Quantum transport in single-molecule systems

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Outline

- Introduction
- Basic concepts
- Key experimental techniques
  - single-molecules
- Beyond conductance measurements
  - thermopower
  - Raman scattering
  - Inelastic signals in conductance
  - shot noise
- Special topics
  - Cross-over from PCS to IETS
- Future directions, open problems

Ref: Molecular electronics: an introduction to theory and experiment, Juan-Carlos Cuevas and Elke Scheer, World Scientific, 2010
Plastic electronics

• Plastic: usually insulators

• Technology for plastic electronics on thin and flexible plastic substrates was developed at Cambridge University’s Cavendish Laboratory in the 1990s.
Mass production at Konarka company, Lowell, MA, USA

Solarmer Energy, El Monte, Ca, USA
OLED
Engineering molecular properties

A unimolecular zwitterionic rectifier

Basic concepts
Standard picture of molecular transport

Coupling →
Different transport regimes

A. Troisi and M. A. Ratner, Small, 2, 172 (2006)
Resonant transport

\[ T = \frac{\Gamma_L \Gamma_R}{(E_F - E_0)^2 + (\Gamma_L + \Gamma_R)^2 / 4} \]

\[ \Gamma_L \approx \Gamma_R \text{ and } (E_F - E_0) \ll \Gamma: \quad T \rightarrow 1 \]

More typically \( (E_F - E_0) \gg \Gamma: \quad T << 1 \)
Gate control

Low current

High current

$E_F$ $V_{bias}$ $V_{gate}$

$E_F$ $e^-$ $V_{gate}$
Limit of weak coupling: Coulomb blockade

\begin{align*}
\partial I_D / \partial V_{SD} & \bigg|_{V_{SD} \to 0} \\
\partial I & \bigg|_{V_{SD} \to 0} \\
\partial V_{SD} & = \frac{C_G}{(C_G + C_D)} (E_c + \Delta)/e \\
\partial V_G & = \frac{C_G}{C_D} (C_{tot}/C_G)
\end{align*}
Limit of strong coupling: conductance eigenchannels

Incoming waves \( \vec{i}_l \)

Outgoing waves \( \vec{\partial}_r \)

Matrix of transmission ampl.

\[ \vec{\partial}_r = \hat{t} \vec{i}_l \]

Landauer:

\[ G = \frac{2e^2}{h} \text{Tr}(\hat{t}^{\dagger} \hat{t}) = \frac{2e^2}{h} \sum_n T_n \]
Limit of very long molecules: hopping

Break-up of coherence due to
Electron-vibration interactions (polarons)
or
Disorder (intra-molecular tunnelbarriers)
plus electron-electron interactions
Distinguishing feature of molecular junctions

In what are molecules different from quantum dots?

Ionic degrees of freedom

Electron-ion interaction
  signatures in differential conductance
  heating
  polaron formation
Bias-induced conformational changes
Key experimental techniques

Single-molecules
The principle of the measurements
Techniques for adjusting the gap: STM
Deposition of molecules: self-assembly

Deposition process:
1. **Solution** with Thiol-ended molecules
2. **Adsorption** onto Au (111)
3. **Organization** over time
4. **STM Image** of the organized molecules
Techniques for adjusting the gap: STM

STM on self-assembled monolayers

Stuart Lindsay and his group, Arizona State University, USA
Paul Weiss and his group, Penn State, USA
UHV-LT-STM: C$_{60}$

Néel, Kröger, Limot, Frederiksen, Brandbyge, Berndt, PRL 98 (2007) 065502
Techniques for adjusting the gap: STM

**Advantages**

- Imaging + electrical measurements
- Tip manipulation
- Versatile and fast (at room temp.)

**Drawbacks**

- Surface preparation requirements
- Combination LT + UHV complicated
- Top-contact poorly defined

References:

Break junction by electromigration

Techniques for adjusting the gap: electromigration break junction

Advantages

- stable for extended periods
- Can be cycled in temperature and field
- Gate electrode coupling

Drawbacks

- Every junction is different
- Limited statistics
- no geometric information
- danger of formation of nanoparticles

References:

H. Park et al, APL 1999
M. Lambert et al., Nanotechnology 2003
Liang et al Nature 2002
Park et al Nature 2002
Mechanically Controllable Break Junction
Lithographically fabricated MCBJ

\[ \frac{\delta l}{\Delta z} = \frac{6ut}{L^2} \]

Conductance for Au contacts at 4.2 K

Conductance (2e^2/h) vs. Piezo-voltage (V)
Deposition of molecules

Experimental procedure

[Diagrams and images showing the experimental procedure]
Thiol-coupled individual molecules

M.A. Reed et al., Science 278, 252 (1997)
Three terminal molecular junctions

Martin, Smit, van der Zant, and van Ruitenbeek, Nano Lett. 9 (2009), 2940
C.A. Martin, PhD thesis
Techniques for adjusting the gap: mechanically controllable break junction

Advantages

- fast and easy, also at low T
- statistical averaging
- any metal for electrodes
- high stability

Drawbacks

- no cycling in field or temperature
- weak gate coupling
- no geometric information

Muller et al Physica C, 1992
Muller et al PRL 1992
Reed et al. Science 1997
Molecules in solution: conductance histograms
(room temperature)

2D histograms: test clean Au in vacuum

Sample 090515_0:
1 nm/s
100 mV bias
5000 indentation
2100 traces

Conductance ($2e^2/h$)

Counts

Length (Å)
Au/OPE3-dithiol

Sample 091116_5:
1 nm/s
50 mV bias
700 nm indentation
500 traces
Au/OPE3 monothiol

Nominally clean Au junction

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Sample 091207_8: 1 nm/s 50 mV bias 20 G indentation 1600 traces

monoSAc-OPE3

Conductance (2e^2/h)

Length (Å)

Conductance (2e^2/h)

Length (Å)
Alkanedithiols: a model system

Li et al., JACS ASAP, 2008
Systematics of alkane conductance

Can the reproducibility be improved?

- compared to thiols the amine-gold bond is weaker
- the low-bias conductance of amines is more clearly defined

Venkataraman et al., Nano Lett. (6) 3, 2006
Beyond conductance measurements:

Thermopower
Principle of thermopower

\[ S = \frac{V}{T_2 - T_1} \]

\[ S \propto \frac{T}{G} \frac{\partial G}{\partial \mu} \]
Principle of thermopower
Principle of thermopower
Thermopower

Reddy, Jang, Segalman & Majumdar, Science 315 (2009) 1568
Thermopower

Reddy, Jang, Segalman & Majumdar, Science 315 (2009) 1568
Raman scattering
Single molecule Raman spectroscopy

Single molecule Raman spectroscopy

Single molecule Raman spectroscopy

Advantages of low temperatures

• Junctions can be held stable for days

• Analysis tools available that are only effective at low T
  * Vibration mode spectroscopy
  * Shot noise
  * Superconducting subgap structure
  * Thermopower

• Interesting effects appear most clearly
Inelastic scattering signals in conductance

1. Weakly coupled molecules
2. Strongly coupled molecules
Coulomb blockade

(a) Source

(b) Drain

(c) 

\[ \frac{\partial I_D}{\partial V_{SD}} \bigg|_{V_{SD} \to 0} \]

\[ V_G \]

\[ V_S \]

\[ V_G \]

slope = \frac{C_D}{C_D + C_B}

\[ \frac{(E_c + \Delta)/e}{(E_c + \Delta)/e} \]

slope = -\frac{C_D}{C_S}

change degeneracy
Vibration modes in Coulomb blockade

I Coulomb blockade

CURRENT

VOLTAGE

E_g

E_{fL}

E_{fR}

LUMO

HOMO
Break junction by electromigration

Break junction by electromigration

Break junction by electromigration

Edgar A. Osorio, Kevin O’Neill, Nicolai Stuhr-Hansen, Ole F. Nielsen, Thomas Bjørnholm, and Herre S. J. van der Zant*
MOLECULAR VIBRATION SPECTRA BY ELECTRON TUNNELING

R. C. Jaklevic and J. Lambe
Scientific Laboratory, Ford Motor Company, Dearborn, Michigan
(Received 18 October 1966)
Principle of inelastic electron tunneling spectroscopy

\[ G \text{ increases for } eV > \hbar \omega \]
Inelastic Electron Tunneling Spectroscopy

Typically low transmission probability

Stipe et al. Rev. Sci. Inst. 70 (1999), 137

$C_2H_2$
Principle of point contact spectroscopy

$G$ decreases for $eV > \hbar \omega$
Deposition of molecules

Molecule dozer

Capillary

Heating wire

Dipstick

Notch

Metal junction

Copper tube

Resistors

Dipstick

Faraday cage
Conductance histogram for Pt

![Conductance histogram for Pt]

Number of counts vs. Conductance ($2e^2/h$)
Conductance curve for Pt/H₂

Conductance (2e²/h)

Piezovoltage (V)
Conductance histogram for Pt/H₄

Bias voltage 140 mV
Conductance curve for Pt/H\textsubscript{2}
Point contact spectrum for Pt/H$_2$

Modulation: 1 mV, 7 kHz
Recording time: 10 s
Temperature: 4.2 K

Pt-H$_2$: Frequencies and stretching dependence

DFT calculations

Vibrational Frequencies for PtH$_2$ (PW91)

Vibration modes for Deuterium, Pt–D$_2$–Pt
The longitudinal mode for Pt-D$_2$-Pt

![Graph showing the longitudinal mode for Pt-D$_2$-Pt]
DFT calculations

Vibrational Frequencies for PtH$_2$ (PW91)

Comparison $H_2$ and $D_2$

Shot noise
Shot noise

Vacuum diode
W. Schottky (1918)
Shot noise

Vacuum diode
W. Schottky (1918)
Shot noise

Vacuum diode
W. Schottky (1918)
Shot noise

W. Schottky (1918)

\[ S_I = 2eI \]
Transmission probabilities from shot noise

\[ I \propto \frac{1}{T^2} \]

For fermions:

\[ I \propto \frac{1}{T^2} \]

\[ I \propto \frac{1}{T^2} \]
General expression:

\[ S_I = 2eV \frac{2e^2}{h} \coth \left( \frac{eV}{2k_B T} \right) \sum_n T_n (1 - T_n) + 4k_B T \frac{2e^2}{h} \sum_n T_n^2 \]

G.B. Lesovik, JETP Lett. 49 (1989) 592
M. Büttiker, Phys. Rev. Lett. 65 (1990) 2901
Experimental technique
Noise signal analysis

(a) Noise Power [pA^2/Hz] vs. Frequency [kHz]

(b) Noise Power [pA^2/Hz] vs. Frequency [kHz] and Counts
Shot noise as a function of current, Au atomic contact at $G = 1.02 G_0$

**Full shot noise**

Best fit $T_1 = 0.99$

$T_2 = 0.03$

**Equal channels $T_1 = T_2 = 0.51$**

**Best fit**

$T_1 = 0.99$

$T_2 = 0.03$

**One channel**

Fully open

$T_1 = 1.00$

$T_2 = 0.02$

Excess noise ($10^{-26} A^2$/Hz)

Bias current (µA)
Conductance curve for Pt

Conductance ($2e^2/h$) vs. Piezovoltage (V) for Pt.
Shot noise on Pt-D$_2$ junctions

Full shot noise

Pt-D$_2$-Pt

g=1.010(5)

T$_1$=0.995

T$_2$=0.015

F=0.02

Excess noise (10$^{-26}$A$^2$/Hz)

Bias current (µA)

D. Djukic & JMvR, Nano Lett. 6 (2006)
Special topic:

cross over between IETS and PCS
Appearance of vibration mode features in experiment

![Graphs showing d²I/dV² and G₀ versus energy and bias voltage](graph.png)
H$_2$O between Pt leads

![Graph showing conductance (G$_0$) vs. number of counts for Pt and Pt+H$_2$O]
Spectra at high and low conductance for Pt/H$_2$O

\[ dI/dV [G_0] \]

\[ \text{Bias Voltage [mV]} \]

G=1.02 $G_0$

G=0.23 $G_0$
Crossover at ~0.55–0.65 (> 0.5). Do we have a single channel?

Inelastic signals in the conductance

\[ \alpha = \frac{\Gamma_L}{\Gamma_R} \]

L. de la Vega, A. Martín-Rodero, N. Agraït, and A. Levy Yeyati, PRB 73, 075428 (2006)


The transmission of the conductance channels from shot noise

Pt-H$_2$O
G = 0.64 ± 0.01$G_0$

Excess noise [$10^{-26}$ A$^2$/Hz]

Bias Current [µA]

$\tau_1 = 0.51 \pm 0.01$
$\tau_2 = 0.13 \pm 0.01$
Cross over between PCS and IETS

Crossover at $G \approx 0.55–0.65$. The main channel crosses 0.5

Increased $G$ by inelastic scattering at $T \ll 1$
Reduction of $G$ by inelastic scattering at $T=1$
Simple argument for cross over at $T = 0.5$
Outlook
Low-temperature STM

R. Temirov, A. Lassise, F.B. Anders, F.S. Tautz, (Bremen) preprint
STM: Pealing off a molecule

Low-temperature STM

\[ \Gamma_s \geq \Gamma_t \quad \text{phase 1} \]

\[ \Gamma_s >> \Gamma_t \quad \text{phase 2} \]

\[ \Gamma_s \geq \Gamma_t \quad \text{phase 3} \]

R. Temirov, A. Lassise, F.B. Anders, F.S. Tautz, (Bremen) preprint
Pealing off a molecule

Two-state molecules: memory

Molecular transport in network arrays

van der Molen, et al., Nano Lett. 9, 76 (2009).
Recent result: Molecular Switch

π-electrons

External stimulus

‘conjugation’ broken

Tokyo, Jan 2011

ON

OFF

1.8 nm

External stimulus

‘conjugation’ broken

Tokyo, Jan 2011
Light controlled conductance switching

Integration to Si

Most important challenges

• Can we understand the IV curves?
• Can we make single molecule devices reproducibly? Or can we work our way around it?
• Can we identify polaron effects in conductance?
• Can we understand and control the heat dissipation in molecular devices?
• Can we make a single-molecule diode with sufficient asymmetry for applications?
• Can we make a reliable voltage controlled switch?
• Can we develop a route towards higher level composite molecular structures?

• How to proceed?
  • → systematic variations in series of molecules
  • → Model systems
  • → UHV-STM
  • → molecule-semiconductor devices