Chapter 10: Beyond Electrical Conductance: Shot Noise and Thermopower

REFERENCES

1) Chapters 4 & 19 of Cuevas & Scheer.


10.0 Reminder: Landauer Formula and Transmission Coefficients

Channels are scattering eigenstates, $\tau_i$ are eigenvalues

Landauer formula: $G = \frac{2e^2}{h} \tau = G_0 \tau$ with $\tau = \sum_{n=1}^{N} \sum_{m=1}^{M} |t_{nm}|^2 = \text{Tr}[tt^\dagger] = \sum_{i=1}^{N} \tau_i$

Problem: $G$ measures sum of $\tau_i$.
No information about individual $\tau_i$ available from measuring $G$!

Note: In this chapter we use $\tau$ instead of $T$ for labeling the transmission coefficients.
10.0 Reminder to Chapter 7: Experimental Determination of Transmission Coefficients of Metallic Contacts

Superconducting IVs: Nonlinearities due to MAR
10.1 Nonlinear Functions of Transport Channels


\[ S \propto \sum \tau_i (1 - \tau_i) \]

**Conductance fluctuations:** Ludoph et al., PRL 82 (1999) 1530

\[ \Delta G \propto \sum \tau_i^2 (1 - \tau_i) \]

**Thermopower fluctuations:**
Ludoph et al., PRB 59 (1999) 12290

\[ \sigma \propto \sum \tau_i^2 (1 - \tau_i) \]

**Supercurrent:** Goffman et al., PRL 85 (2000) 170

\[ I_J \propto \sum \tau_i (1 - \tau_i \sin^2(\delta/2))^{-1/2} \cos(\delta/2) \]

**Superconducting IVs/MAR:** Scheer et al., PRL 78 (1997) 3535

→ can be used for measuring channels
10.1 Shot noise

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:
  
  Johnson/Nyquist noise
  
  \[ S_I = 4k_B T G \]

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

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

(W. Schottky 1918)
10.1 Shot noise in atomic contacts


\[ S_I(V) = \int \left( \langle I(t)I(0) \rangle - \langle I \rangle^2 \right) dt = 2eV \frac{2e^2}{h} \sum \tau_n (1 - \tau_n) \]
10.1 Shot noise in atomic contacts

H.E. van den Brom et al, Phys. Rev. Lett. 82, 1526 (1999)
10.1 Pt-hydrogen-Pt junctions: Conductance histograms


- The hydrogen molecule forms a stable bridge between Pt electrodes.
- The conductance is $G \approx G_0$ and is largely dominated by a single conduction channel.
10.1 Pt-hydrogen-Pt junctions: Shot noise measurements

D. Djukic and J.M. van Ruitenbeek, Nano Lett. 6, 789 (2006).

\[ S_I = 2eV \coth\left( \frac{eV}{2k_BT} \right) \frac{2e^2}{h} \sum_i \tau_i (1 - \tau_i) + 4k_BT \frac{2e^2}{h} \sum_i \tau_i^2 \]

If \( k_BT \gg eV \):

\[ S_I = 2eI \left( 1 - \frac{\sum_i \tau_i^2}{\sum_i \tau_i} \right) = 2eIF(\{\tau_i\}) \]

\( F \) = Fano factor

**Diagram:**
- Graph showing excess noise (in 10^26 A^2/Hz) plotted against energy (meV) and bias current (\( \mu A \)).
- Graph for Pt-D_2 with data points and trend lines.
- Diagram of Pt-D_2 molecule.
10.1 Pt-benzene-Pt junctions: Conductance histogram


- The introduction of benzene supresses the formation of pure Pt contacts.
- New junctions with preferred conductance of $1G_0$ and sometimes $0.2G_0$ are formed while stretching the contact.
Several channels contribute to transport for high conductances (ca. $1G_0$).

The number of channels is reduced to one when the conductance is reduced to around $0.2G_0$. 

\[ S_I = 2eV \coth\left( \frac{eV}{2k_BT} \right)G_0 \sum \tau_i (1 - \tau_i) + 4k_B T G_0 \sum \tau_i^2 \]
10.2 Thermopower

- **Thermopower (or Seebeck coefficient):**

\[ S = -\frac{\Delta V}{\Delta T} \]

\( \Delta V = \) thermoelectrical voltage
\( \Delta T = \) temperature difference

- **Thermopower in the coherent transport regime:**

\[ S = \frac{1}{eT} \int_{-\infty}^{\infty} (E - \mu) \tau(E) \left[ \frac{\partial f(T, E)}{\partial E} \right] dE \]
\[ \int_{-\infty}^{\infty} \tau(E) \left[ \frac{\partial f(T, E)}{\partial E} \right] dE \]

\( \tau(E) = \) transmission
\( f(E) = \) Fermi function

**Low-temperature expansion:**

\[ S = -\frac{\pi^2 k_B^2 T}{3e} \frac{\tau'(E_F)}{\tau(E_F)} \]

\[ \left[ \tau'(E_F) = \frac{d\tau}{dE} \bigg|_{E=E_F} \right] \]
10.2 Thermopower measurements of Au atomic contacts


Break-junction setup

Thermopower vs. piezo voltage

![Diagram of a break-junction setup with labels for 25 μm gold wire, RuO₂ heaters, RuO₂ thermometers, notched 100 μm gold wire, phosphor bronze bending beam, and piezo. The graph shows thermopower vs. piezo voltage with data points and labels for S (μV/K) and G (2e²/h).]
10.2 Thermopower measurements of Au atomic contacts


- The thermopower can be both positive and negative, but it vanishes on average.
- The thermopower fluctuations of Au reach a minimum close to $1G_0$.
- **Interpretation:** the thermopower is due to interference effects induced by the presence of impurities nearby the contact region.
10.2 Why thermopower of molecular junctions?


- It is measurable.
- It gives valuable information about the location of the Fermi level.
- It is rather insensitive to the details of the coupling to the contacts.

**Thermopower or Seebeck coefficient**

\[
S = \frac{1}{eT} \int_{-\infty}^{\infty} \frac{(E - \mu) \tau(E) \left[ \partial f(T, E) / \partial E \right] dE}{\int_{-\infty}^{\infty} \tau(E) \left[ \partial f(T, E) / \partial E \right] dE}
\]
10.2 Thermopower measurements in molecular junctions

10.2 Probing the chemistry of molecular heterojunctions using thermoelectricity


Study of the effect of different substituents and end groups

- Electron-withdrawing groups
- Electron-donating group
- Electron-withdrawing groups
- Different end group

Reference molecule
10.2 Thermopower measurements in molecular junctions


Thermopower or Seebeck coefficient

\[
S = \frac{1}{eT} \int_{-\infty}^{\infty} \frac{(E - \mu)\tau(E)\left[ \frac{\partial f(T, E)}{\partial E} \right] dE}{\int_{-\infty}^{\infty} \tau(E)\left[ \frac{\partial f(T, E)}{\partial E} \right] dE}
\]
10.2 Probing the chemistry of molecular heterojunctions using thermoelectricity


- The electron-withdrawing groups reduce the thermopower: HOMO lies further away from Fermi level.
- The electron-donating groups increase the thermopower by moving the HOMO closer to the Fermi level.
- BDCN has a negative thermopower: Transport is dominated by the LUMO.
10.2 Ab-initio studies of the thermopower

Length dependence

\[ \tau(E) \approx \alpha(E) \exp(-\beta(E)N) \]

\[ S = S^{(0)} + S^{(1)}N \]

Exp.: P. Reddy et al., Science 2007
Theory: F. Pauly et al., PRB 2008

Influence of conjugation

\[ q_1 + q_2 \cos^2(\varphi) \]

Exp.: F. Pauly et al., PRB 2008
Theory: M. Bürkle et al., PRB 2012

C\textsubscript{60} junctions

S. Bilan et al., PRB 2012
10.2 Towards efficient thermoelectrics

Thermoelectric elements
• Conversion of waste heat into electrical energy
• Nanorefrigerators

Figure of merit: $ZT = S^2GT/\kappa$

Thermopower $S$
Temperature $T$
Electric conductance $G$
Thermal conductance $\kappa$

$\kappa = \kappa_{el} + \kappa_{ph}$

Ultimate Goal: Enhancement of $ZT$ through appropriate nanostructuring