Chapter 7

1. The conductance of a single atom

7.1.1 Landauer approach to conductance

real system

\[ G_0 = \frac{2e^2}{h} \approx (12.9 \text{ k}\Omega)^{-1} = \text{conductance quantum} \]

\[ G = \frac{2e^2}{h} T(E_F) = G_0 \sum_{n} T_n \]

\( T(E_F) \) = total transmission at \( E_F \)

\( T_n \) = transmission coefficients

Landauer formula

(low-temperature conductance)

electron reservoirs

scattering region

\( E_F + eV \)

\( S \)

\( E_F \)

incoming

\( N_L \)

outgoing

incoming

\( N_R \)

outgoing
7.1.2 Conductance of atomic-scale contacts

1. Scanning tunneling microscope (STM)

2. Break junctions (MCBJ)

Binning & Rohrer (1982)  
Gimzewski & Möller (1987)  
Agraït et al. (1992)

...........

J.M. van Ruitenbeek et al. (1992, 1996)
7.1.2 Conductance of atomic-scale contacts

7.1.2 Conductance of atomic-scale contacts

Reminder: Conductance quantization in 2DEG point contacts

Point contact defined in a 2D electron gas by means of a split gate on top of a semiconductor heterostructure.

Point contact conductance as a function of gate voltage at 0.6 K. The constriction width increases with increasing voltage on the gate (see inset).

7.1.2 Conductance of atomic-scale contacts


STM experiments (4.2 K for Al and 1.5 K for Pb)

- The conductance traces differ significantly from metal to metal and, in the case of multivalent metals, there are no plateaus at multiples of the conductance quantum.

- Notice that the traces depend also on whether the contact is being opened or closed.
7.1.2 Conductance of atomic-scale contacts


- Simultaneous measurement of the conductance and force in a Au contact at room temperature.

- Notice the stress accumulation on the plateaus and the coincidence of the stress relief events with the jumps in the conductance.

**Conclusion:** The conductance jumps correspond to sudden atomic rearrangements in which some atomic bonds are broken and the cross section of the contact varies in an abrupt manner.
7.1.3 Conductance histograms

Au Histogram
STM, 300 K

Conductance quantization?

Pt and Ni Histograms
MCBJ, 4.2 K

M. Brandbyge et al., PRB 52, 8499 (1995)

Not always!

A.I. Yanson, PhD thesis, University of Leiden (2001)
7.1.3 Conductance histograms

The conductance histograms are in general sensitive to experimental conditions such as temperature, voltage, breaking speed, environmental conditions, etc.

7.1.3 Conductance histograms

Summary of the findings regarding the conductance histograms:

- With exception of alkali metals, the highest peak is always lying at the lowest frequently occurring conductance value.

- The position of this peak for all the elements falls in the range between 0.7 and 2.3\(G_0\). There is no structure related to metallic conductance in the histograms below the position of the first peak.

- For free electron-like alkali metals the first peak is extremely sharp and is located almost exactly at 1\(G_0\). This statement also extends to the noble metals.

- For divalent metals (zinc, magnesium) and trivalent ones (aluminum) the first peak is rather sharp and located slightly below 1\(G_0\). Other multivalent metals, and in particular transition metals, exhibit a broad first peak located well above 1\(G_0\) and in some cases like niobium it lies even above 2\(G_0\).
7.1.4 Determining the conduction channels


One can determine experimentally the transmission coefficients in superconducting materials.

$V = \text{voltage}$

$\Delta = \text{energy gap}$

Break junctions: Al single-atom contacts (30 mK)
7.1.4 Determining the conduction channels

Theoretical results for the I-V curves of a single-channel superconducting quantum point contact.

I-V curves (zero temperature)  Differentical conductance vs. voltage

The same results with different methods: Averin & Bardas (95), Shumeiko et al. (97).
7.1.4 Determining the conduction channels

Transport between superconducting electrodes:
tunnel regime $\rightarrow$ single-particle processes

$E_{F,L} - E_{F,R} = eV > 2\Delta$

| Probability: $T$ | Charge transfer: $1e$ |
7.1.4 Determining the conduction channels

Andreev reflection: a two-particle tunneling process

Superconductor

\[ eV > \Delta \]

Superconductor

Probability: \[ T^2 \]

Charge transfer: \[ 2e \]

\[ I \]

\[ \Delta \quad 2\Delta \quad eV \]
Multiple Andreev reflection: a multi-particle tunneling process

\[ eV > 2\Delta/3 \]

**Probability:** \( T^3 \)

**Charge transfer:** \( 3e \)
7.1.4 Determining the conduction channels

Fitting the experimental I-V curves
(Al MCJB, 30 mK, last conductance plateau)

- experimental data
  (Total transmission = 0.807)

\[ \frac{\tau_n}{\Delta} = \begin{cases} 
0.652 \\
(0.390, 0.388) \\
(0.405, 0.202, 0.202)
\end{cases} \]
7.1.4 Determining the conduction channels


In the last plateau of an Al contact, where $G < G_0$, two or three channels contribute to the transport.

![Graph showing conductance vs. energy](image)

<table>
<thead>
<tr>
<th>$T_{\text{total}}$</th>
<th>0.875</th>
<th>0.817</th>
<th>0.807</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.682</td>
<td>0.399</td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>0.12</td>
<td>0.254</td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>0.154</td>
<td></td>
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</tr>
</tbody>
</table>

[Yanson and van Ruitenbeek PRL (1997)]
### 7.1.5 Chemical nature of the conduction channels of one-atom contacts


\[
\hat{H} = \sum_{i\alpha,\sigma} \varepsilon_{i\alpha} \hat{c}^+_{i\alpha,\sigma} \hat{c}_{i\alpha,\sigma} + \sum_{i \neq j, \alpha\beta,\sigma} t_{i\alpha, j\beta} \hat{c}^+_{i\alpha,\sigma} \hat{c}_{j\beta,\sigma}
\]

\[i, j \rightarrow \text{atoms} \quad \alpha, \beta \rightarrow \text{orbitals}\]

- \(t_{i\alpha, j\beta} \rightarrow\) (nearest neighbors) bulk parameterization (Papaconstantopoulos, 1986).

- Orthogonal basis and Slater-Koster two-center approximation.

**Ingredients**

- **Chemistry:** minimum basis \(\rightarrow\) valence orbitals.

<table>
<thead>
<tr>
<th>Material</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali and noble metals: Li, Na, K, ..., Cu, Au, and Ag</td>
<td>(s)</td>
</tr>
<tr>
<td>sp-like metals: Al, Pb, Zn, Cd, Mg, etc.</td>
<td>(s) and (p)</td>
</tr>
<tr>
<td>Transition metals: Nb, Pt, Pd, Ti, Fe, Co, etc.</td>
<td>(s) and (d)</td>
</tr>
</tbody>
</table>

- **Geometry:** importance of the local environment.

- **Charge neutrality:** self-consistent determination of the on-site energies.
7.1.5 Chemical nature of the conduction channels of one-atom contacts

Electrical current (Landauer formula):
\[ I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \text{Tr} \{ t^+ t \} [ f_L - f_R ] \]

Transmission matrix expressed via Green’s functions:
\[ t(E, V) = 2\Gamma_L^{1/2} (E, V) G_{CC}^r (E, V) \Gamma_{R}^{1/2} (E, V) \]

- Scattering rates: \( \Gamma_X = \text{Im} \{ \Sigma_X^a \} \), where \( \Sigma_X^a = t_{CX} g_{XX}^a t_{XC} \) (\( X = L, R \))

- The central Green’s functions are given by:
  \[ G_{CC}^{r,a} = \left[ (E \pm i\eta)1 - H_{CC} - \Sigma_{L}^{r,a} - \Sigma_{R}^{r,a} \right]^{-1} \]

- \( \text{Dim}(t^+ t) = N_C \rightarrow \) number of orbitals in the first layer (due to nearest neighbor couplings).

Linear regime:
\[ G = \frac{2e^2}{h} \sum_{i=1}^{N_C} T_i \]

\( T_i = \) eigenvalues of \( t^+ t \) at the Fermi energy.
7.1.5 Chemical nature of the conduction channels of one-atom contacts

- Transmission evaluated at the central atom: $\text{Dim}(t^+ t) = N_{orb}$

The number of channels is controlled by the number of valence orbitals in the central atom

- In the case of one-atom contacts the channels are linear combinations of the atomic orbitals of the central atom:

$$|\text{channel}_i\rangle = c_{is} |\bigcirc\rangle + c_{ip} |\bigcirc\rangle + c_{id} |\bigcirc\rangle$$

- Assuming that there is a single relevant orbital per atom, the transmission adopts the form:

$$T(E) = \frac{4\Gamma_L(E)\Gamma_R(E)}{[E - \tilde{\varepsilon}_0]^2 + [\Gamma_L(E) + \Gamma_R(E)]^2}$$

- If there are several relevant orbitals per atom (sp-like metals, transition metals, etc.), then it is difficult to satisfy the “resonant” condition for all the channels at the same time. This implies that in multivalent metals there are often several channels with intermediate transmissions and therefore, there is no conductance quantization!!!
7.1.5 Chemical nature of the conduction channels of one-atom contacts

Aluminum: [Ne]3s²3p¹  
Lead: [Xe]6s²6p²
Experimental confirmation that the chemical valence determines the number of channels of one-atom contacts.
7.1.5 Chemical nature of the conduction channels of one-atom contacts

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductance (G₀)</th>
<th>Number channels</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali and noble metals</td>
<td>~ 1</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td>Al</td>
<td>0.6 – 1.1</td>
<td>3</td>
<td>s und p</td>
</tr>
<tr>
<td>Pb</td>
<td>1.5 - 2.5</td>
<td>3</td>
<td>s und p</td>
</tr>
<tr>
<td>Nb</td>
<td>2 - 3</td>
<td>5</td>
<td>s und d</td>
</tr>
</tbody>
</table>

Macroscopic wires: Resistivity (x 10⁻⁸ Ωm) at T = 300 K

<table>
<thead>
<tr>
<th>Material</th>
<th>Ag</th>
<th>Cu</th>
<th>Au</th>
<th>Al</th>
<th>Na</th>
<th>Zn</th>
<th>Pt</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>1.61</td>
<td>1.72</td>
<td>2.27</td>
<td>2.73</td>
<td>4.93</td>
<td>6.01</td>
<td>10.8</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Small is different!!
7.1.6 Atomic chains: discovery

A.I. Yanson, G. Rubio Bollinger, H.E. van den Brom, N. Agraït, J.M. van Ruitenbeek,


Conductance as a function of the displacement of the two gold electrodes with respect to each other in a MCBJ experiment at 4.2 K.

Distribution of lengths for the last conductance plateau for Au, obtained from 10000 experiments.
7.1.6 Atomic chains: discovery

TEM images of a gold contact recorded while withdrawing the tip from the sample.

TEM image of a gold atomic chain (four yellow dots) forming a bridge between two gold banks (yellow areas above and below).
Observation of parity oscillations in the conductance of atomic chains of Au, Pt, and Ir.

Length histograms and averaged conductance.