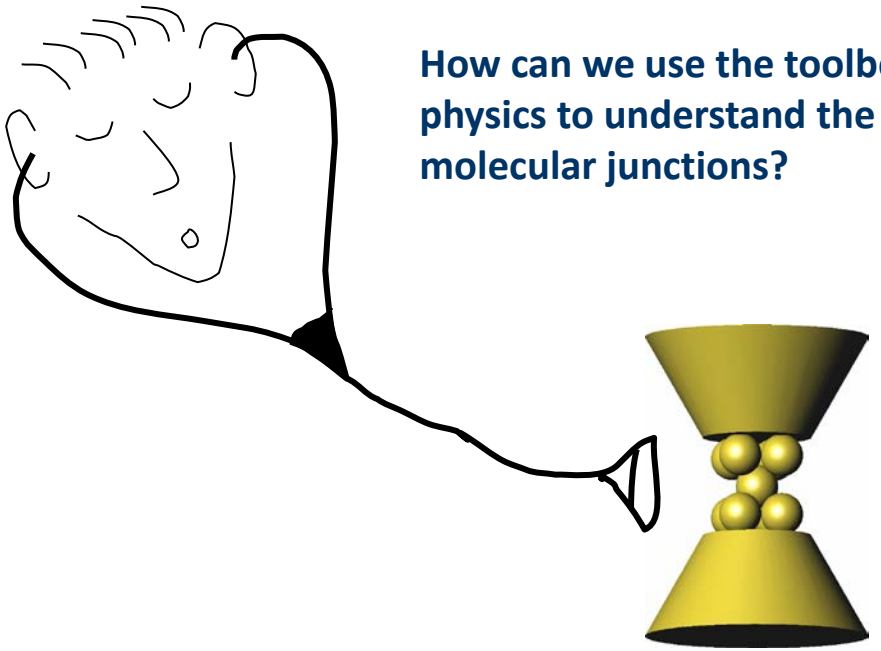
Mesoscopic phenomena in atomic and molecular nanojunctions

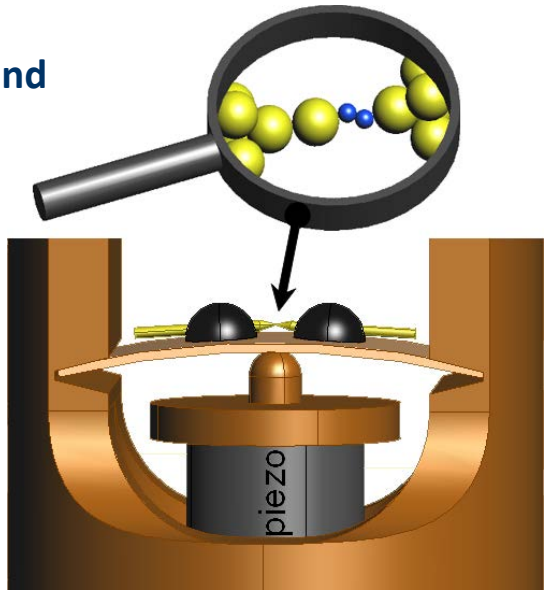
Literature:

N. Agrait, A. L. Yeyati, and J. M. van Ruitenbeek:
Quantum properties of atomic-sized conductors
Physics Reports 377, 81 (2003)

E. Scheer and J.C. Cuevas, Molecular Electronics (World Scientific, 2010)

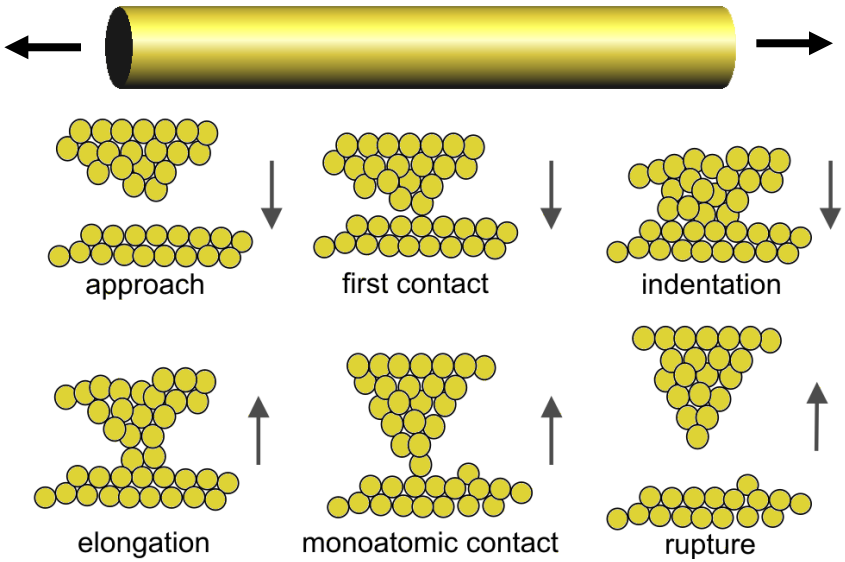


How can we use the toolbox of mesoscopic physics to understand the behavior of atomic and molecular junctions?

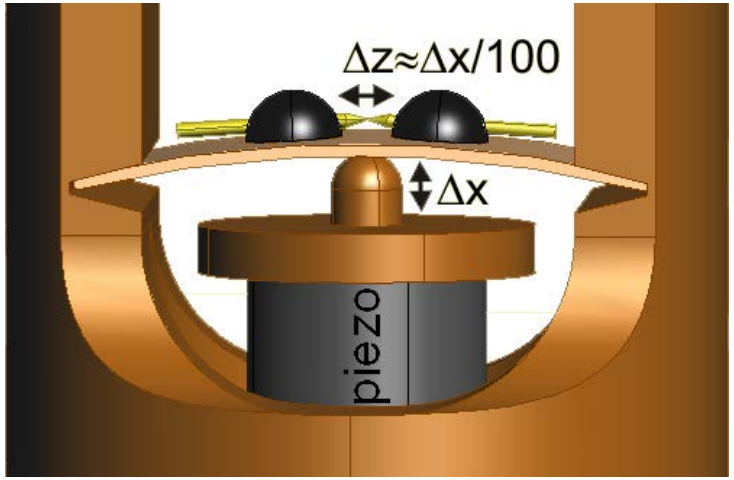


Creating atomic-sized metallic junctions

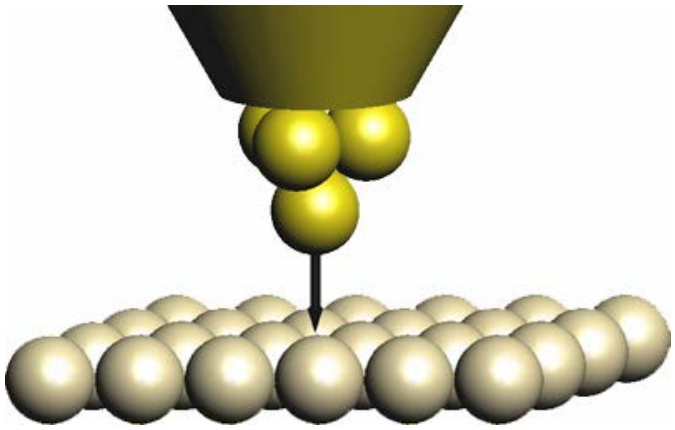
During the rupture of a metallic wire at the final stage a single atom connects the two sides



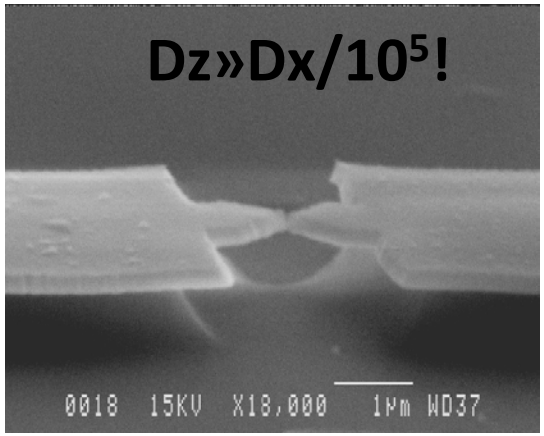
A possible method to create high stability atomic-sized junctions: **M**echanically **C**ontrollable **B**reak **J**unction technique



An atomic-sized contact can be created by pushing an STM tip into the sample surface

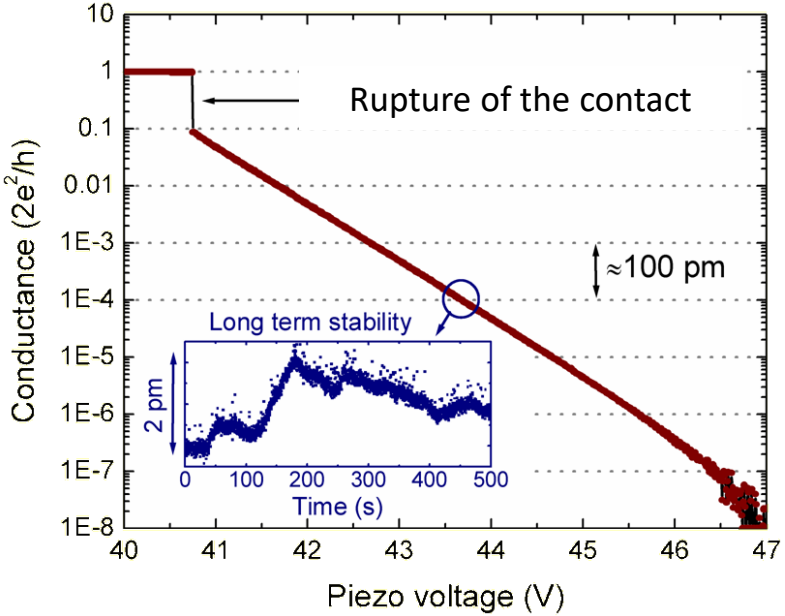


With a nanofabricated break junction a displacement ratio of $1:10^5$ can be reached



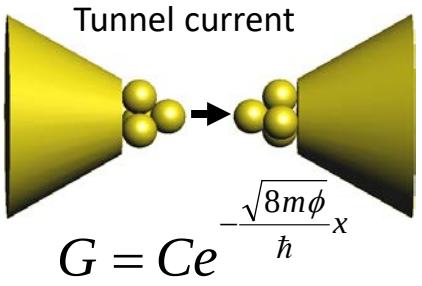
Stability, conductance histograms

The measurement of tunnel current as a function of piezo voltage can be used for calibration and to measure the stability of the system

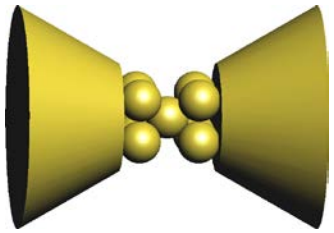


A clear exponential dependence is observed over 6 orders of magnitude in the conductance. A displacement of 100pm approximately corresponds to a change by a decade in the conductance.

The system has a stability of 2pm during 10 minutes.

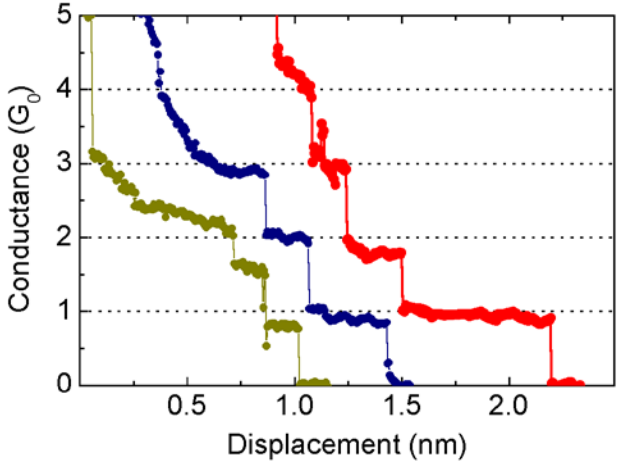


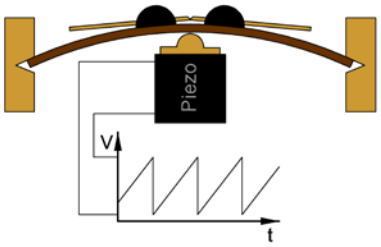
$$G = Ce^{-\frac{\sqrt{8m\phi}}{\hbar}x}$$

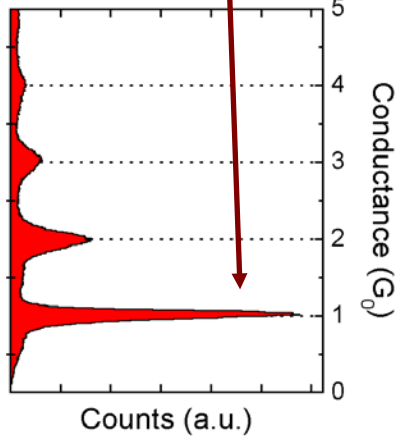


The first peak in the histogram tells the conductance of a single atom junction

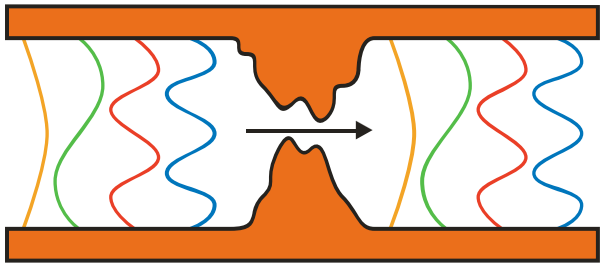
Individual conductance traces -> thousands of ruptures -> conductance histogram







Reminder: Landauer formula



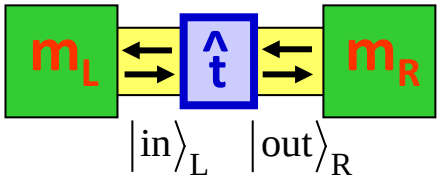
The system is considered as two ideal quantum wires with quantized transverse modes connected by a small constriction, characterized by a transmission matrix

$$|\mathrm{out}\rangle_R = \hat{t}\,|\mathrm{in}\rangle_L$$

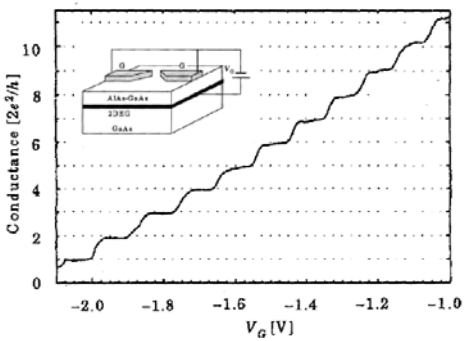
transmission matrix

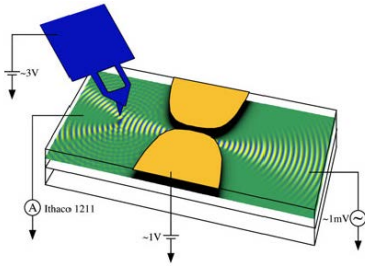
The conductance is given by the Landauer formula:

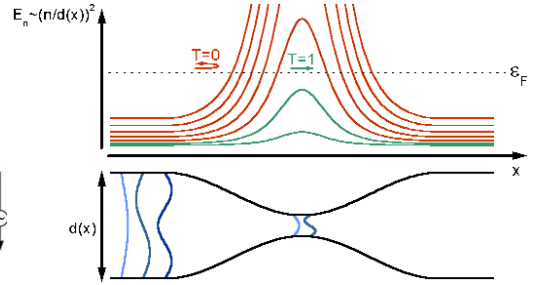
$$G = \frac{2e^2}{h}\mathrm{Tr}(\hat{t}^{\dagger}\hat{t}) = \frac{2e^2}{h}\sum_{i=1..N} T_i$$



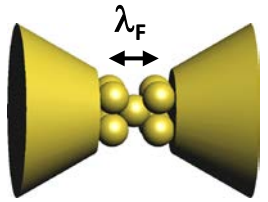
In the appropriate eigenchannel basis the conductance can be given as a sum transmission eigenvalues, the so called „mesoscopic PIN code"







In semiconductor **2DEG heterostructures** the Fermi wavelength is large due to the small electron density, λ_F»40nm. -> a "smooth", adiabatic contact can be made by e-beam lithography -> conductance quantization is observed

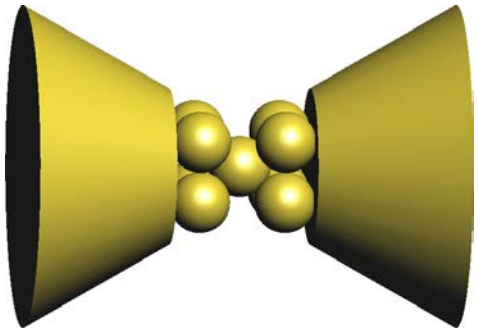


In metals the Fermi wavelength is comparable to the lattice constant. According to a simple approximation (3D Sharvin formula) a single-atom contact has a conductance in the range of conductance quantum, G»$2e^2/h$. Due to the atomic granularity of the matter such a small contact cannot be treated as an adiabatic one.

Mesoscopic PIN code of single-atom contacts

The conductance of a single atom contact can be determined from conductance histogram measurement.

But how many channels contribute to the conductance, and what is the transmission probability of the individual channels?



$$G = \frac{2e^2}{h} \sum_{i=1..N} T_i$$

$$\{T_i\} = ?$$

Mesoscopic PIN code

The number of conductance channels are expected to be related to the band structure of the material.

Element	*Type of atom*	*Number of modes*	*Conductance for one atom*
Au	*s*	?	1 G_0
Al	*s-p*		~0.8-1.2 G
Pb	*s-p*		~2.5-3 G
Nb	*s-d*		~2.5-3 G

To get more information about the mesoscopic PIN code further quantities should be measured, like:

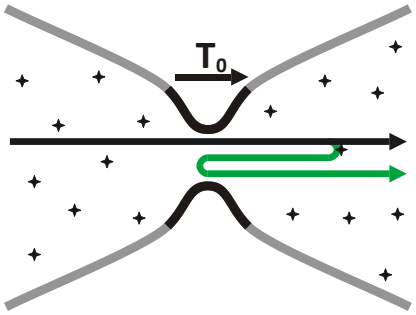
-Conductance fluctuations

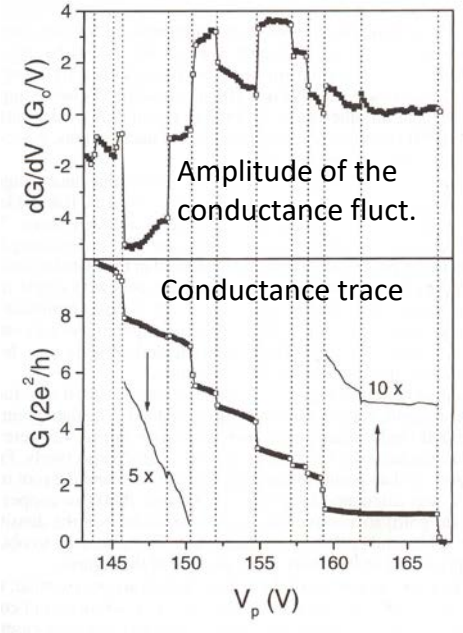
-Shot noise

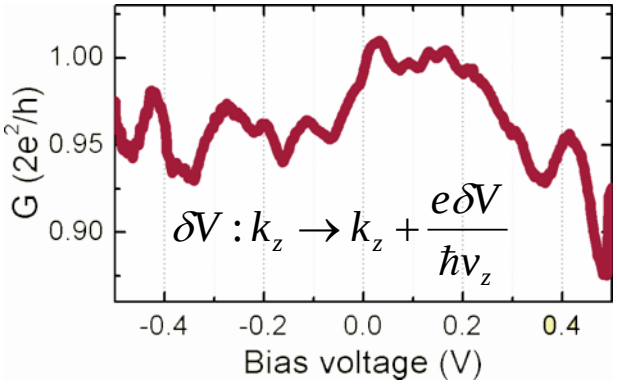
-Superconducting subgap structure

Conductance fluctuations

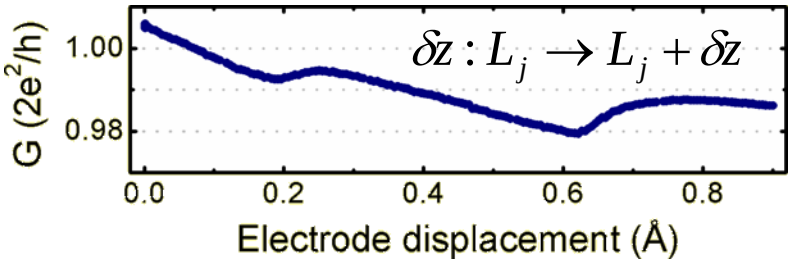
The electron wave transmitted through the contact can be partially reflected by the diffusive electrodes. This partial wave is reflected again by the contact, and interferes with the direct wave.



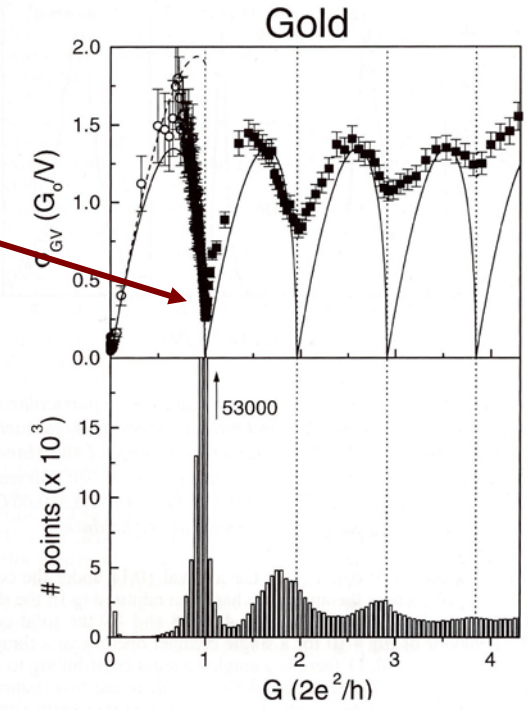




The interference conditions can be changed by the voltage (changing the wavelength) or by tuning the electrode separation, causing conductance fluctuations.



For a single-atom gold contact the conductance fluctuations are suppressed -> a single channel with perfect transmission gives the conductance of $1G_0$



The amplitude of the conductance fluctuations is:

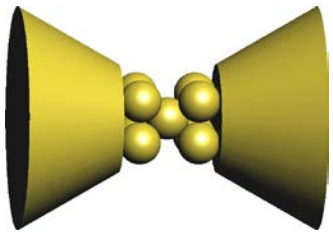
$$\sigma_{GV} \propto \sqrt{\sum_{n=1}^{N} T_n^2 (1 - T_n)}$$

For channels with perfect transmission the conductance fluctuations are suppressed (the partial wave cannot be reflected back by the contact)

Source: B. Ludoph et al. Phys. Rev. Lett., **82**, 1530 (1999); A. Halbritter et al. Phys. Rev. B, **69**, 121411 (2004)

Estimating the number of channels from noise

The conductance of a single atom contact:



In Au: G = 1G_0
In Al: G=0.7-1G_0

But how many channels?

The conductance:

$$G = \frac{2e^2}{h}\underbrace{\sum_{n=1}^{N} T_n}_{g}$$

The noise:

$$S = 2eV \cdot \frac{2e^2}{h}\sum_{n=1}^{N} T_n\,(1-T_n)$$

The Fano factor:

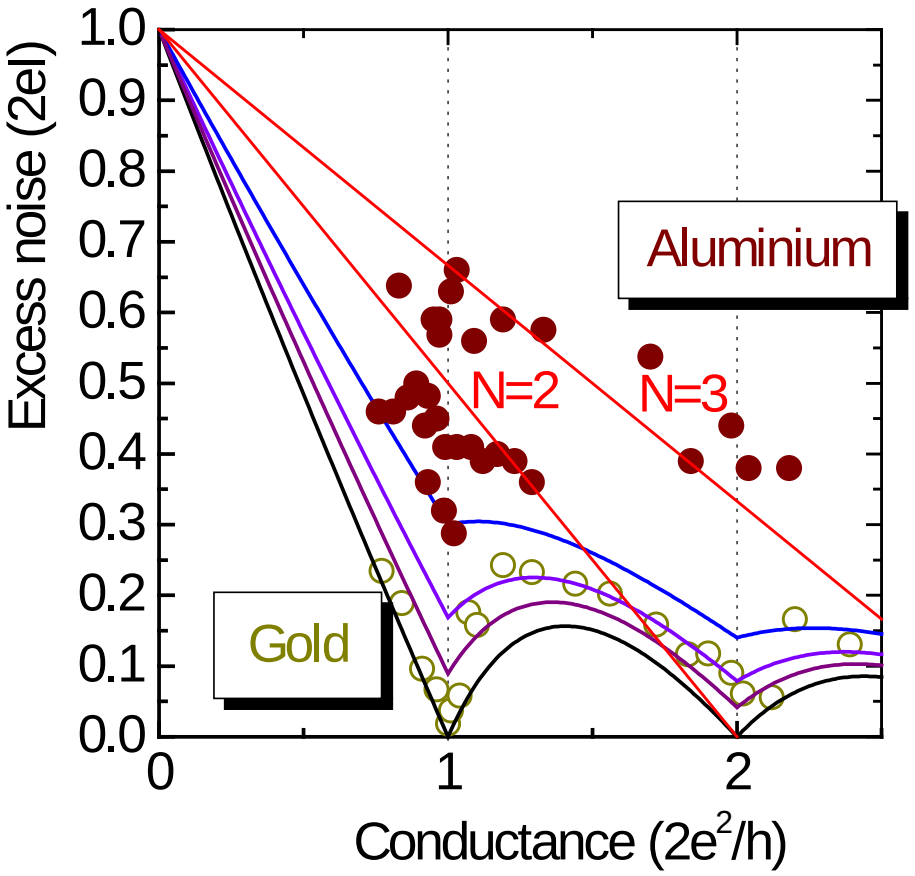
$$F = \frac{S}{2eI} = \frac{\sum T_n\,(1-T_n)}{\sum T_n}$$

For a given conductance, *g* and a given number of open conductance channels, *N* the noise is maximal when all T_n are equal (T_n=*g*/*N*):

$$F_{\max} = 1 - g/N$$

The noise is minimal if all T_n = 0,1, except one, say T_j:

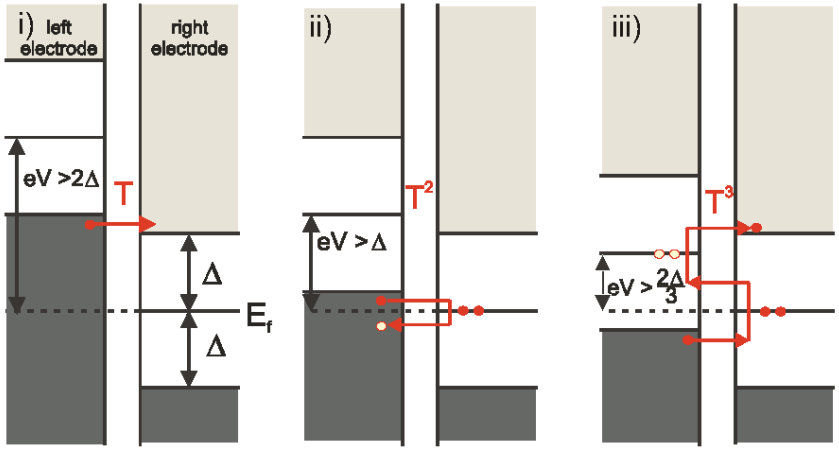
$$F_{\min} = \frac{T_j\,(1-T_j)}{g}$$



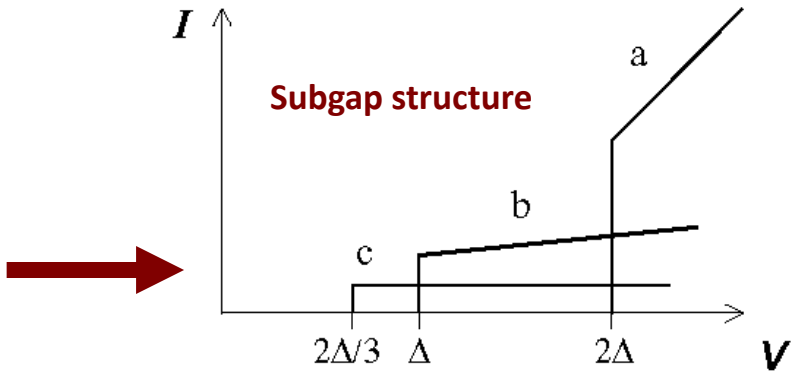
-A single atom Au contact has 1 channel with perfect transmission + „saturation of channel transmission"

-A single atom Al contact has 2-3 channels

Charge transfer in a superconducting nanoconstriction with multiple Andreev reflections:

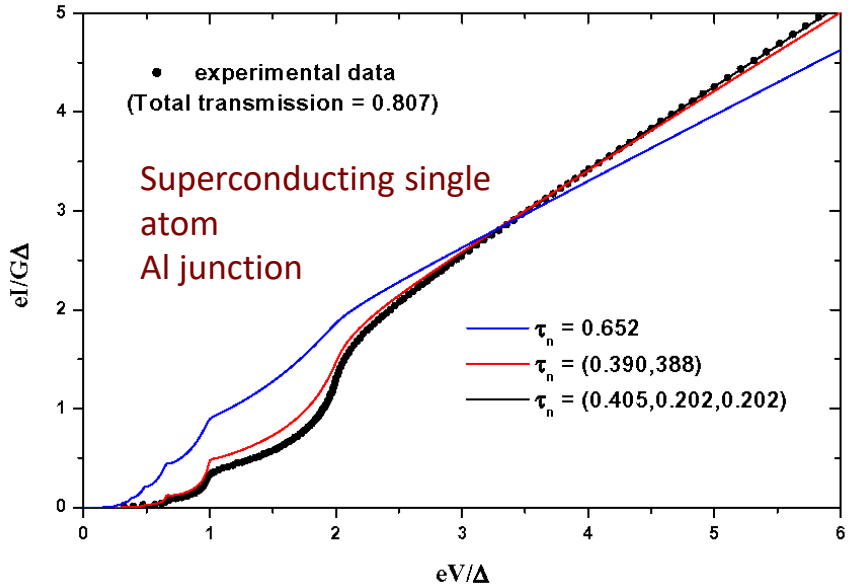


SC subgap structure



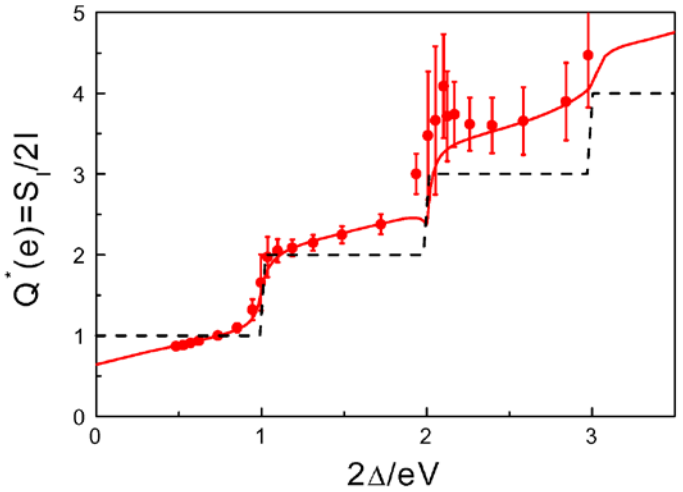
The n^{th} order process where a charge of n*e is transmitted is allowed at eV>2Δ/n with a probability of t^n. For contacts with large transmissions the higher order processes are important.

Experimental I-V curve and theoretical fits:

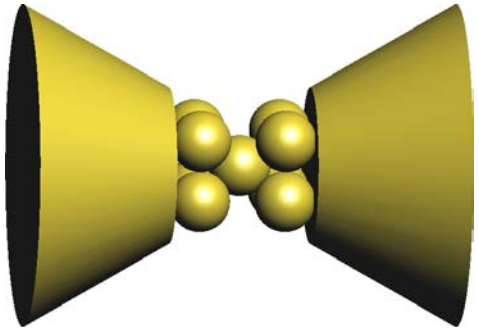


By fitting the subgap structure in the I-V curve the whole mesoscopic PIN code can be determined. E.g. a single-atom Al junction with $G=0.8G_0$ has 3 partially open channels

The noise measurement shows the transfer of multiple charge quanta in the subgap regime:



Mesoscopic PIN code of single-atom contacts



$$G = \frac{2e^2}{h}\sum_{i=1..N} T_i$$

$$\{T_i\} = ?$$

Mesoscopic PIN code

Element	*Type of atom*	*Number of modes*	*Conductance for one atom*
Au	*s*	1	1 G_0
Al	*s-p*	3	~0.8-1.2 G
Pb	*s-p*	3	~2.5-3 G
Nb	*s-d*	5	~2.5-3 G

-Conductance fluctuations

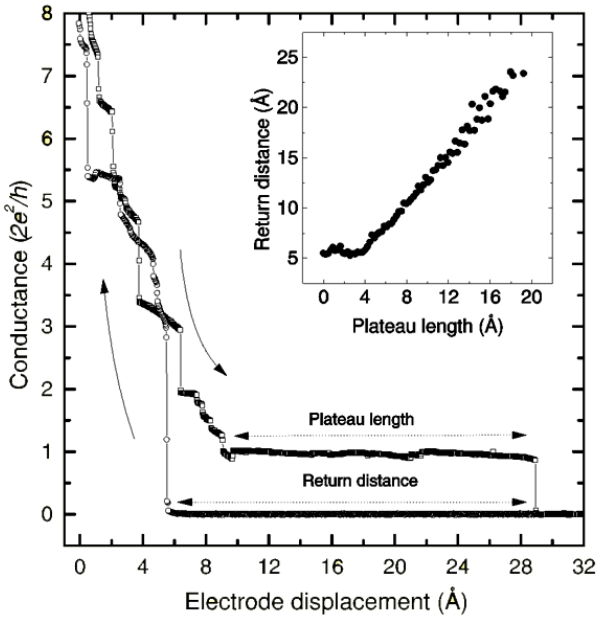
-Shot noise

-Superconducting subgap structure meas.

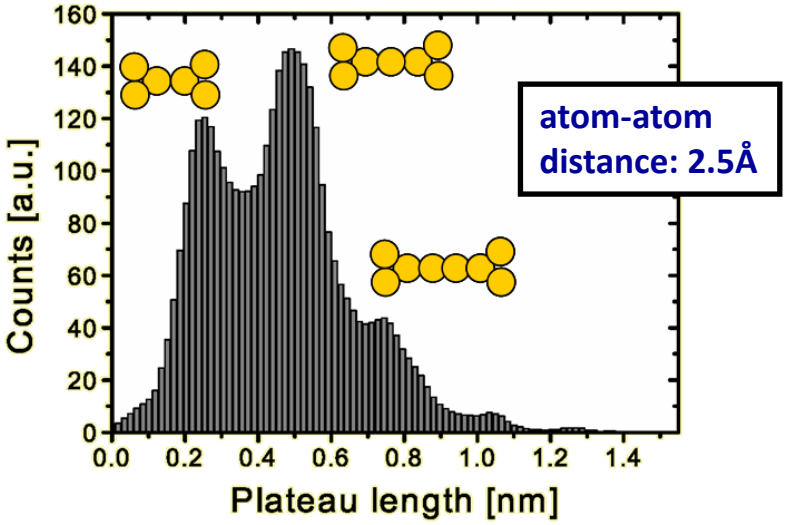
-Theoretical simulations

In *s* metals (e.g. noble metals) a single-atom contact has a single conductance channel.
In p metals (e.g. Al, Pb, In, ...) a single-atom contact has a 3 open channels
In d metals (e.g. Nb, Pt, ...) a single-atom contact has 5 open channels

Atomic chain formation

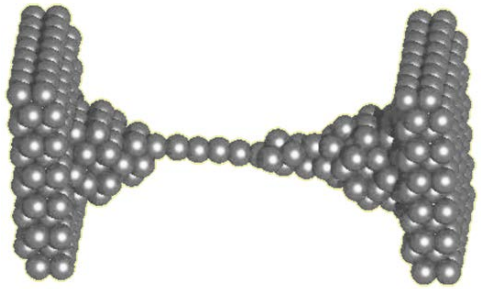


In gold contacts the last plateau on the conductance trace is much longer than a typical Au-Au distance.



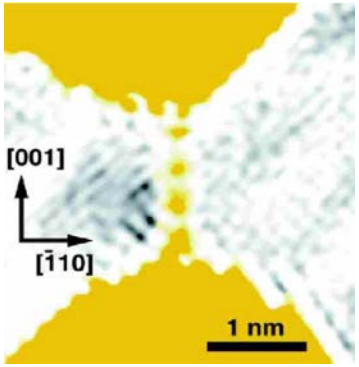
The distribution of the length of the last plateau shows peaks at equidistant displacements with a spacing of 2.5 Å

A. I. Yanson et al. Nature, **395**, 783 (1998)



If a single-atom gold contact is pulled, it does not break, but a monoatomic Au chain is pulled from the electrodes. Note, that the chains with different number of atoms have the same G=2e2/h conductance, i.e. **the conductance of a perfect quantum wire does not depend on the wire length (see Sharvin-formula!)**

HTEM picture:

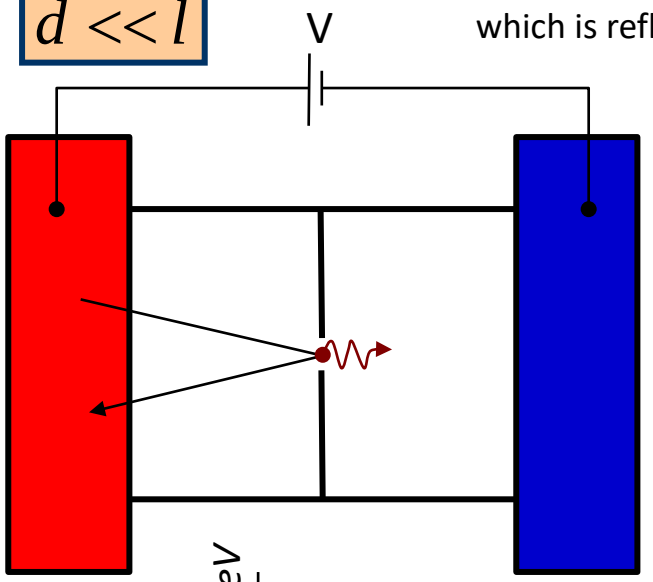


Ohnishi et al. Nature, **395**, 780 (1998)

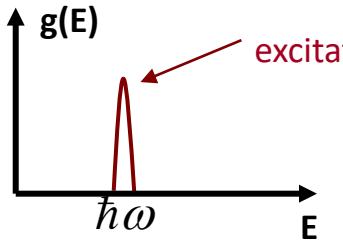
Point-contact spectroscopy

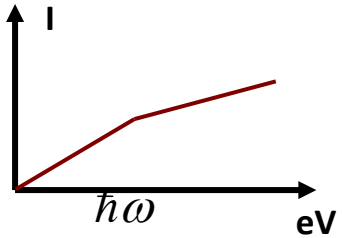
A.G.M. Jansen et al. J. Phys. C **13**, 6073. (1980)
A. Halbritter, L. Borda, A. Zawadowski
Advances in Physics **53**, 939 (2004)

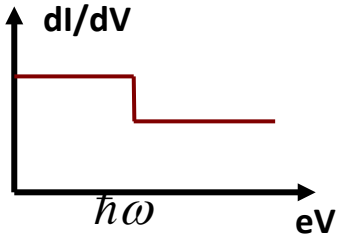
$d \ll l$

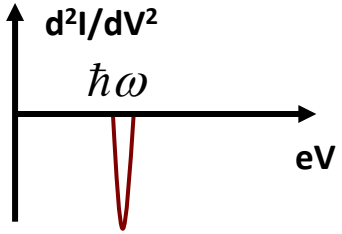


The inelastic scattering can cause backscattering through the contact, which is reflected by a nonlinearity in the I-V curve:

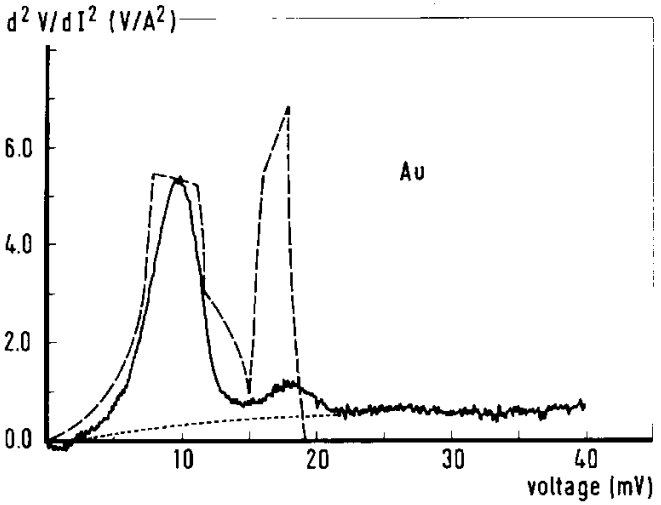




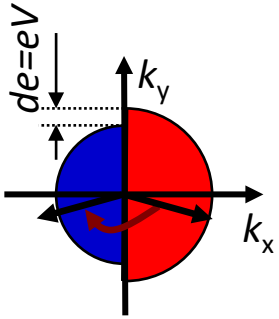




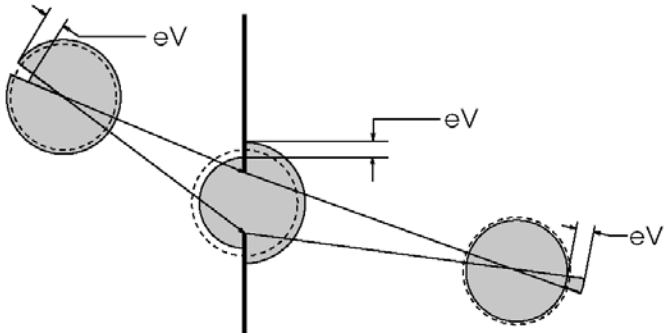
d^2I/dV^2 shows the spectrum of the inelastic excitations in the close vicinity of the contact



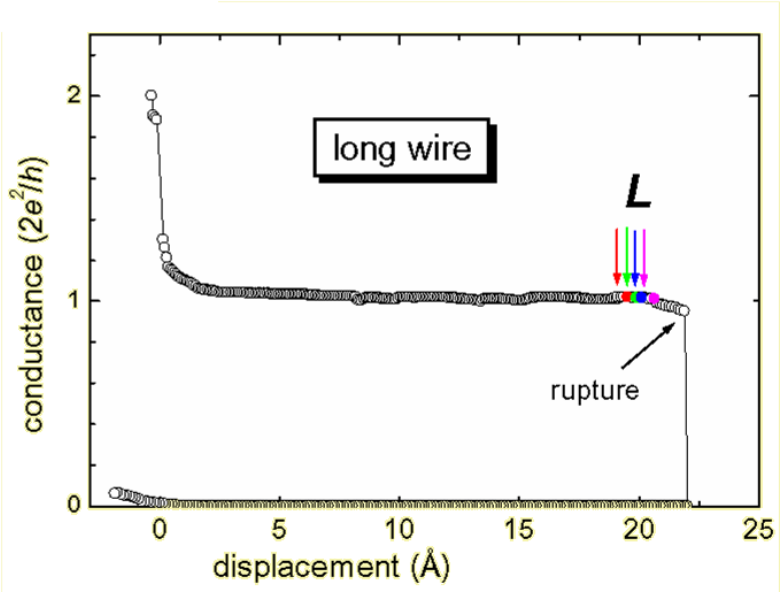
Distribution function at the middle of the contact:



At T=0 an electron at the contact going to the right cannot be scattered to the occupied right-going states, but it can be scattered to the unoccupied left-going states

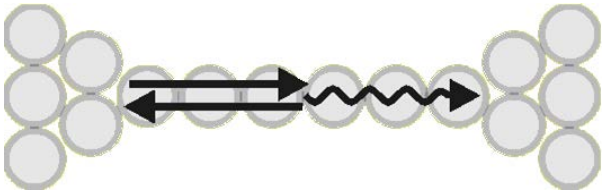


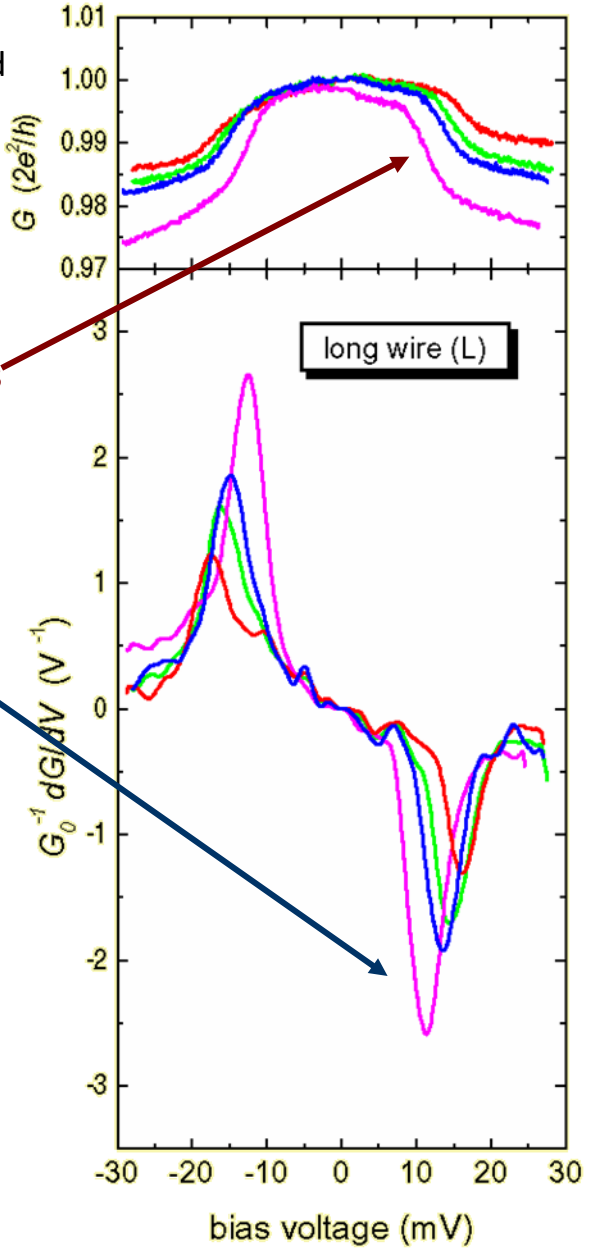
Vibrational spectroscopy of atomic wires



The vibrational modes of an atomic chain can be determined by measuring I-V curves.

At the excitation energy of a vibrational mode the differential conductance shows a step-like decrease due to the enhanced probability of back-scattering. This is reflected by sharp peaks in the d^2I/dV^2 curves.

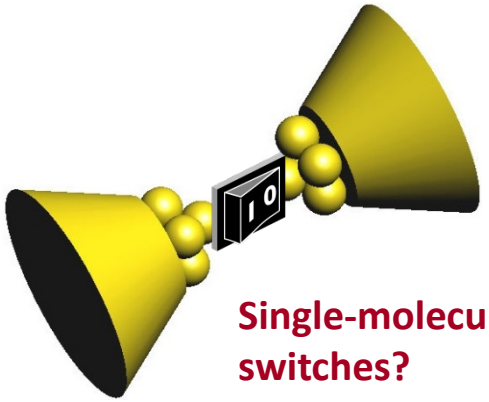




When the contact is stretched the energy of the vibrational mode is decreasing → longitudinal mode (as the chain is stretched, the spring constant becomes smaller)

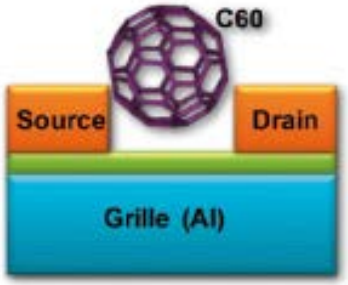
Source: N. Agrait et al. Phys. Rev. Lett., **88**, 216803, (2002)

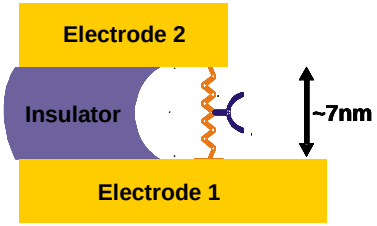
Molecular electronics



Single-molecule switches?

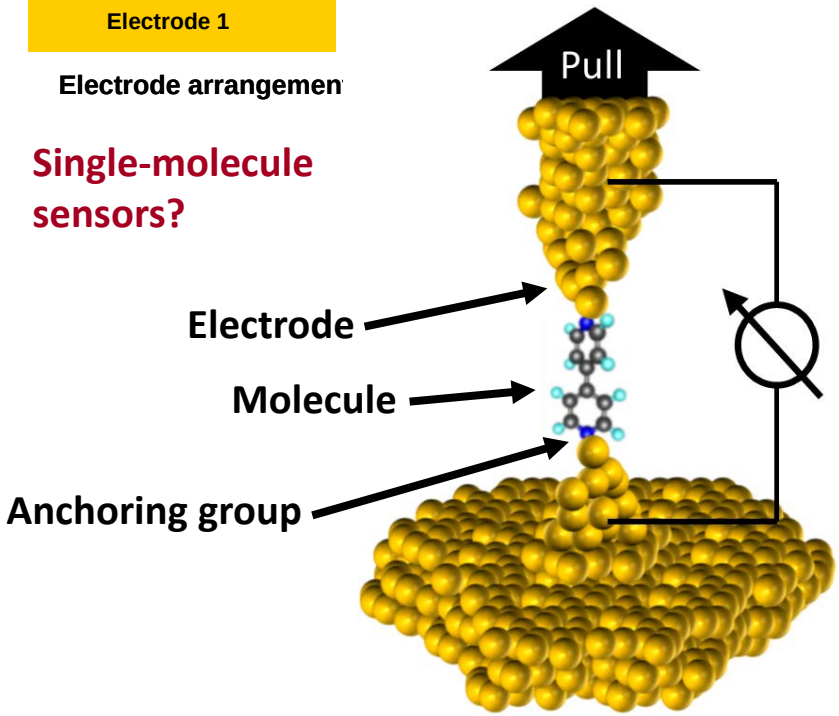
Single-molecule transistors?

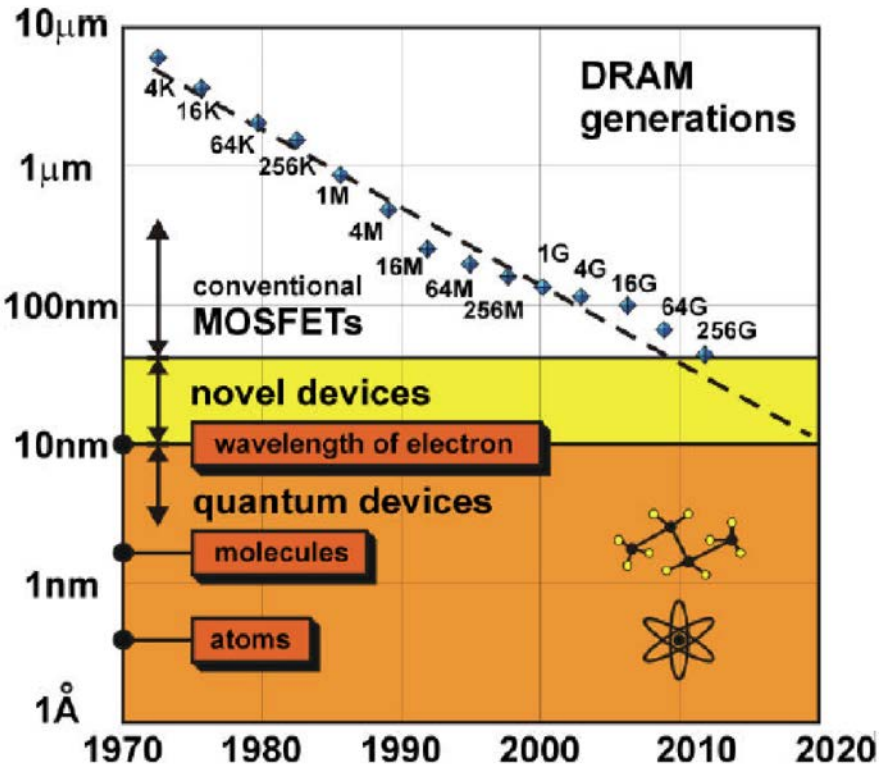




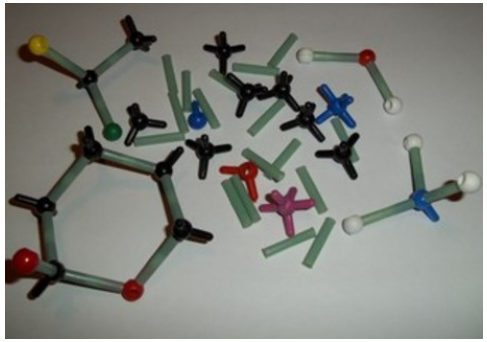
Electrode arrangemen

Single-molecule sensors?

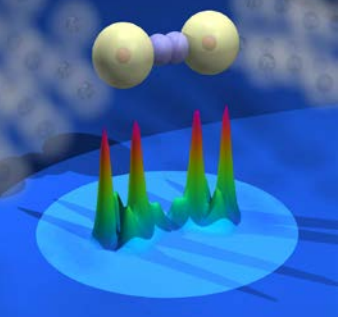


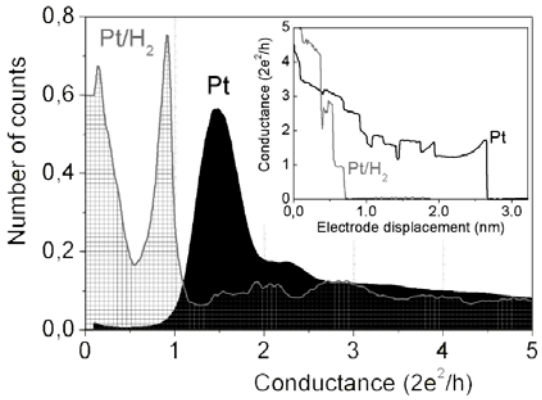


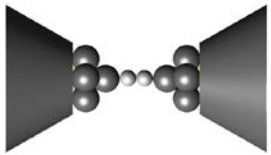
Bottom-up



Conductance of a single H_2 molecule







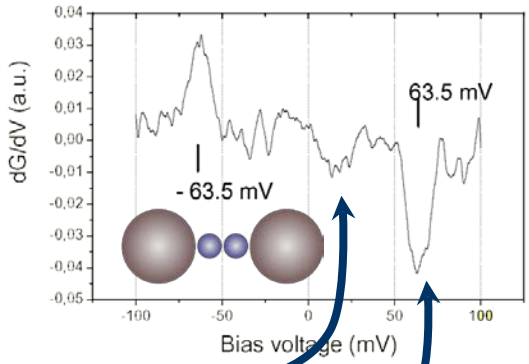
If hydrogen molecules are admitted to atomic-sized Pt junctions the characteristic peak of single-atom Pt contacts at $G=1.5G_0$ disappears and a new peak grows at $1G_0$.

→ formation of a new, well-defined molecular configuration

The details of this configuration can be understood by measuring various mesoscopic phenomena, and comparing the results with ab-initio simulations

Vibrational modes

The d^2I/dV^2 curves shows distinct peaks at 63.5mV, whereas the phonon modes of pure Pt are at ~10mV.



Ph. modes of Pt

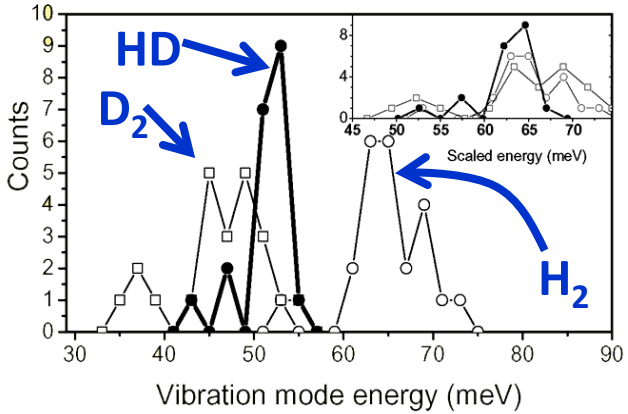
New, high ω mode

Source: R.H.M. Smit et al. Nature **419,** 906 (2002)

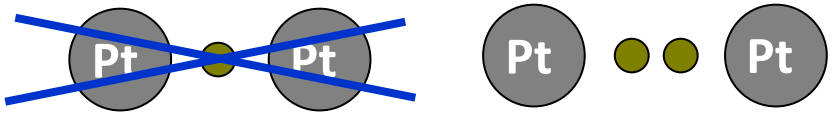
$$E = \hbar\omega \propto \sqrt{\frac{\kappa}{m}}$$

$$m_H : m_{Pt} \cong 1:195$$

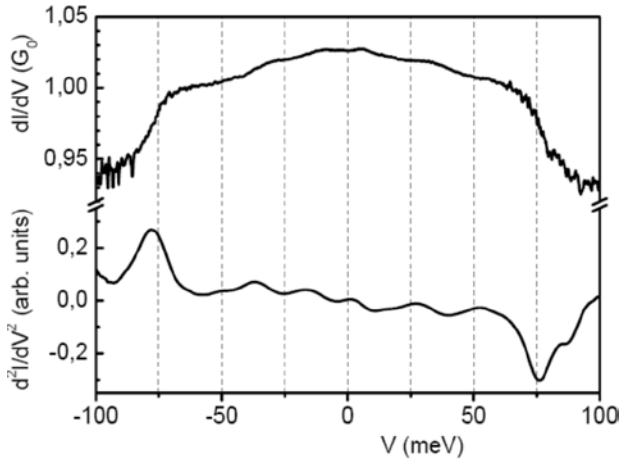
It can be tested by the measurement of isotope shift, whether the new vibrational mode is related to hydrogen.



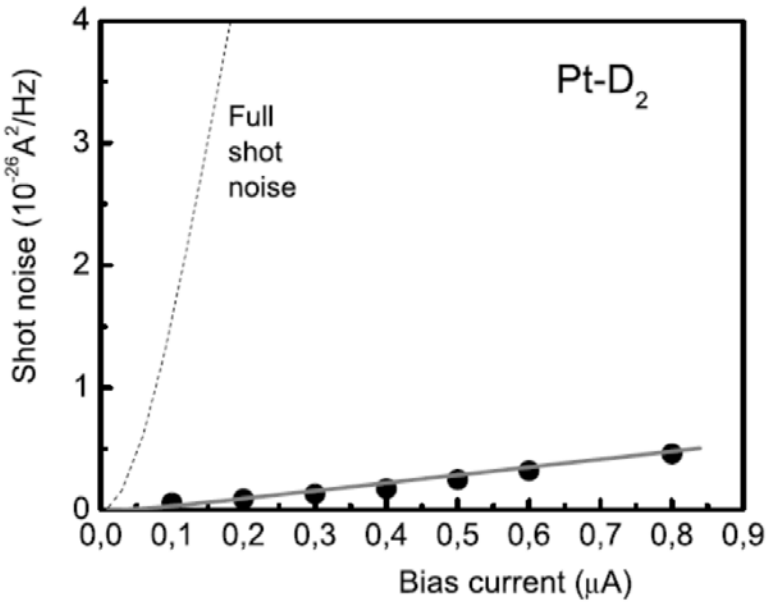
The isotope shift is clearly detectable for H_2, D_2 and HD molecules. The fact that HD has an intermediate vibrational energy proves that the vibrational mode of a molecule, and not that of a dissociated atom is observed.



Shot noise



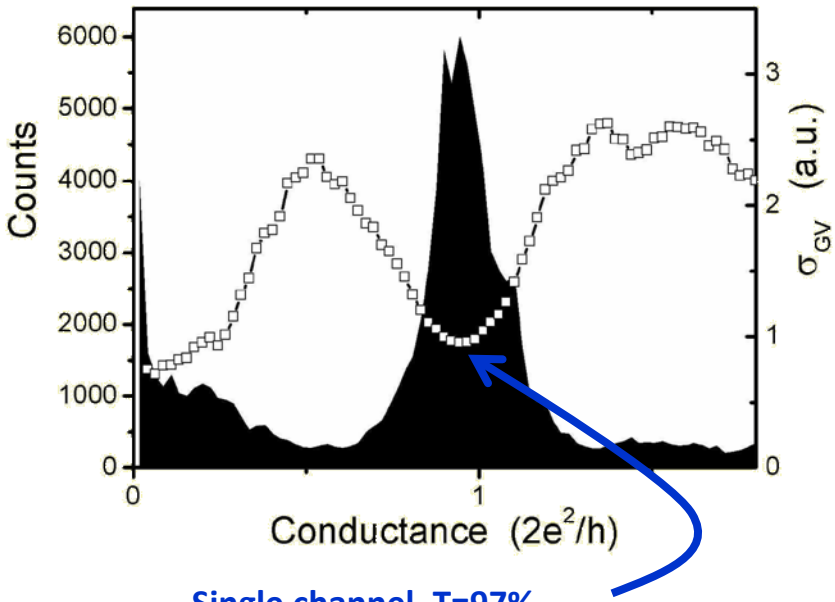
A single configuration with characterized vibrational modes can be selected



The shot noise measurement shows that the selected configuration indeed has a single, almost perfectly transmitting channel

Source: R.H.M. Smit et al. Nature **419,** 906 (2002)

Conductance fluctuations



Single channel, T=97%

The conductance fluctuation measurement shows that in average, for a large number of junctions the new configuration has a single, almost perfectly transmitting channel.

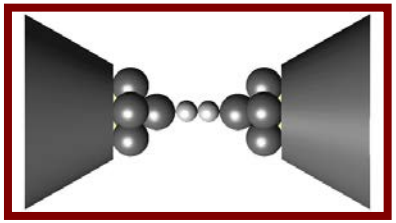
Conclusions:

Vibr. spectroscopy -> hydrogen molecule

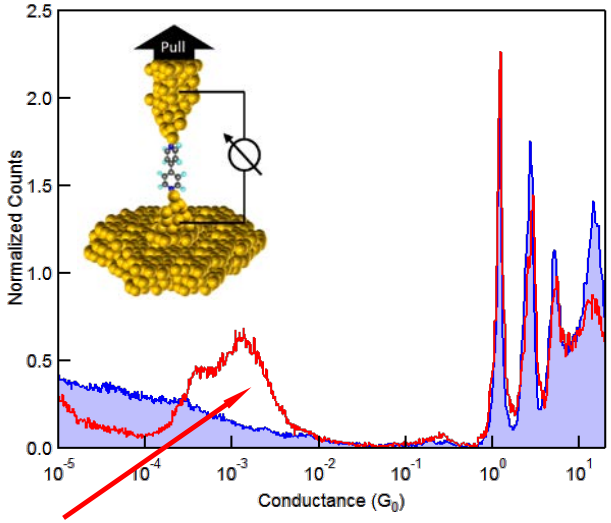
Shot noise, cond. fluct. -> single channel

single hydrogen molecule

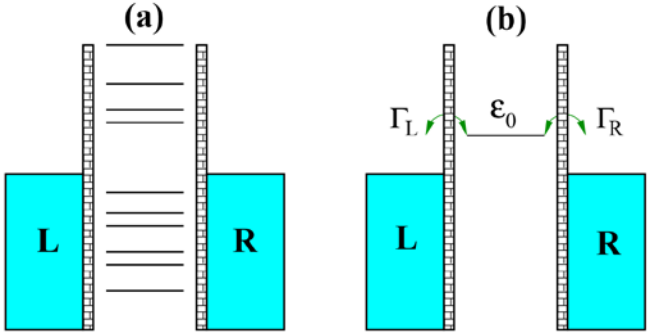
+ ab initio simulations
-> molecules is aligned parallel with the axis



Conductance through single organic molecules



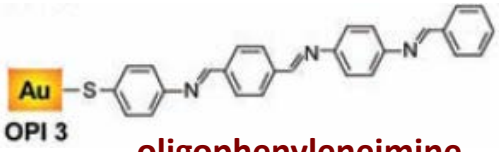
Dosing the molecules a new peak appers in the conductance histogram



Simplest model: transport through a single level (the HOMO or the LUMO) (Resonant tunneling model, Breit-Wigner formula):

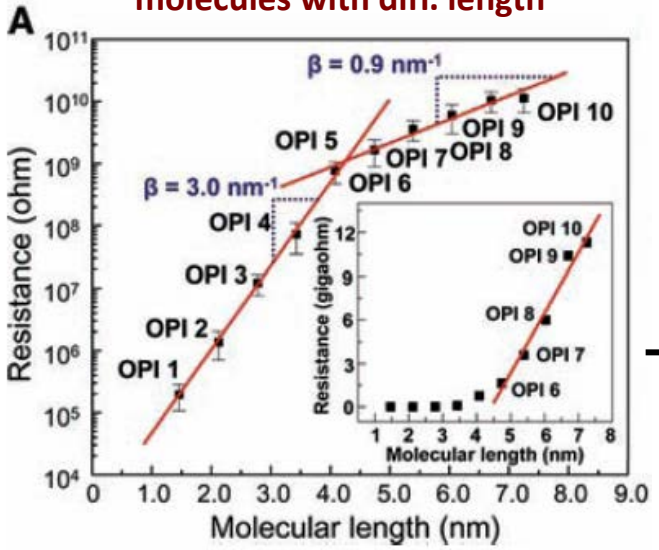
$$T(E,V) = \frac{4\Gamma_L\Gamma_R}{[E-\epsilon_0(V)]^2 + [\Gamma_L+\Gamma_R]^2}$$

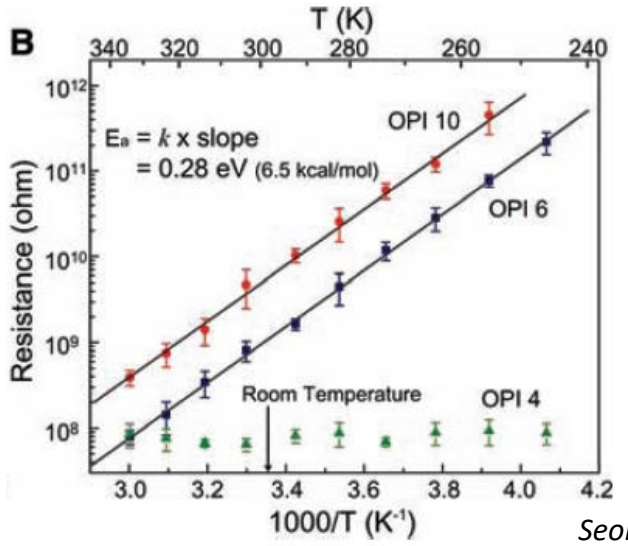
Conductance as a function of molecular length



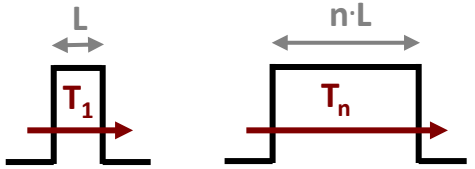
OPI 3

oligophenyleneimine molecules with diff. length



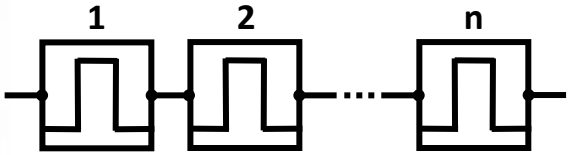


Coherent transport:



$$G_n \approx Ae^{-B\cdot n\cdot L} \approx G_1^n$$

Incoherent transport (Ohm's law):



$$G_n = G_1 / n$$

OPI1-5: coherent transport

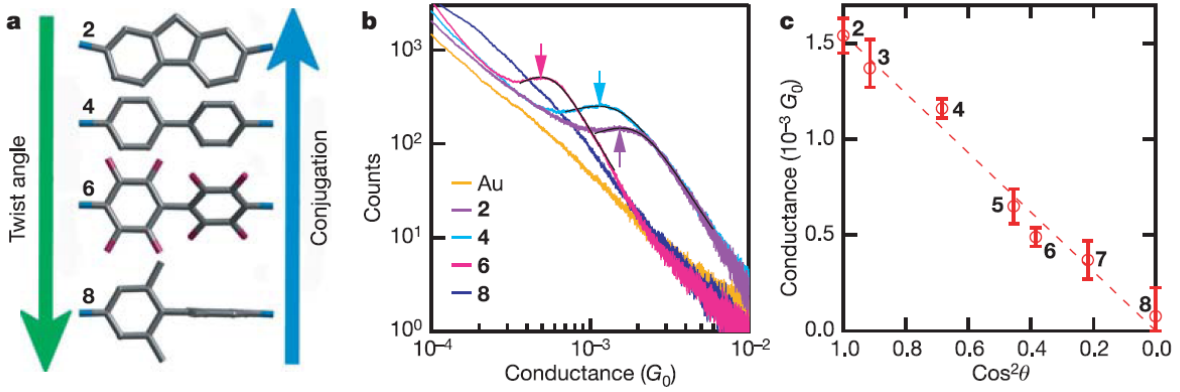
- exponential dependence of G on the length
- no T dependence

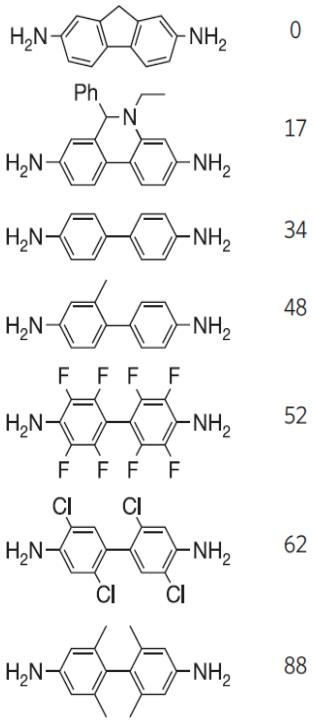
OPI6-10: incoherent hopping

- linear dependence of G on the lenth
- exponential T dependence, activated behavior

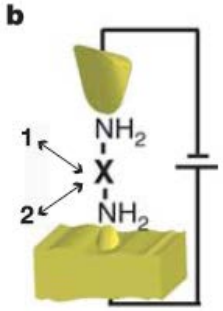
*Seong Ho Choi, et al., Science **320**, 1482 (2008);*

Conformation dependent conductance





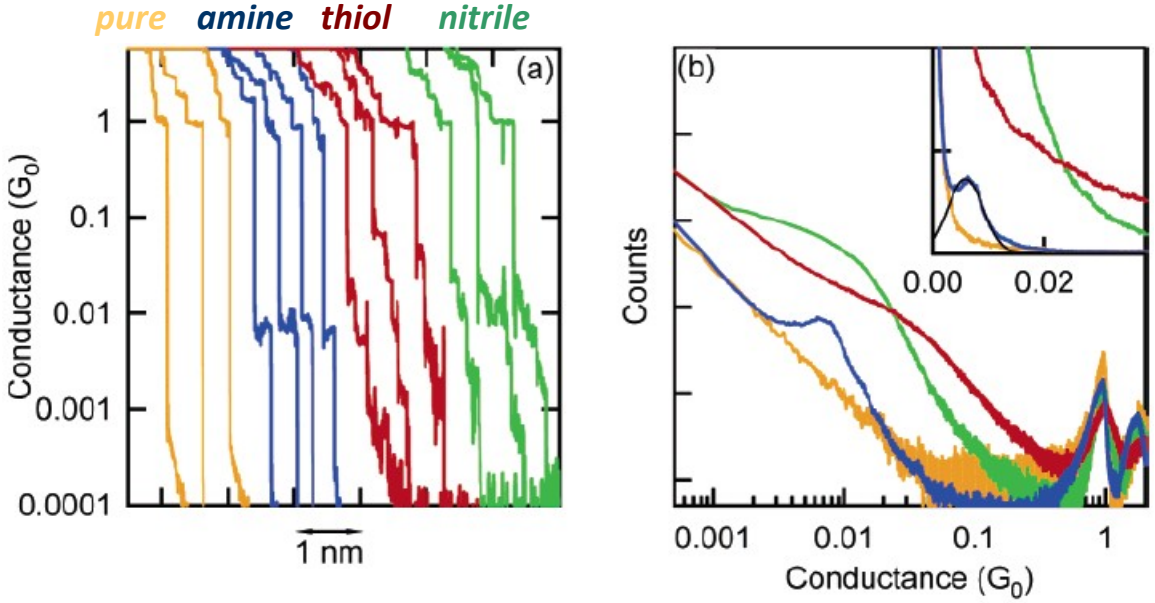
- Tuning twist agle by chemical design
- Conductance depends on the delocalization of the orbitals, **p-conjugated molecules** are good candidates for high transmission
- As the twist angle increases, the conductance decreases, $T(\varepsilon) \sim t^2$, $t \sim \cos\theta$
- The effect of substituents does not matter, the real effect comes from the $\pi-\pi$ overlap



L. Venkataraman et al., Nature 442, 904-907 (2006)

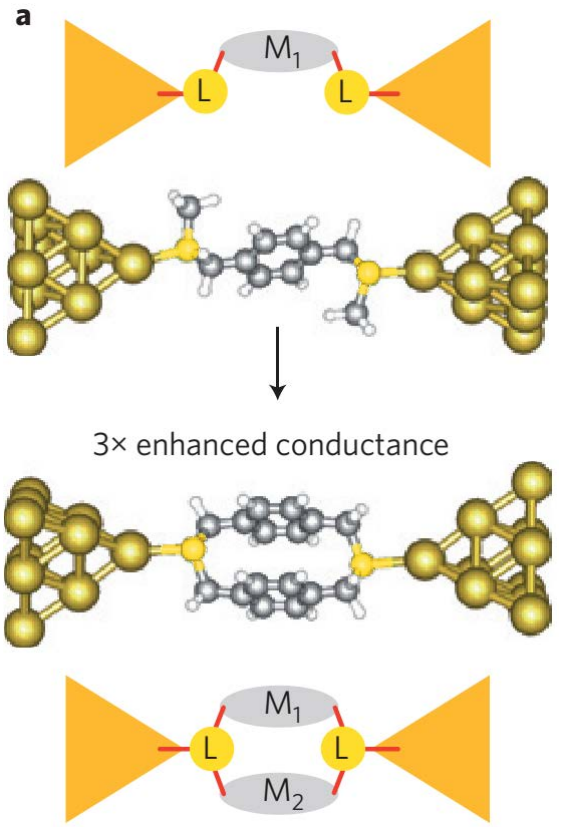
Role of the anchoring group

Venkataraman et al., Nano Lett., 6, 3 (2006)



- Generally **gold electrodes** and **thiol (SH) linking groups** are used
- Problems with thiol:
  - Low conductance
  - Not so well-defined binding site
- Amine (NH_2) group gives much better defined plateaus and histogram peak
- **Amine group is selective to low coordinated Au sites**
- Isonitrile (NC) also gives less well-defined configurations
- Further possibility: fullerene-based groups (larger conductance, higher stability due to multiple bonds)

Quantum interference?



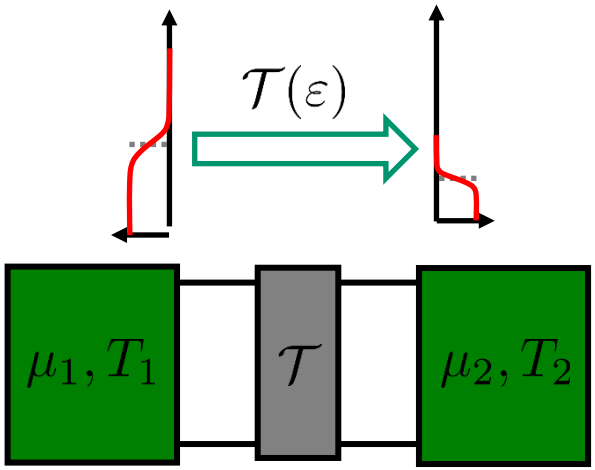
Parallel connected molecules give more than twice as large conductance due to quantum interference phenomenon!

Vazquez et al., Nature Nanotechnology 7, 663 (2012)

Thermoelectric power in a single-channel nanowire

The calculation of the current in the presence of temperature difference between their electrodes:

$$I = \frac{2e}{h} \cdot \int \mathcal{T}(\varepsilon) \cdot [f_1(\varepsilon, \mu_1, T_1) - f_2(\varepsilon, \mu_2, T_2)] \, \mathrm{d}\varepsilon$$

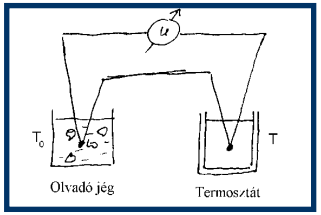


Sommerfeld-expansion: (see e.g. the derivation of Pauli paramagnetism)

$$\int_{-\infty}^{\infty} H(\varepsilon) \cdot f(\varepsilon, \mu, T) \, \mathrm{d}\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon) \, \mathrm{d}\varepsilon + \frac{\pi^2}{6}(kT)^2 H'(\mu) + \mathrm{O}\left(\frac{kT}{\mu}\right)^4$$

$$I \approx \frac{2e}{h} \cdot \int_{\mu_2}^{\mu_1} \mathcal{T}(\varepsilon) \, \mathrm{d}\varepsilon + \frac{2e}{h}\frac{\pi^2}{6}(kT_1)^2 \mathcal{T}'(\mu_1) - \frac{2e}{h}\frac{\pi^2}{6}(kT_2)^2 \mathcal{T}'(\mu_2) \approx \frac{2e}{h} \cdot eV \cdot \bar{\mathcal{T}}(\varepsilon) + \frac{2e}{h}\frac{\pi^2 k^2}{3} \cdot \Delta T \cdot T \cdot \mathcal{T}'(\mu)$$

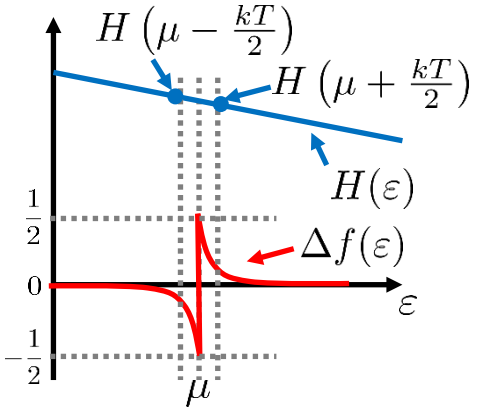
$$\Delta T = T_1 - T_2; \quad T = \frac{T_1 + T_2}{2}; \quad \mu = \frac{\mu_1 + \mu_2}{2}$$



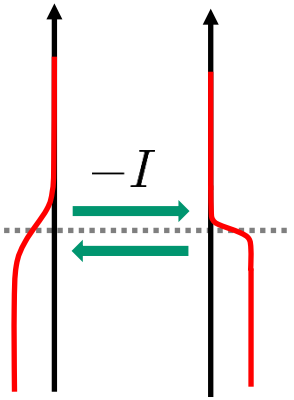
Putting a voltmeter with infinity internal resistance on the electrodes (I=0!):

$$V\big|_{I=0} = \underbrace{-\frac{\pi^2 k^2 T}{3e} \cdot \frac{1}{\mathcal{T}} \frac{\partial \mathcal{T}(\varepsilon)}{\partial \varepsilon}\bigg|_{\mu}}_{S} \cdot \Delta T$$

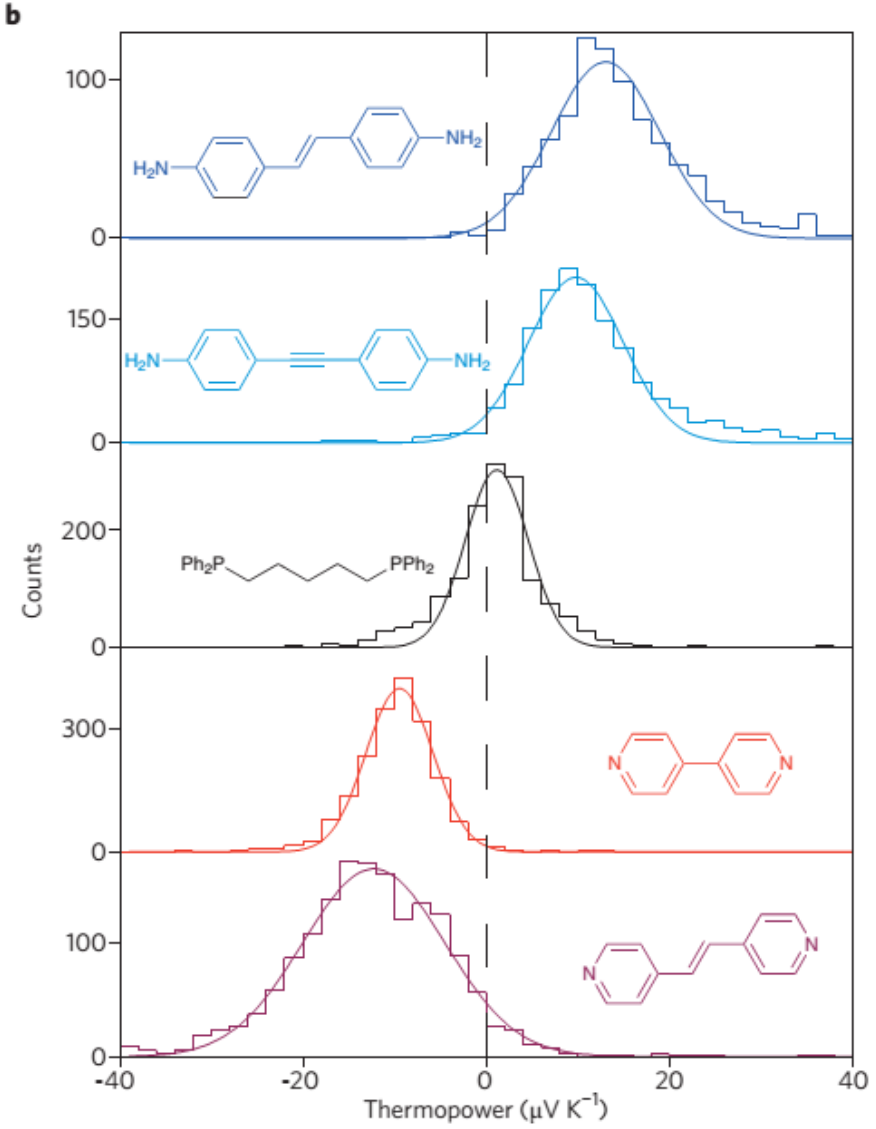
← Cutler-Mott-formula



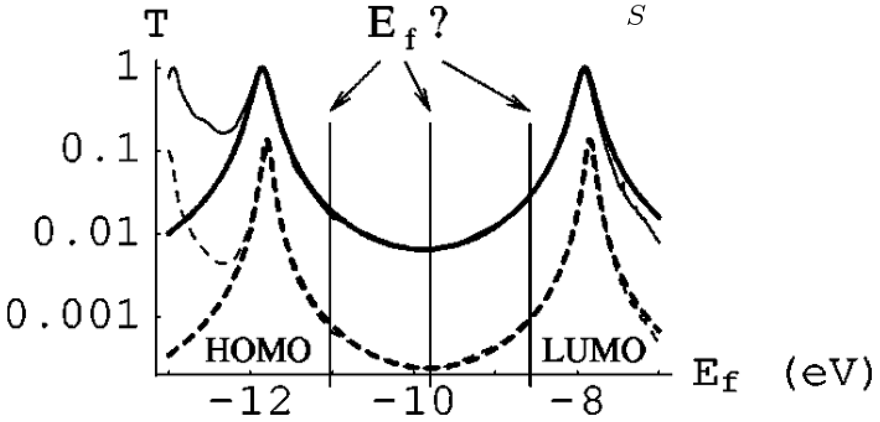
Due to the temperature difference a thermoelectric power is observed (Seebeck-effect, S – Seebeck-coefficient). This only arises in case of energy dependent transmission. At V=0 it is clear that for an energy independent transmission the current flow bellow the chemical potential cancels the opposite direction current flow above the chemical potential.



Thermopower in single-molecule junctions



$$V\big|_{I=0} = \underbrace{-\frac{\pi^2 k^2 T}{3e}\cdot\frac{1}{\mathcal{T}}\frac{\partial \mathcal{T}(\varepsilon)}{\partial \varepsilon}\bigg|_{\mu}}_{S}\cdot\Delta T$$

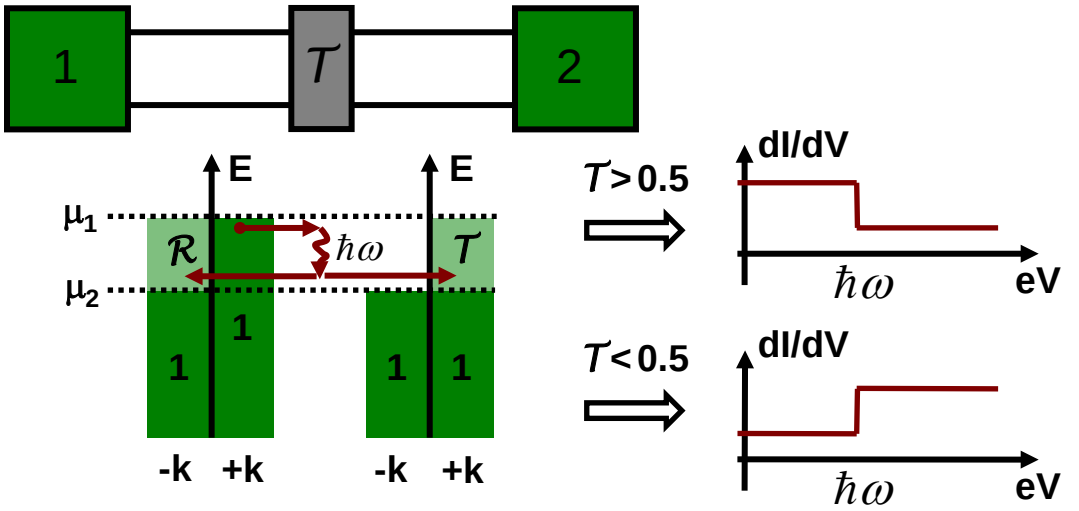


In a single molecule junction the sign of $d\mathcal{T}/d\varepsilon$ is positive if the LUMO state dominates the current, and it is negative if the HOMO dominates. Therefore, the thermopower measurement can make difference between the HOMO and LUMO conduction! (The conductance alone cannot make difference.)

J.R. Widawsky, P. Darancet, J.B. Neaton, L. Venkataraman, *Simultaneous Determination of Conductance and Thermopower of Single Molecule Junctions*, **Nano Letters, 12**, 354−358, (2012)

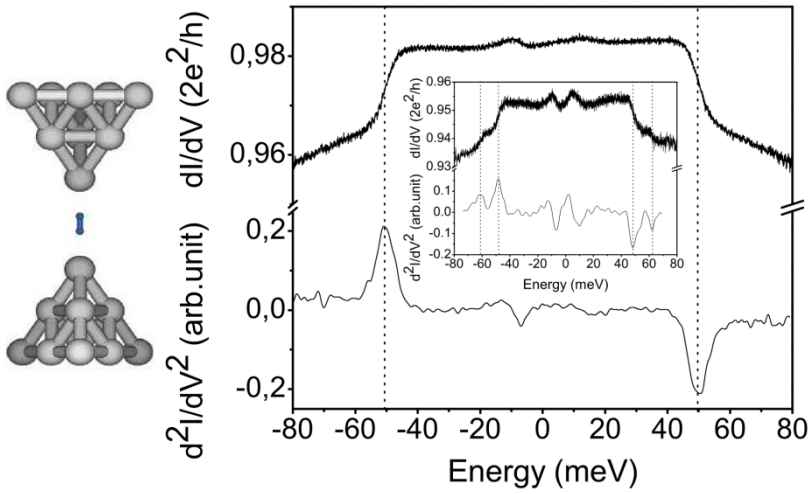
Point-contact spectroscopy/inelastic electron tunneling spectroscopy

A single channel conductor with $\mathcal{T}$ transmission is considered. In the scattering region the electrons can also excite a vibrational mode with $\hbar\omega$ energy. An $eV=\mu_1-\mu_2$ voltage is applied on the electrodes. At the right side of the scattering region all the states are occupied till μ_2, and at $\mu_2<E<\mu_1$ the +k states are occupied with $\mathcal{T}$ probability, and the –k states are unoccupied. At the left side the +k states are all occupied till μ_1, and the –k states till μ_2, whereas at $\mu_2<E<\mu_1$ the –k states are occupied with $\mathcal{R}=1-\mathcal{T}$ probability. If the electrons scatter on the vibrational mode, they need to end up in an unoccupied state. Scattering forward it has $1-\mathcal{T}$ probability, whereas scattering backward it has $1-\mathcal{R}$ probability. The former gives rise to current increase, the latter to current decrease. The net inelastic current correction:



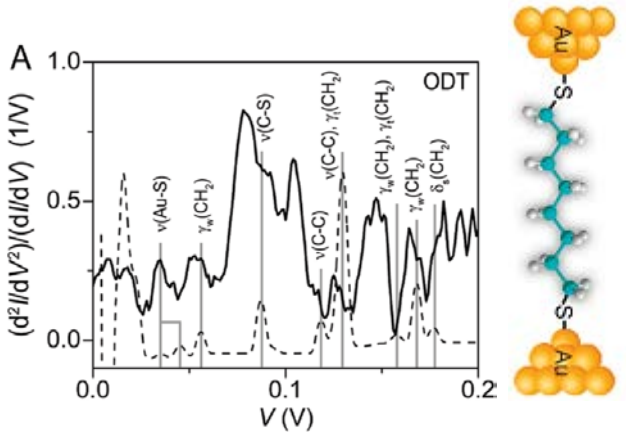
$$\delta I^{\mathrm{in}} \sim (eV-\hbar\omega)\left((1-\mathcal{T})-(1-\mathcal{R})\right)=(eV-\hbar\omega)(1-2\mathcal{T})$$

At $\mathcal{T}>0.5$ the conductance decreases at $\hbar\omega$ (this is called point-contact spectroscopy), at $\mathcal{T}<0.5$ it increases (inelastic electron tunneling spectroscopy, IETS). The crossover at T=0.5 was experimentally demonstrated in O. Tal et al., PRL **100,** 196804 (2008)



Smit et al. Nature 419, 906 (2002), Djukic et al. PRB 71, 161402 (2005)

The various different molecular vibrational modes are determined simply from the second derivative of the I(V) curve. (the step in dI/dV is a peak in d^2I/dV^2!)



Kim et al. ACS Nano 5, 4104 (2011)