

H. B. Heersche et al., PRL 96, 206801 (2006)

also: M.-H. Jo et al., cond-mat/0603276

black: negative differential conductance \( dI/dV < 0 \)
Theory

Molecular electronics

electronic manipulation of molecular charge, spin, conformation…:

Inelastic transport through single molecules

- coupling to internal degrees of freedom, here: spin
- using magnetic molecules as memory devices:
  - write spin information electronically
  - store spin information
  - read spin information electronically
Inelastic tunneling due to coupling to molecular spin

system: endohedral $N@C_{60}$

nitrogen retains its spin $S_N=3/2$ (Hund's 1st rule)

$C_{60}$ has 3-fold degenerate LUMO

$$H_{\text{mol}} = (\epsilon_{\text{LUMO}} - eV_g) \hat{n} + \frac{U}{2} \hat{n}(\hat{n} - 1) - J S_{C_{60}} \cdot S_N$$

$U$: Hubbard repulsion on $C_{60}$

$J$: ferromagnetic exchange

$$H_{\text{leads}} = \sum_{\alpha=L,R} \sum_{k\sigma} \epsilon_{k\sigma} a_{\alpha k\sigma}^\dagger a_{\alpha k\sigma}$$

$$H_t = \sum_{\alpha=L,R} \sum_{nk\sigma} (t_{\alpha} a_{\alpha k\sigma}^\dagger c_{n\sigma} + t_{\alpha}^* c_{n\sigma}^\dagger a_{\alpha k\sigma})$$

$$H = H_{\text{mol}} + H_{\text{leads}} + H_t$$

production by ion implantation:

Almeida Murphy et al., PRL 77, 1075 (1996)

Density matrix formalism

von Neumann equation for density matrix:

\[ \frac{d\rho_I(t)}{dt} = -i[H_{tI}(t), \rho_I(t)] \]

interaction rep.

\[ \rho_I(t) = \rho_I(0) - i \int_0^t dt' [H_{tI}(t'), \rho_I(t')] \]

iteration:

\[ \frac{d\rho_I(t)}{dt} = -i[H_{tI}(t), \rho_I(0)] \]

\[ - \int_0^t dt' [H_{tI}(t), [H_{tI}(t'), \rho_I(t')]] \]

reduced density matrix of molecule:

\[ \rho_{\text{mol}I}(t) \equiv \text{Tr}_{\text{leads}} \rho_I(t) \]

Born approximation:

\[ \rho_I(t) \approx \rho_{\text{mol}I}(t) \otimes \rho^0_{\text{leads}} \]

Markov approximation

\[ \rho_{\text{mol}I}(t') \approx \rho_{\text{mol}I}(t) \]

at this stage leads to perturbation theory of second order in tunneling

\[ \frac{d\rho_{\text{mol}I}(t)}{dt} \approx - \int_0^t dt' \text{Tr}_{\text{leads}}[H_{tI}(t), [H_{tI}(t'), \rho_{\text{mol}I}(t) \otimes \rho^0_{\text{leads}}]] \]

(sequential tunneling)
Back in Schrödinger picture:

\[
d\rho_{\text{mol}}(t)/dt \approx -i \left[ H_{\text{mol}}, \rho_{\text{mol}} \right] - \text{Tr}_{\text{leads}} \int_0^\infty dt' \left[ H_t, e^{-i(H_{\text{mol}} + H_{\text{leads}})t'} H_t e^{i(H_{\text{mol}} + H_{\text{leads}})t'}, \rho_{\text{mol}}(t) \otimes \rho_{\text{leads}}^0 \right]
\]

\text{cf. Mitra, Alleiner, and Millis, PRB 69, 245302 (2004).}

Can evaluate this now. Alternative derivations:
- diagrammatics on Keldysh time contour [König et al., PRB 54, 16820 (1996)]
- time-convolutionless master equation [Tokuyama and Mori, Prog. Theor. Phys. 54, 918 (1975)]

Assuming fast dephasing = rapid decay of off-diagonal components of $\rho_{\text{mol}}$ obtain rate equations for probabilities $P_n$ of molecular many-body states

\[
\dot{P}_n = \sum_{m \neq n} P_m R_{m \rightarrow n} - P_n \sum_{m \neq n} R_{n \rightarrow m} \equiv \sum_m A_{nm} P_m
\]

Stationary state: \[ 0 = \sum_m A_{nm} P_m \]

Tunneling through magnetic molecules
Results for stationary state

gate voltage
\[ V_g = 0 \text{ V} \]

temperature
\[ T = 0.01 \text{ K} \]


Tunneling through magnetic molecules
Differential conductance

Tunneling through magnetic molecules

Fine structure at temperature $T = 0.1$ K:

Map of crossover points
Origin of fine structure:

- **selection rules** for single-electron tunneling
- **occupation** of initial state

Tunneling through magnetic molecules
Tunneling through molecule with magnetic anisotropy

\[ H_{\text{mol}} = (\epsilon - eV_g) \hat{n} + \frac{U}{2} \hat{n}(\hat{n} - 1) - J \mathbf{s} \cdot \mathbf{S} - K_2 (S^z)^2 \]

C.T. and F. Elste, PRB 73, 235304 (2006)

Energy barrier for spin reversal

Tunneling through magnetic molecules
Relaxation of spin becomes slow

The transitions $X$ become thermally suppressed around $K_2 = 0.04$

Tunneling through magnetic molecules
The only energetically allowed transitions from $n = 0, m = 2$ is to $n = 1, m = 5/2 \rightarrow$ spin-down electron tunnels in (from right) then tunnels out (to left)
A spin-polarized current is flowing until the molecular spin relaxes (very slowly) → A macroscopic magnetic moment is transferred through the molecule

Here: relaxation due to thermal activation. Also possible due to spin tunneling from “up” to “down”, see C. Romeike et al., cond-mat/0511391

Macroscopic spin transfer is due to the small quantum spin $S$ of the molecule → Giant spin amplification

Possible read-out mechanism for molecular electronics

Anisotropy also leads to negative differential conductance (NDC)

$$\frac{dI}{dV} < 0$$
Tunneling through magnetic molecules

C.T. and F. Elste, PRB 73, 235304 (2006)

can write the spin by applying a bias voltage (no magnetic field):

swtiching down $\rightarrow$ up

switching up $\rightarrow$ down

Tunneling through magnetic molecules
Ferromagnetic/nonmagnetic leads: Spin blockade

vanishing anisotropy, $K_2 = 0$

transition $n = 1 \rightarrow 0$, $m \rightarrow m + 1/2$

(spin-down electron out) is suppressed by DOS in ferromagnetic lead

molecule trapped in low-spin state: spin blockade
Conclusions

Molecular electronics

Inelastic transport through single molecules

Theory for magnetic molecules:
- coupling to spin: fine structure
- anisotropy: slow relaxation
- anisotropy: giant spin amplification
- one ferromagnetic lead: spin writing
- one ferromagnetic lead: spin blockade
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