Chapter 11

Electronic transport measurements

1. Measurements of the linear conductance (DC)
2. Measurement of current-voltage characteristics
3. Measurements of differential conductance $dI/dV$ and IETS/PCS ($d^2I/dV^2$)
4. Thermopower
5. Shot Noise

REFERENCES

1) Chapter 5 of the lecture script
Typical Properties of Functional Structures

1. **Diode**: Au-SAM-Thiol-Au (Nanopore) 4-thioacetatebiphenyl, M. Reed, APL (1997)

2. **Switch**: Nanopore (60 K) M. Reed et al., Science (1999)


Non-linear IVs: Current bias vs. Voltage bias

Resonant case: transport through molecular level

Off resonant case: molecules as tunneling junctions

Design of the electrical measurement circuit

- What is the property to measure?
- Energy resolution? Which voltage range?
- Absolute & relative amplitude of signal?
- Small relative signal on constant background?
  -> Lock in technique
- Large variations of the background (high dynamic range)
  -> I & V have to be measured
- Which absolute resistance/conductance regime?
- Expected size of voltage signal:
  ~ 1 nV or 1 pA possible with RT electronics (thermal noise),
  for smaller voltages: SQUID or cold amplifiers
Intrinsic current fluctuations of an electrical resistor:

\[ S_I(\omega) = 2 \int dt e^{i\omega t} \langle \Delta \hat{I}(t + t_0) \Delta \hat{I}(t_0) \rangle \]

\[ \Delta \hat{I}(t) \equiv \hat{I}(t) - \langle \hat{I}(t) \rangle \]

* Thermal fluctuations:
  \[ S_I = 4k_B T \]

/Nyquist noise:

* Non-equilibrium fluctuations (shot noise): randomly distributed tunneling of \( q \) discrete charges.

\[ S_{\text{Poisson}} = 2q |I| \]

(W. Schottky 1918)
Typical Measurement Task in Molecular Electronics:

Aluminium few-atom contacts

Histogram calculated from >6200 scans

Aluminium T < 100 mK

Electrode distance (nm)

Conductance (2e^2/h)

Conductance (2e^2/h)

Counts

A Yanson, Leiden "classical" breakjunction T = 4.2 K
Particular requirements for electronic measurement of atomic and molecular contacts

- Wide range of conductance from $10^{-5} \, G_0$ (10 GΩ) to few $G_0$ (kΩ)
- Measurement of linear conductance, e.g. for conductance histograms: Correct choice of bias voltage to assure working in the linear regime - difficult because nonlinearities appear on varying voltage scales ($\mu$V to V)
- Self-heating of the contacts due to Joule dissipation is difficult to detect & to discriminate from intrinsic properties
- Sudden voltage spikes and jumps may destroy the sample.
- Extreme variation of the differential conductance within small changes of the bias.
- Strongly nonlinear IVs with negative differential resistance NDR or hysteresis -> voltage bias vs. current bias -> hysteresis effects
- Limited lifetime of the junctions.
11.1 Conductance vs. Resistance measurements

Ohm’s law – linear conductance

Conductance $G = \frac{\text{Current } I}{\text{Voltage } V}$

Differential Conductance $= \frac{dI}{dV}$

High resistance $R_x > R_s$: (Low conductance $G_x < G_s$)
Voltage bias, current measurement – effective conductance measurement

Low resistances $R_x < R_s$: (High conductance $G_x > G_s$)
Current bias, voltage measurement – effective resistance measurement
Example: IVs of a superconducting atomic contact

- $B = 0$
- $B = 5\,\text{mT}$
- $B = 13\,\text{mT}$

$T = 30\,\text{mK}$
Example: IVs of a superconducting atomic contact

Hysteresis!
Example: IVs of a superconducting atomic contact

![Graph showing IV characteristics of a superconducting atomic contact with Al bridge, C18-21, 170696.](image)

- **Very high differential conductance**
- **Very low differential conductance**

\[ \Delta = 180 \, \mu V \]

**T = 30 \, mK**

Similar: SET
11.2 Nonlinear-Conductance Measurements with high dynamic range & high spectral resolution

Set-up for measuring IVs of atomic contacts with strongly varying linear and differential conductance (corresponding to differential resistances of kΩ to MΩ)

$V$: Bias voltage applied to series of $R_s + R_x$
$R_s$: series resistance, chosen according to expected differential resistance
For $R_s < R_x$: Voltage bias, for $R_s > R_x$: effective current bias
Minimum $R_s$ necessary for current limitation
$F$: Low-pass filters, necessary for achieving high energy resolution

After amplification:
$V \rightarrow x$-channel, $I \rightarrow y$-channel of oscilloscope or analogue-digital converter
Measurement of the conductance of a hydrogen molecule between Pt leads with the break-junction technique
11.3 Scanning probe spectroscopy and Inelastic Electron Tunneling Spectroscopy

„negative“ atoms?

oxygen / Pt(111)

J. Wintterlin, Berlin

Courtesy: G. Costantini, MPI Stuttgart
Tunneling spectroscopy

\[ E_F = -E_F \]

\[ \Phi_{\text{tip}} \]

\[ \Phi_{\text{sample}} \]

\[ eV \]

\[ I \]

\[ V \]
Tunneling spectroscopy

- $E_F$
- $\Phi_{\text{tip}}$
- $\Phi_{\text{sample}}$
- $eV$

Tip

Sample
Tunneling spectroscopy

\[ \Phi_{\text{tip}} \]

\[ \Phi_{\text{sample}} \]

\[ -E_F \]

\[ 0 \]

\[ E \]

\[ z \]

\[ eV \]

\[ I \]

\[ V \]
Tunneling spectroscopy

$-E_F$

Sample

Tip

$\Phi_{\text{tip}}$

$\Phi_{\text{sample}}$

$I$

$V$
Tunneling spectroscopy

- $E_F$
- $\Phi_{\text{tip}}$
- $\Phi_{\text{sample}}$
- $eV$

Sample

Tip
Tunneling spectroscopy
Tunneling spectroscopy

$E_F$: Fermi level
$\Phi_{\text{tip}}$: Tip potential
$eV$: Energy difference between tip and sample
$\Phi_{\text{sample}}$: Sample potential

$I$: Current
$V$: Voltage

Diagram showing the energy levels and current-voltage characteristics in tunneling spectroscopy.
Tunneling spectroscopy

- $E_F$
- $\Phi_{\text{tip}}$
- $\Phi_{\text{sample}}$
- $eV$

Graph: $I$ vs $V$
Tunneling spectroscopy

The diagram illustrates the principle of tunneling spectroscopy. The energy levels of the tip and sample are shown as $-E_F$ and $eV$, respectively. The Fermi level in the tip ($\Phi_{\text{tip}}$) and in the sample ($\Phi_{\text{sample}}$) are indicated. The graph on the right shows the current $I$ as a function of the voltage $V$, with $dI/dV$ peaks indicating the presence of electronic states in the sample.
surface state Cu(111)  

\[ \text{dI/dV (a.u.)} \]

\[ \text{Bias Voltage (V)} \]

L. Vitali, MPI-FKF

\[ n\text{-InAs(110)} \]

\[ \text{dI/dV [arb. units]} \]

\[ \text{sample voltage [V]} \]


HBC molecules on Au(001)  

\[ \text{dln/dnV} \]

\[ \text{Voltage / V} \]

T. Fritz, TU Dresden

YBCO films  

\[ \Delta = 16 \text{ meV} \]

\[ \text{dI/dV (a.u.)} \]

\[ \text{Sample Bias (meV)} \]

Pentacene on thin layer of NaCl on Cu (111) for decoupling the molecular states from the electronic states of the metal surface (reducing $\Gamma_s$).

- Functionalization of tip changes the "active" orbital.
Elastic tunneling

\[ -E_F \]

\[ 0 \]

\[ E \]

\[ \Phi_{\text{tip}} \]

\[ eV \]

\[ \Phi_{\text{sample}} \]

\[ I \]

\[ V \]
Elastic tunneling

\[-E_F\]

\[0\]

\[E\]

\[\Phi_{\text{tip}}\]

\[\Phi_{\text{sample}}\]

\[eV\]
Elastic tunneling
Elastic tunneling

\[ -E_F \quad 0 \quad E \]

\[ \Phi_{\text{tip}} \]

\[ eV \]

\[ \Phi_{\text{sample}} \]
Elastic tunneling

$-E_F$  
$0$  
$E$

$\Phi_{\text{tip}}$

$\Phi_{\text{sample}}$

$eV$

$I$

$V$
Elastic tunneling

\(-E_F\)

\(0\)

\(E\)

\(z\)

\(\Phi_{\text{tip}}\)

\(\Phi_{\text{sample}}\)

\(eV\)

\(dI/dV\)

\(V\)
Inelastic tunneling

possibility of vibrational "channels"
Inelastic tunneling

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Inelastic tunneling

\( -E_F \)

\( \Phi_{\text{tip}} \)

\( \Phi_{\text{sample}} \)

\( eV \)

Possibility of vibrational “channels”
Elastic tunneling

\[ \frac{dI}{dV} \sim LDOS \]

\[ \frac{d^2I}{dV^2} \]

Inelastic Electron Tunneling Spectroscopy

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

\[ \frac{d^2I}{dV^2} \sim vDOS \]
Reminder: 9.1 Signatures of vibrational modes

(a) IETS:
Weak e-ph coupling
Off-resonant tunneling

(b) PCS:
Weak e-ph coupling
High conductance (~ $G_0$)

(c) RIETS:
Strong e-ph coupling
Weak electronic coupling
Measurement of LDOS by STS

1. Order perturbation theory

\[ I = \frac{2me}{h} \int_{-\infty}^{\infty} \left[ f(E_F - eV + \varepsilon) - f(E_F + \varepsilon) \right] \rho_S(E_F - eV + \varepsilon) \rho_T(E_F + \varepsilon) M_{\mu\nu} d\varepsilon \]

mit \( \rho_{T,S} \) Density of states of tip and sample

\( M_{\mu\nu} \) Tunnel matrix element: overlap of wave functions of tip and sample, depends on chemical nature and geometry

Für \( M_{\mu\nu} = \text{const.} \) and low temperature it follows:

\[ I \propto \int_{0}^{eV} \rho_S(E_F - eV + \varepsilon) \rho_T(E_F + \varepsilon) d\varepsilon \]

If \( \rho_T = \text{const.} \):

\[ \frac{dI}{dV} \propto \rho_S \]

Local Density of States (LDOS) of the sample
9.3 Measurement of IV, dI/dV and d²I/dV² of molecular contacts

Source: Y. Kim, A. Karimi, D. Weber
11.3 Lock-in technique

Purpose: low-noise amplification by phase sensitive detection in a narrow frequency band and cross-correlation (narrow band pass filter)

Main ingredients of a lock-in amplifier:
- Preamplifier for input signal $V_{in}(t)$
- Channel for reference signal (internal or external)
- Phase shifting unit ($\Delta \phi$), applies phase between signal and reference
- Mixer (multiplier)
- Low pass for integrating the cross correlation

Cross correlation: $V_{out}(t)$ non-zero if $f_{in} = f_{ref}$

$V_{out}(t) = \frac{1}{T} \int_{t-T}^{t} \sin[2\pi f_{ref} \cdot s + \Delta \phi]V_{in}(s)ds$

For sinusoidal signals: $V_{out}(t) \propto V_{in}(t) \cos(\Delta \phi)$
11.3 Lock-in Technique for measuring \( \frac{dV}{dI} \) and \( \frac{d^2V}{dI^2} \)

Superposition of DC signal and harmonic AC signal: \( I = I_0 + I_1 \cos \omega t \)

\[
V_{PK}(I) = V_{PK}(I_0) + \frac{dV_{PK}}{dI} \bigg|_{I_0} I_1 \cos \omega t + \frac{1}{4} \frac{d^2V_{PK}}{dI^2} \bigg|_{I_0} I_1^2 \cos 2\omega t + \cdots .
\]

1st harmonic \( \propto \frac{dV}{dI} \)

2nd harmonic \( \propto \frac{d^2V}{dI^2} \)

MCBJ at low temperature:
Opening Traces and Conductance Histograms

Examples:
I-Vs and IETS of HDT@ 4.2 K

\[ \Gamma_{L,R} = 120 \text{ meV}, \ E_0 = 2.35 \text{ eV} \]

\[ \Gamma_{L,R} = 110 \text{ meV}, \ E_0 = 1.93 \text{ eV} \]
Symmetry of IETS spectra

Black/blue: as measured

Red: symmetrized signal

\[ y = \frac{[f(x) - f(-x)]}{2} \]

Linewidth broadening of IETS of ODA

Experimental linewidth $W_{\exp}$ given by intrinsic linewidth $W_I$, thermal broadening $k_B T$ and modulation voltage $V_{ac}$:

$$W_{\exp} = [(5.4k_B T)^2 + (1.7V_{ac})^2 + (W_I)^2]^{1/2}$$

a) $V$ dependence at fixed $T$: black line: linear fit $\rightarrow W_I = 4.9 \pm 0.8$ meV

b) $T$ dependence at fixed $V_{ac}$: black squares: theoretical expectation, red dots: experimental findings

$T = 4K$: $5.4k_B T = 1.8$ meV
Assignment of modes

Vibrational modes of free molecules known from Raman spectroscopy

-> For molecules in junctions: Theory required!
11.4 Measuring thermopower of metallic contacts (with MCBJ)

Thermopower (Seebeck coefficient) $S = \frac{V_{th}}{\Delta T}$

$T_{base} = 4.2$ K

Typical values

$\Delta T \sim 0.1$–1 K

$V_{th} \sim nV - \mu V$

-> requires 2 well-calibrated (resistive) thermometers and high-resolution voltage measurement (e.g. SQUID) or switching to same DVM at low $T$ (avoiding thermopower contributions from wiring)
11.4 Measuring thermopower of molecular contacts with STM

Thermopower (Seebeck coefficient) \( S = \frac{V_{th}}{\Delta T} \)

Typical values
\( \Delta T \sim 10 - 30 \text{ K} \)
\( V_{th} \sim \mu\text{V} - \text{mV} \)

\( T_{\text{base}} = 300 \text{ K} \)

Step 0
Stabilize \( \Delta T = T_{\text{hot}} - T_{\text{amb}} \)

Step 1: V bias, I-meas. while approaching until \( G = 0.1 G_0 \)

Step 2: V bias = 0, \( V_{th} \) – meas. while withdrawing

K. Baheti, J.A. Malen, P. Doak, P. Reddy, S.-Y. Jang, T. Don Tilley, Arun Majumdar, and R. A. Segalman,
11.5 Shot noise in atomic contacts


\[ S_I(V) = \int \langle I(t)I(0) \rangle - \langle I \rangle^2 \, dt = 2eV \frac{2e^2}{\hbar} \sum_n \tau_n (1 - \tau_n) \]
11.5 Correlation set-up for noise measurements

Problem: Signal of interest $S_I$ is smaller than noise of measurement circuit
Solution: Correlation measurement

Current-biasing sample $R_D$ via $R_B$

Cross-correlation eliminates all uncorrelated voltage noise (from leads and amplifiers)

Voltage-noise sources

Current-noise sources
11.5 Correlation set-up for noise measurements

\[
S_{V_1V_2}(v) = \frac{R_\parallel^2}{1 + (2\pi v R_\parallel C)^2} \times \left[ S_I + S_B + 2 \left(1 + \frac{R_L}{R_\parallel}\right) S_{\text{Amp}}\right]
\]

where

\[
R_\parallel = \frac{R_B R_D}{(R_B + R_D)}
\]

\(S_B\) and \(S_{\text{Amp}}\) have to be measured independently.
11.5 Correlation set-up for noise measurements

\[ S_{V_1V_2}(\nu) = \frac{R^2_{||}}{1 + (2\pi \nu R_{||} C)^2} \times \left[ S_I + S_B + 2 \left( 1 + \frac{R_L}{R_{||}} \right) S_{Amp} \right] \]

where

\[ R_{||} = \frac{R_B R_D}{R_B + R_D} \]

Examples of equilibrium Noise spectra \( V = I = 0 \)
11.6 Lock-in Technique for measuring $\text{dI/dV}$ and shot noise with simple wiring

- Measuring the conductance (opening and closing curves)
- First and second differential conductance
- Measurements of the noise in a rather broad range of conductance values from $0.01 \, G_0$ to $1 \, G_0$

Source: Y. Kim, A. Karimi, D. Weber
Example: Inelastic shot noise

Quantum mechanical scattering & discreteness of charge generate shot noise.