ICN2 Institut Català de Nanociència i Nanotecnologia
EXCELENCIA SEVERO OCHOA

Tel Aviv Siesta/TranSiesta Tutorial - 10 September 2014

TranSiesta Session I:
Quantum Electronic Transport:
TranSiesta basics

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Patrons: Generalitat de Catalunya
CSIC Consejo Superior de Investigaciones Científicas
UAB Universitat Autònoma de Barcelona

OUTLINE

1. Motivation: Nanoelectronics & Molecular Electronics
2. Transport in the Bulk: A Brief Reminder
3. Meso-Nanoscale Transport: Basic Concepts
4. Coherent Transport: Landauer Formulation
5. Some Math: Green's Functions
6. Formulation at Equilibrium (non-interacting electrons)
7. Away from Equilibrium: Non-Equilibrium Green's Functions (non-interacting electrons)
8. Some Examples
9. Beyond elastic scattering and independent electrons: e-e, e-ph

TranSIESTA - Main Reference

PHYSICAL REVIEW B, VOLUME 65, 165401

Density-functional method for nonequilibrium electron transport

Mads Brandbyge,[1,*] José-Luis Mozos,[2] Pablo Ordejón,[2] Jeremy Taylor,[1] and Kurt Stokbro[1]
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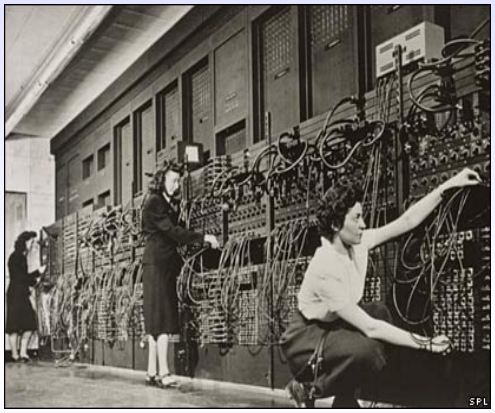
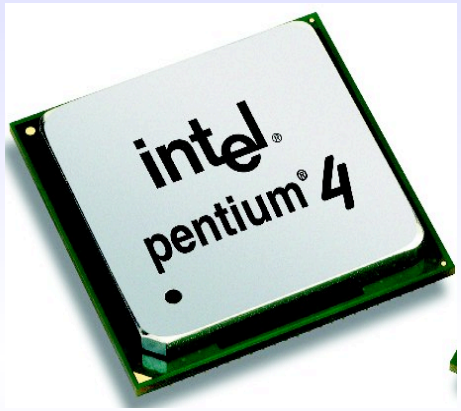
(Received 29 September 2001; published 22 March 2002)

New Challenges: Transport at the Nanoscale

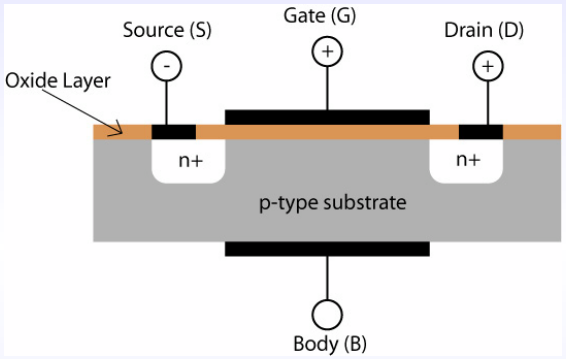
Miniaturization of (standard) Electronic Devices (top-down)



Eniac computer
(1947)



Pentium processor
(2000)



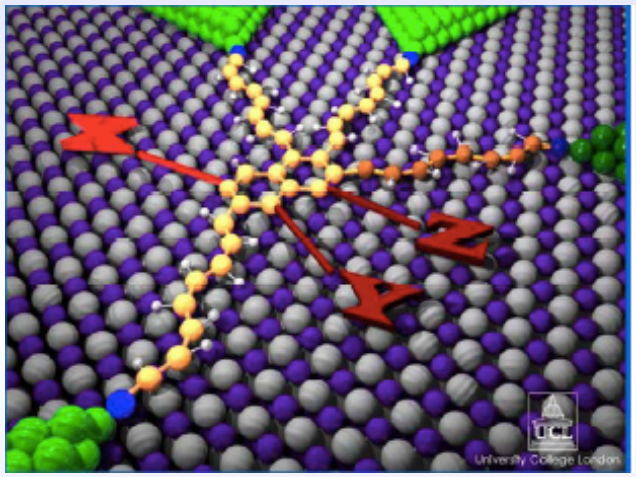
Current technologies:
65 to 22 nm

Challenges:

- Leakage (tunneling) currents at gate oxide
- Quantum confinement effects (semi-classical theory starts to fail)
- Lithographic top-down printing of smaller features
- Atomic limit: doping becomes unreliable

Molecular or Nano-electronics

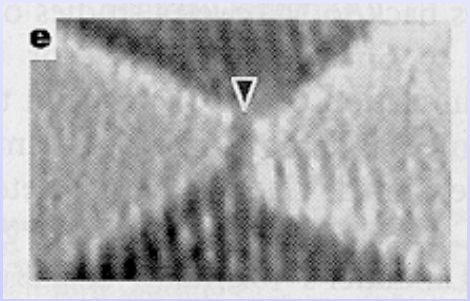
New approach to electronics: Bottom-up design

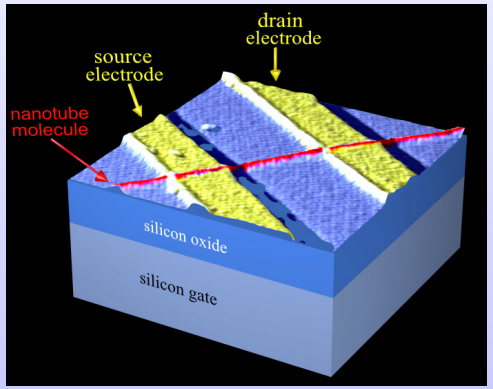


R. Stadler, M. Forshaw and C. Joachim, Nanotechnology 14, 138 (2003)

Huge experimental progress in fabrication and characterization

- Atomic wires: quantized conductance
- Diodes (with single molecules)
- Negative differential resistance
- Molecular Transistors (e.g., with nanotubes)
- Single-electron Transistor - Coulomb blockade
- Inelastic effects (phonons – IETS)
- Kondo resonances ....

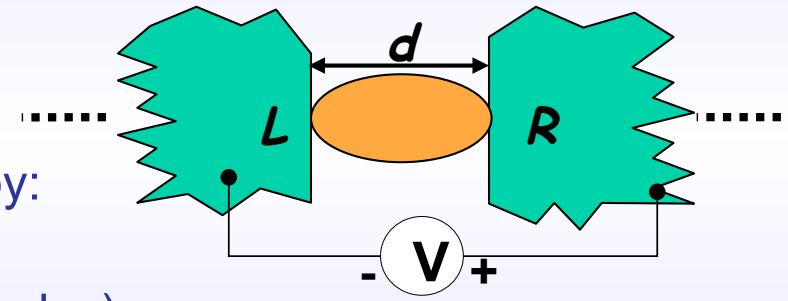




Theory of Transport at the Nanoscale

Strong need for theoretical methods for molecular electronics and nanoeletronics:

Quantum Behavior (semiclassical models are not applicable)



Simplest case:

I/V curves in 2-terminal devices, externally driven by:

- different μ in L,R
- external electric field (screened inside bulk electrodes)

Challenges

- Open system (non-periodic boundary conditions)
- Non-equilibrium conditions (two different chemical potentials)
- Many sources of scattering:
  - elastic - potential of constriction; impurities; ...
  - inelastic - e-e interactions; phonons; magnetic excitations...

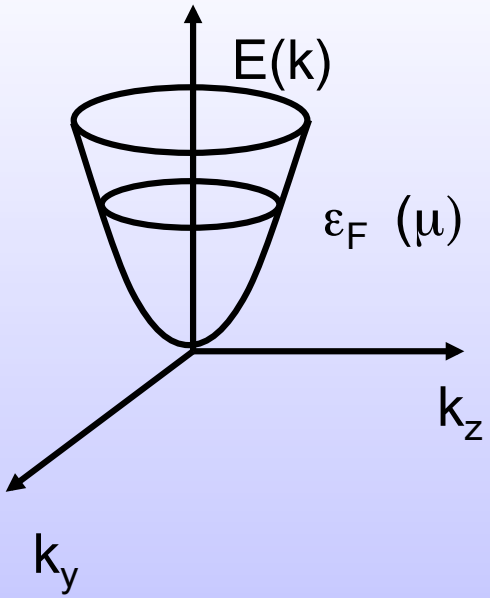
Bulk conductors (a reminder)

Distribution function at equilibrium:

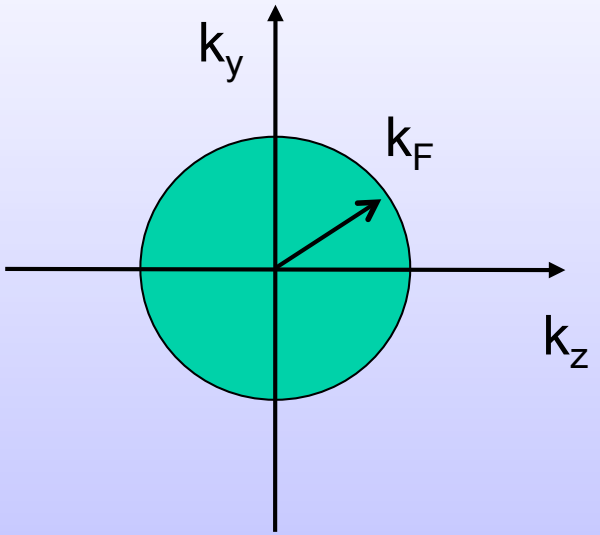
$$f_0(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/kT] + 1}$$

Free electron gas

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}$$

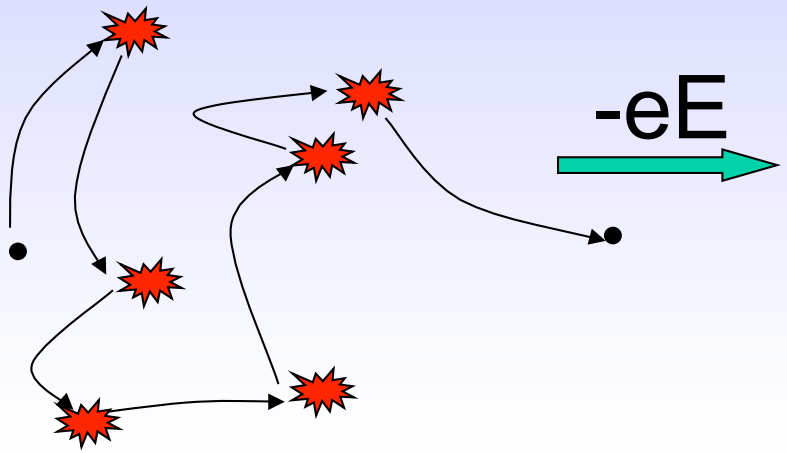


Zero net current



Out of Equilibrium (electric field)

Classical Picture: collisions + drift



Semiclassical Theory: Boltzmann

Quantum effects:

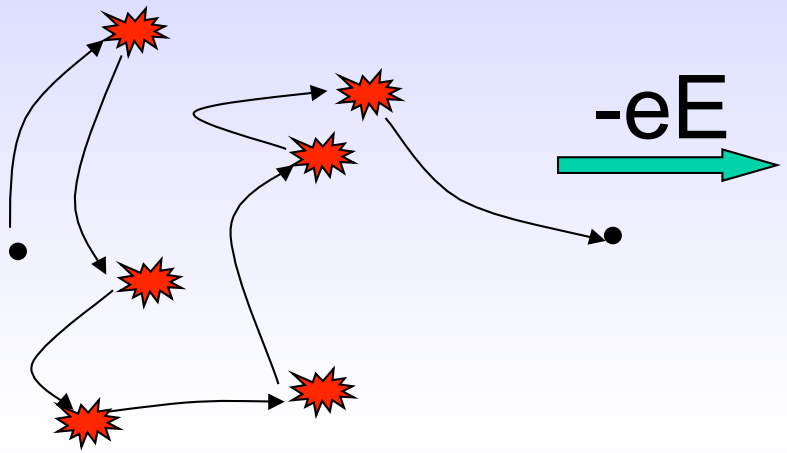
$$v(k) = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k}$$

non-equilibrium distribution function, $f_{\mathbf{p}}(\mathbf{r},t)$

$$\begin{aligned}\frac{df_{\mathbf{p}}(\mathbf{r},t)}{dt} &\equiv \frac{\partial f}{\partial t}+\frac{\partial f}{\partial \mathbf{r}}\frac{d\mathbf{r}}{dt}+\frac{\partial f}{\partial \mathbf{p}}\frac{d\mathbf{p}}{dt}+I_{\text{coll}}\\ &= \frac{\partial f}{\partial t}+\mathbf{v}\frac{\partial f}{\partial \mathbf{r}}+\mathbf{F}\frac{\partial f}{\partial \mathbf{p}}+I_{\text{coll}}\\ &= 0\end{aligned}$$

Out of Equilibrium (electric field)

Classical Picture: collisions + drift



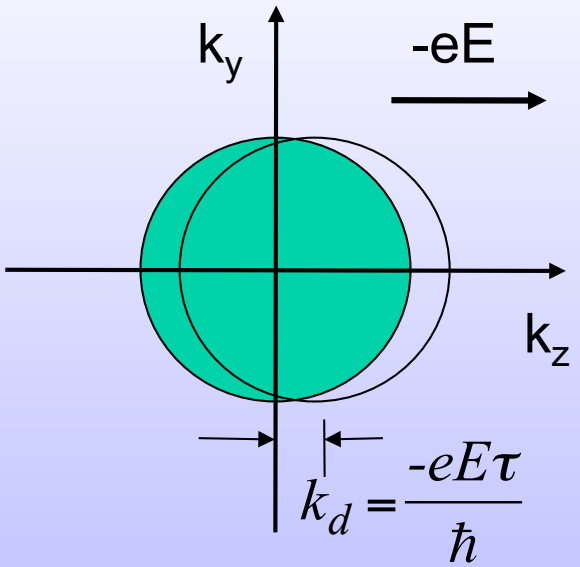
Semiclassical Theory: Boltzmann

Quantum effects:

$$v(k) = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k}$$

current density

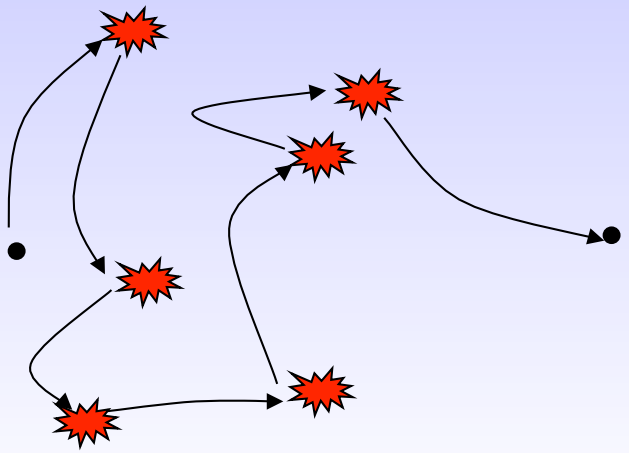
$$\mathbf{j}(\mathbf{r},t) = e\int (d\mathbf{p})\,\mathbf{v}\,f_{\mathbf{p}}(\mathbf{r},t)\,.$$



Drude conductivity

$$\sigma_0 = \frac{ne^2\tau_{\rm tr}(\epsilon_F)}{m}$$

Relevant Length Scales



1. Nature of the collisions:

- Elastic (static impurities)

These change the momentum k, but not the quantum coherence of the wf's
Characterized by a Relaxation Time (τ) and **Mean Free Path** ($l_m = v\tau$)

- Inelastic (phonons; e-e interactions; spin excit; impurities with internal deg. of free.)

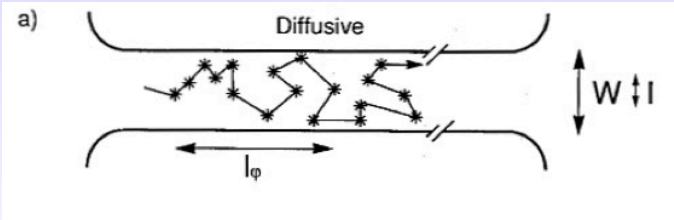
They change momentum, and introduce random phases (decoherence)
Temperature-dependent (phonons)
Characterized by a **Phase Relaxation Length** (l_ϕ)

2. Quantum Nature of Electrons: **de Broglie wavelength**: ($\lambda = 2\pi/k$)

Defines the lengths at which quantum effects become important

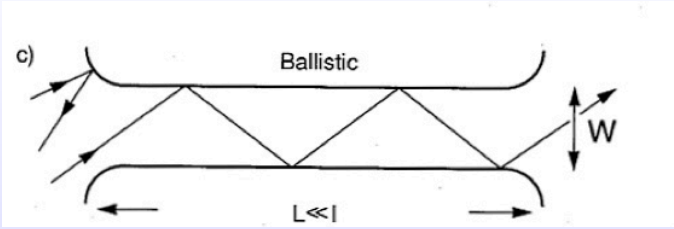
Transport Regimes:

1. Classical Diffusive Transport:
   - macroscopic samples, with $L \gg l_m, l_\phi$
   - semiclassical Boltzmann eq. is valid

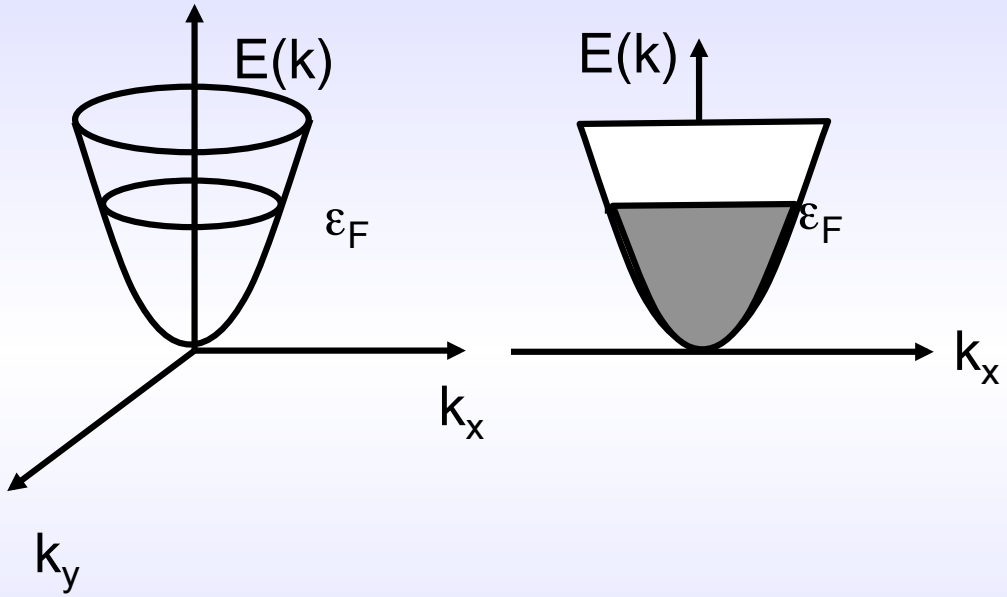


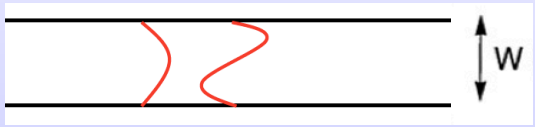
2. Coherent Transport:
   - macroscopic or microscopic samples, with $L < l_\phi$
   - quantum interference effects
     (weak and strong localization due to impurity disorder)

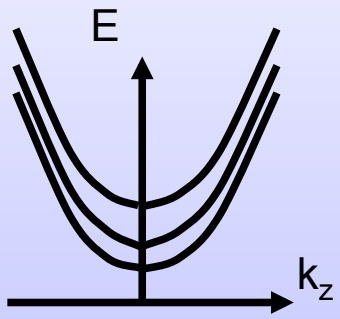
3. Ballistic Transport:
   samples with $L < l_m, l_\phi$
   - Momentum distribution deviates from Boltzmann;
   - Breaking of Ohm's law.

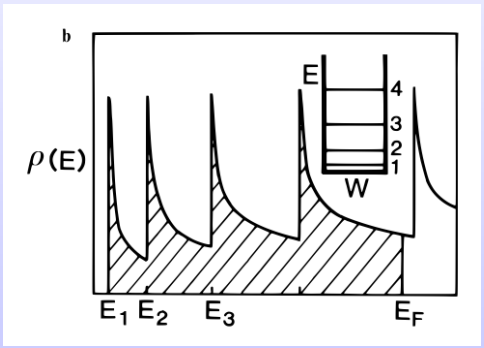


Wide conductor vs. narrow conductor:









Transport Regimes: "Quantum Transport"

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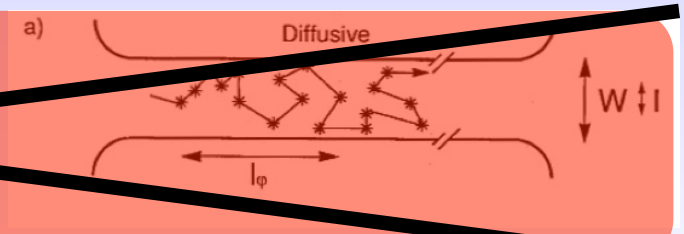

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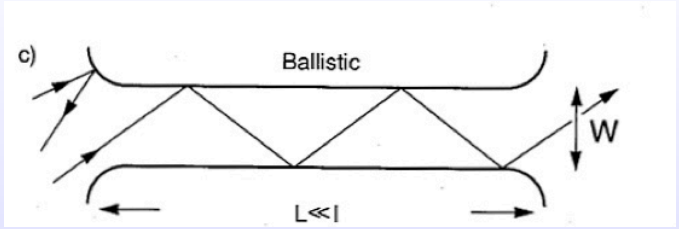
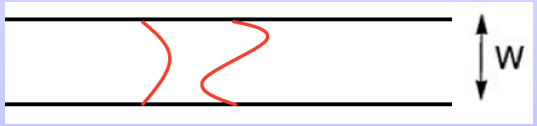
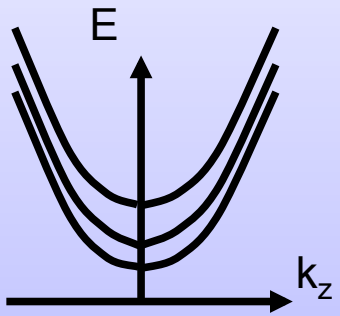
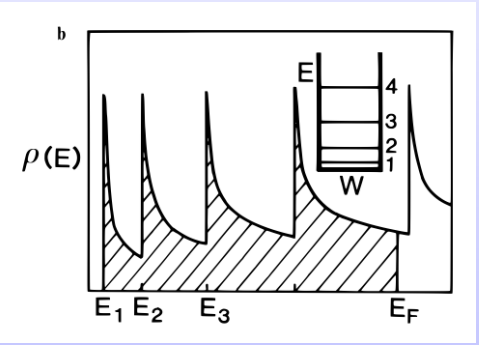


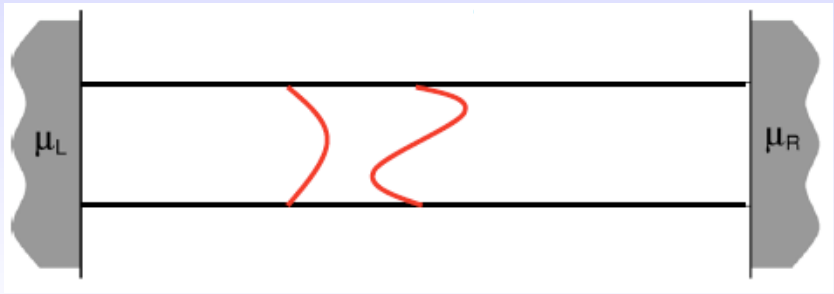
4. Quantum Size Effects:
   - samples with $L_{x,y,z} \sim \lambda$
   - quantization of levels in that dimension

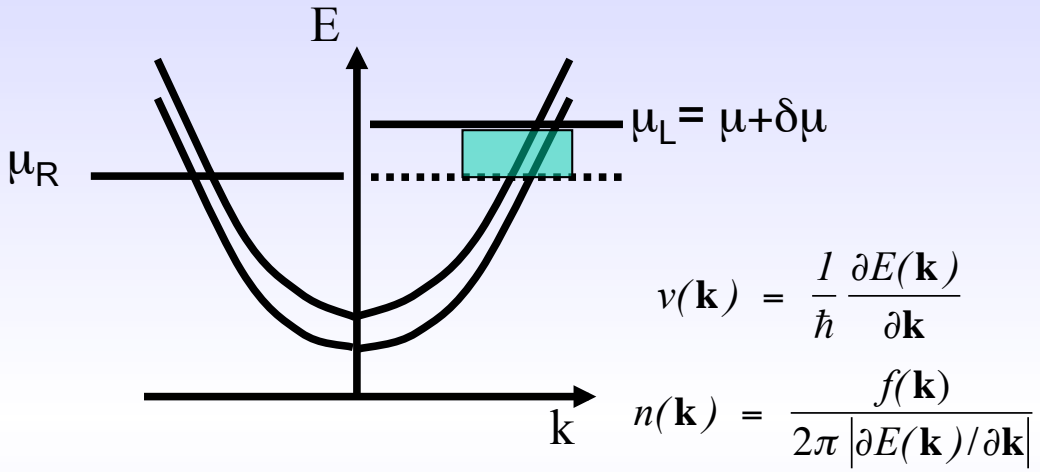






Quantum Transport: Long, reflectionless contact





$$v(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial E(\mathbf{k})}{\partial \mathbf{k}}$$

$$n(\mathbf{k}) = \frac{f(\mathbf{k})}{2\pi\,|\partial E(\mathbf{k})/\partial \mathbf{k}|}$$

$$\mu_L - \mu_R = \delta\mu = -eV$$

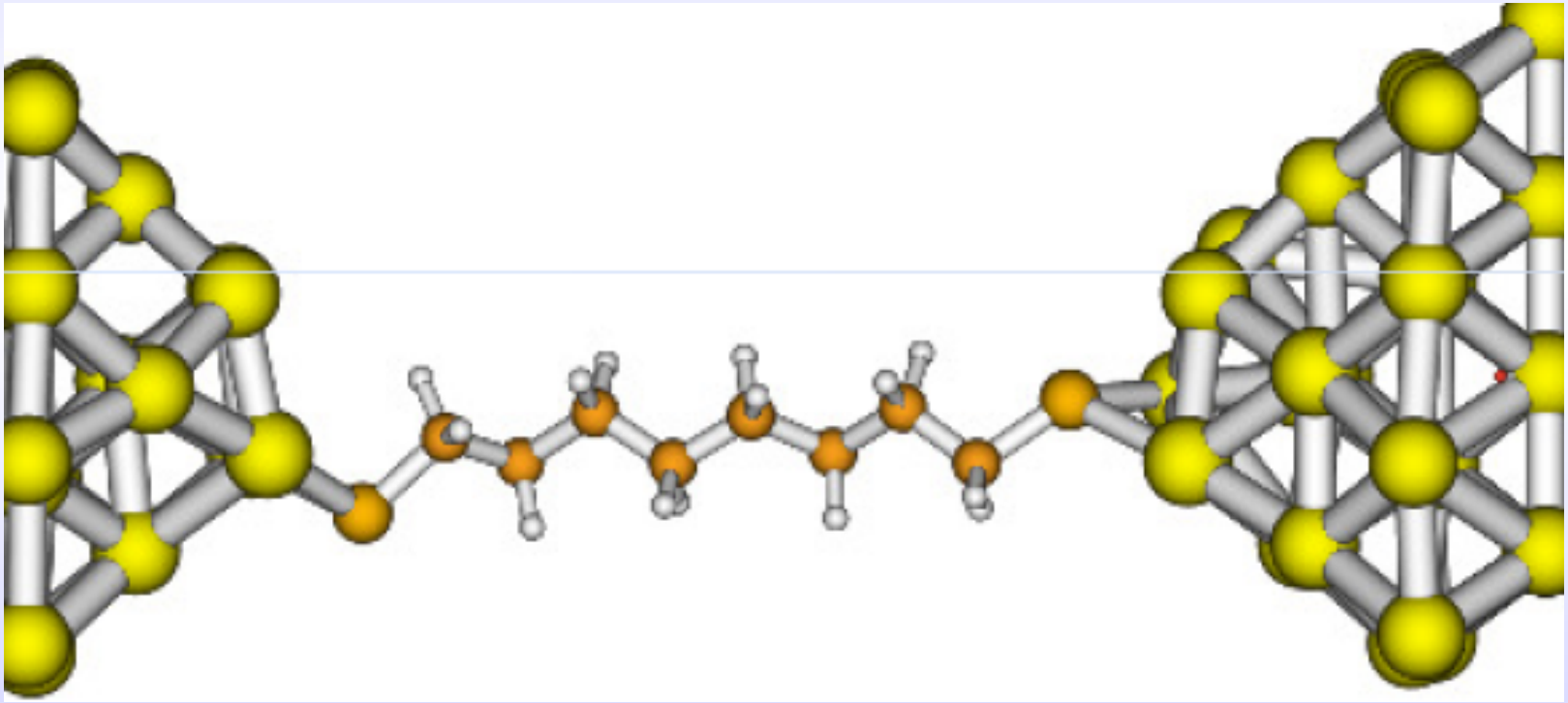
$$I = -2e\sum_{i}^{bands}\int_{BZ} dk\, n(k) v_g(k,i) = \frac{2e^2}{h} V N_{bands}(E_F)$$

$$G = \frac{I}{V} = N_{bands}\frac{2e^2}{h} = N_{bands} G_0$$

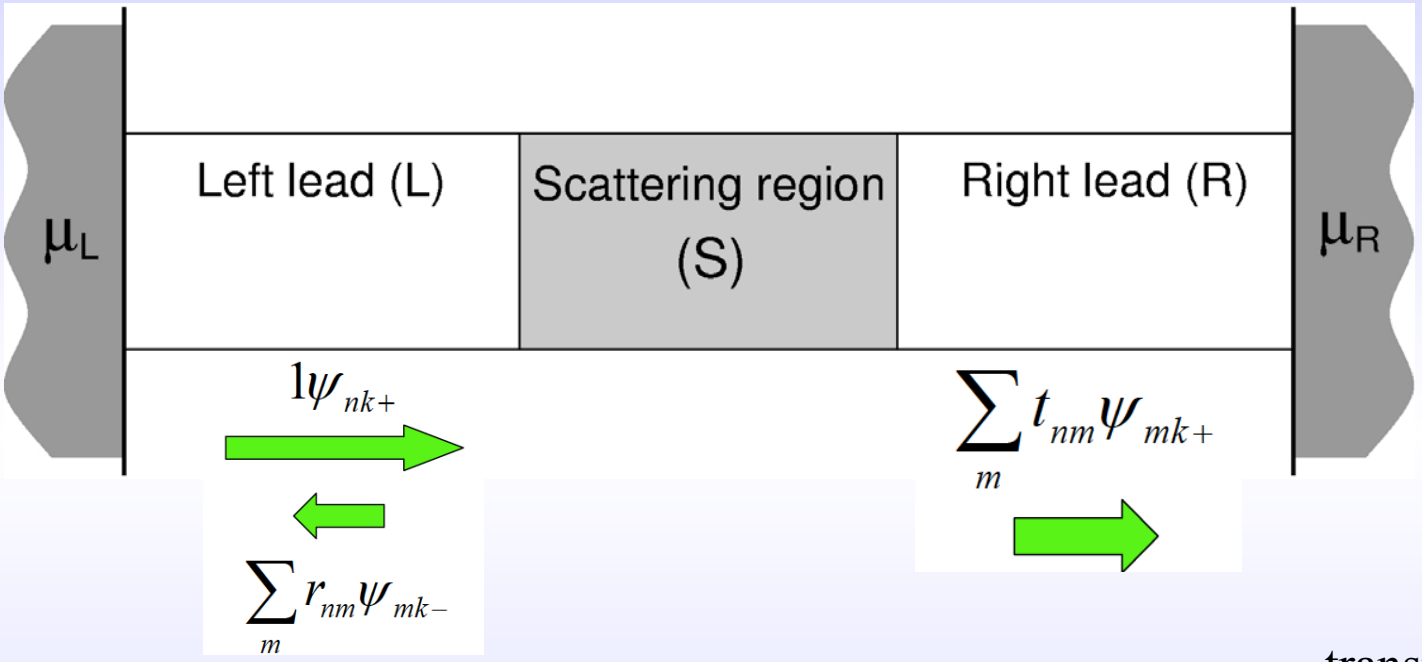
QUANTUM OF CONDUCTANCE

$$G_O = \frac{2e^2}{h} \Rightarrow 12.9\,k\Omega$$

Transport: Scattering at Nanoconstriction

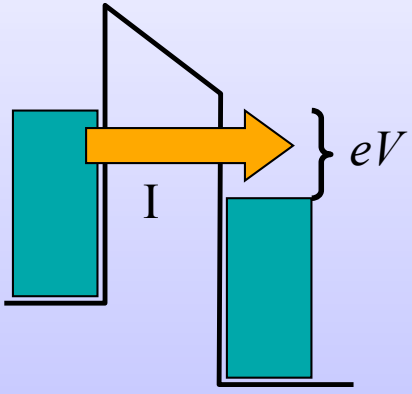


Transport: Scattering at Nanoconstriction



transmission matrix:

$$T(\varepsilon) = Tr\,[t^{+}t]\,(\varepsilon) \qquad \psi_{out} = t\,\psi_{in}$$



$$I = \frac{2e}{h}\int d\varepsilon\,\left(f_L(\varepsilon) - f_R(\varepsilon)\right)T(\varepsilon)$$

LANDAUER - BÜTTIKER

Transport: Scattering

$$I = \frac{2e^2}{h}\int d\varepsilon \; \left(f_L(\varepsilon) - f_R(\varepsilon)\right) T(\varepsilon)$$

For small voltage (linear response):

$$G = \frac{I}{V} = \frac{2e^2}{h} T(E_F) \; = \; G_0 \, T(E_F)$$

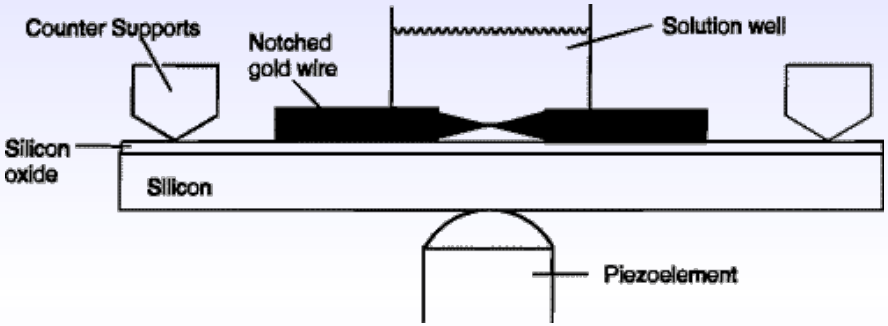
Limitations:

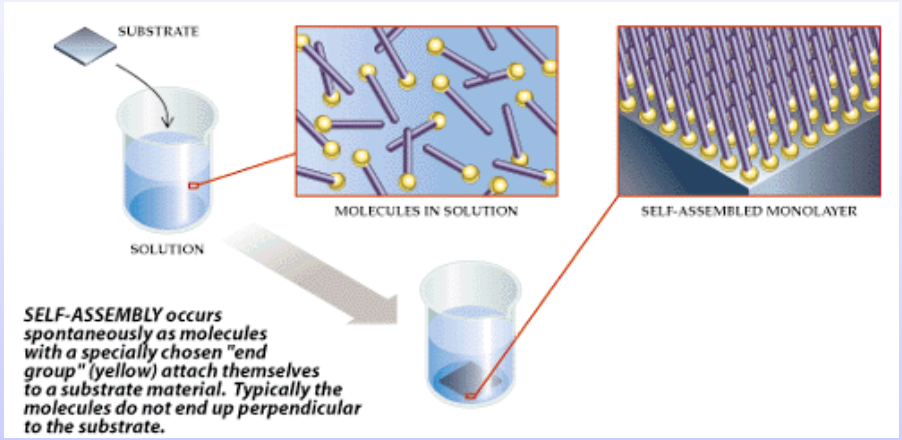
- Coherent Transport
- Non-interacting electrons

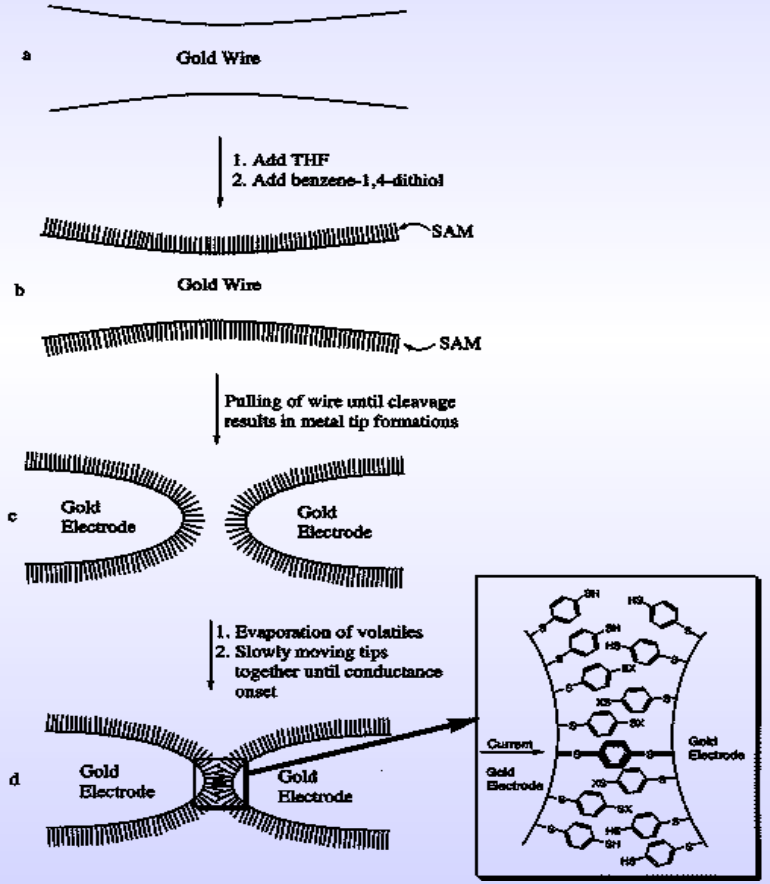
- Electrons incident from left/right are in thermal equilibrium with left/right reservoirs.
- Complete thermalisation of electrons upon entering reservoir
- No back-scattering at lead-reservoir interface

"Single" Molecule Experiments

Mechanical break junctions



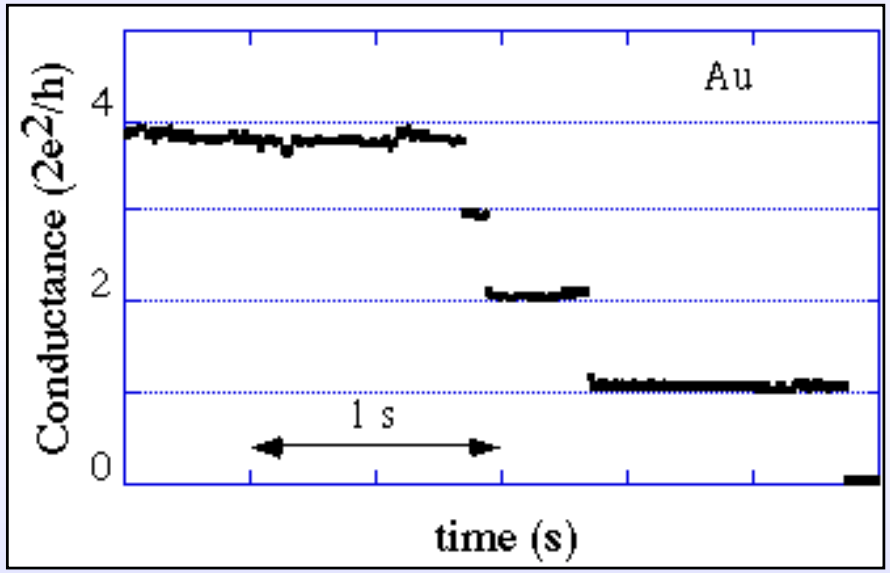




M. A. Reed *et al*, Science **278**, 252 (1997)

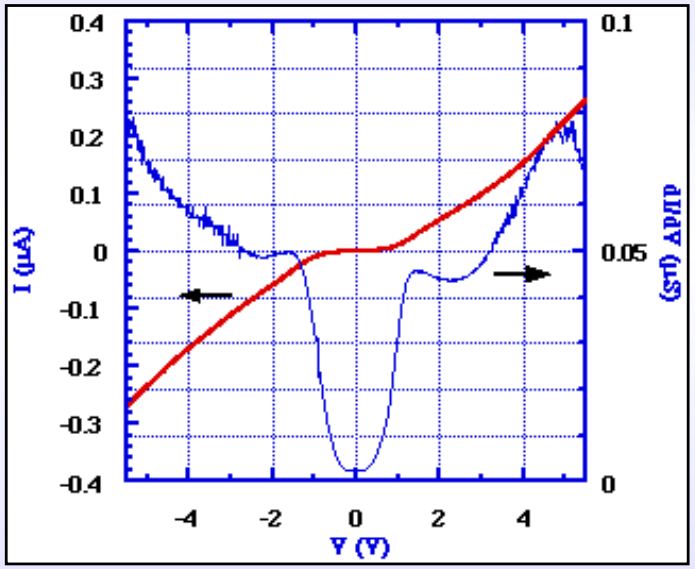
I/V Curves and Conductance

No Molecules/Solution



Wires formed (up to 1 atom thick!)
Conductance quantization
Atomic short-circuit

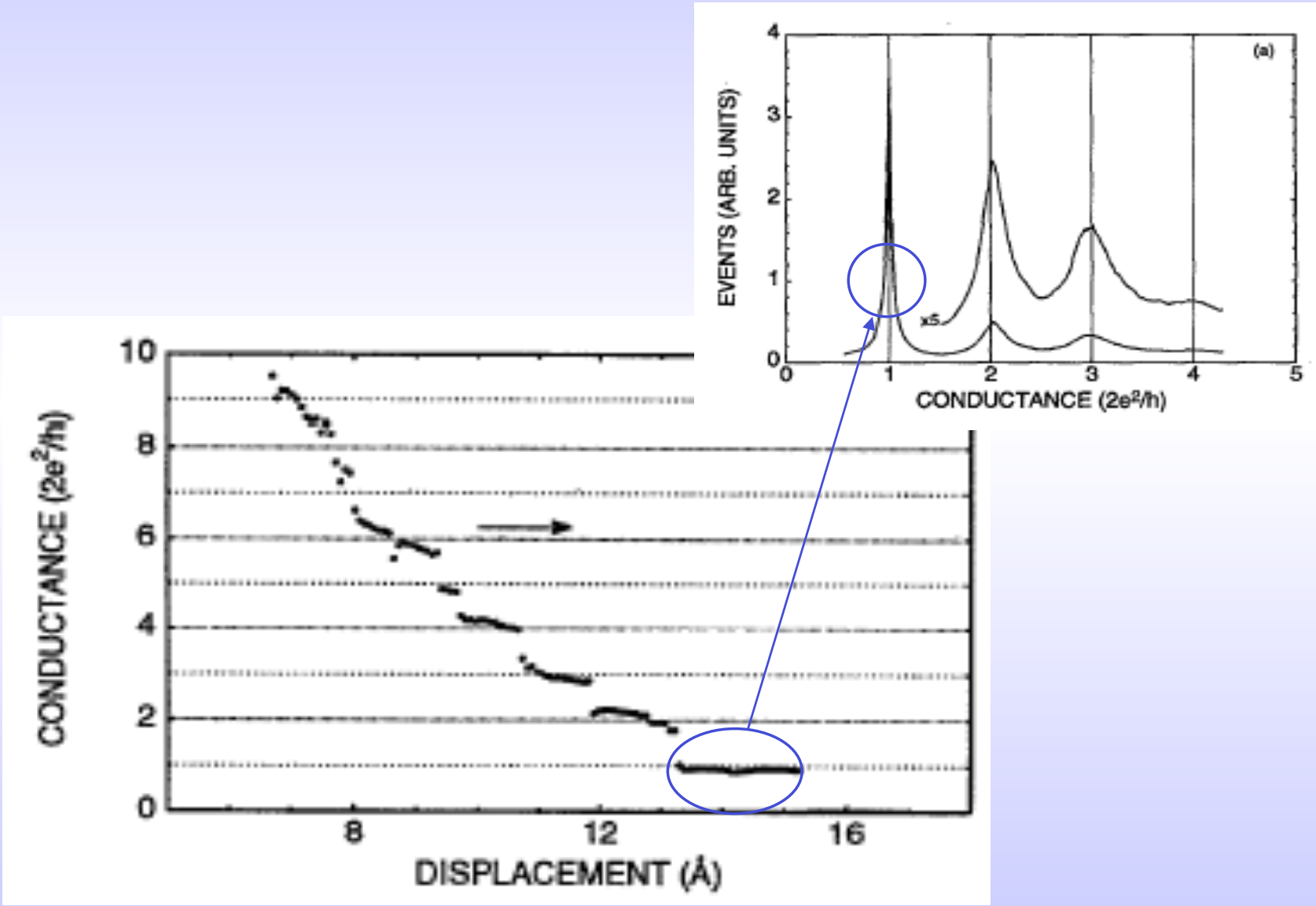
Molecules in Solution



Nonlinear I/V curves
Molecular levels (channels)

M. A. Reed *et al*, Science **278**, 252 (1997)

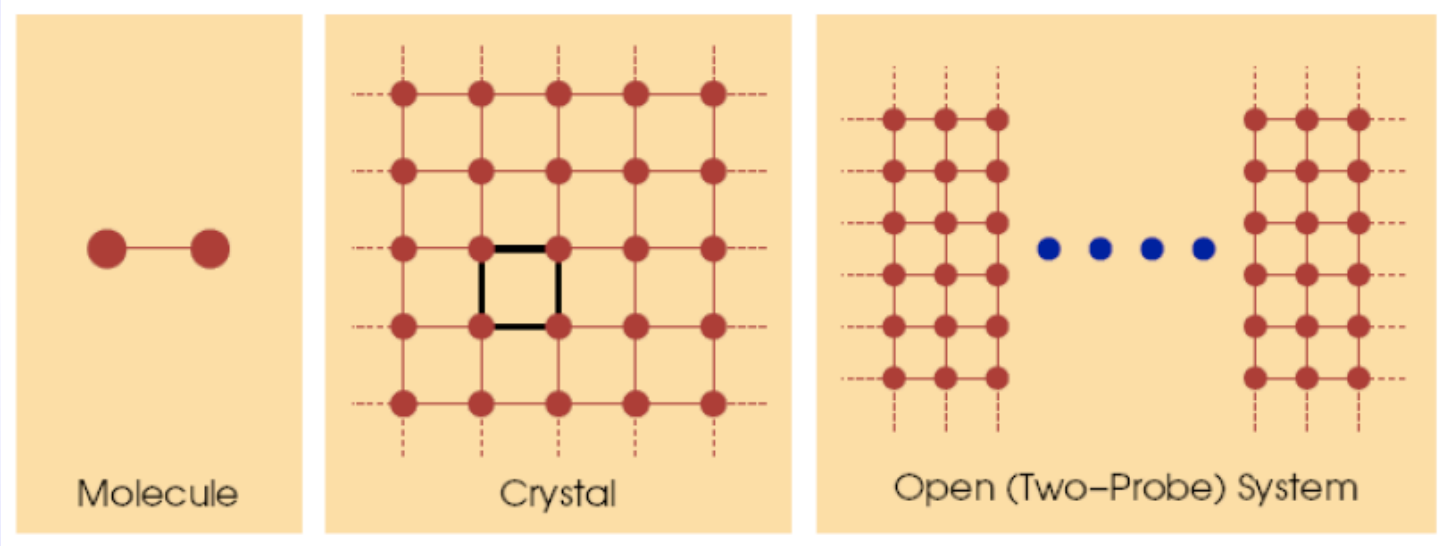
4. Coherent Transport: Landauer



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

Open systems

Infinite but non-periodic systems:



How to deal with them??

- Often, these systems can be seen as a finite system coupled to one or more (semi)infinite periodic systems
- Periodic system solved by standard methods
- Solve finite system + coupling using Green's Functions

Green's Functions

Retarded Green's Function

$$G^r(E) = (E^+ - H)^{-1} \qquad \left[E^+ = \lim_{\delta \to 0^+} E + i\delta \right]$$

$$G^r = \sum_i \frac{|i\rangle\langle i|}{E + i\delta - \varepsilon_i} \qquad G^r_{\mu\nu} = \sum_i \frac{\langle \mu|i\rangle\langle i|\nu\rangle}{E + i\delta - \varepsilon_i}$$

At equilibrium:

$$\rho(E) = -\frac{1}{\pi} \mathrm{Im}\, G^r(E)$$

Density of States

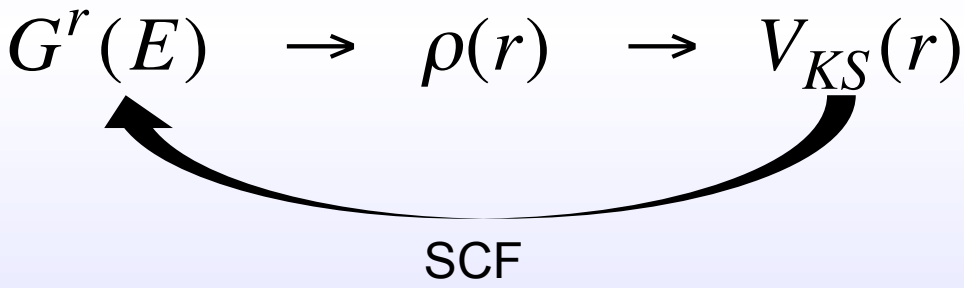
$$\rho = -\frac{1}{\pi} \mathrm{Im} \left[\int_{-\infty}^{\infty} n_{FD}(E) G^r(E)\, dE \right]$$

Particle Density (matrix)

Green's Functions

- Can be used in practice to compute the density matrix and the charge density without computing the eigenvectors/eigenvalues

- In DFT: Charge Density obtained from Green's Functions instead of eigenvectors -- Self Consistency cycle



- Useful for solving systems with 'extra' interactions (for instance, among different subsystems) -- Open systems!

Dyson's Equation

Suppose that the Hamiltonian can be split in two parts: an 'unperturbed' term plus a perturbation:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

Define the 'unperturbed' Green's Function as:

$$G_0(z) = (z - H_0)^{-1}$$

Then, it can be easly shown (Exercise!) that G fullfils Dyson's Equation:

$$\hat{G}(z) = \hat{G}_0(z) + \hat{G}_0(z)\hat{V}G(z)$$

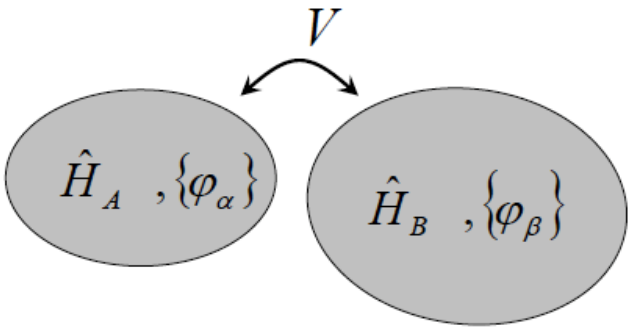
These can be used to compute the G.F. of the system with the perturbation V, if the G.F. of the unperturbed system G_0 is known.

Practical solution for Open Systems!!

Dyson's Equation and Self-Energies

If the system can be divided into two sub-systems, we can take the couping V as the 'interaction' in Dyson's equation (note that V needs not to be small!):

$$H = H_0 + V = \begin{pmatrix} H_A & 0 \\ 0 & H_B \end{pmatrix} + \begin{pmatrix} 0 & V_{AB} \\ V_{BA} & 0 \end{pmatrix}$$



We have:

$$G_0 = \begin{pmatrix} G_{0,AA} & 0 \\ 0 & G_{0,BB} \end{pmatrix}$$

with

$$G_{0,AA} = (z - H_A)^{-1}$$

$$G_{0,BB} = (z - H_B)^{-1}$$

Using Dyson's eq. it is easy to prove that:

$$G_{AA}(z) = (z - H_A - \underbrace{V_{AB} G_{0,BB}(z) V_{BA}}_{\Sigma_B(z)})^{-1}$$

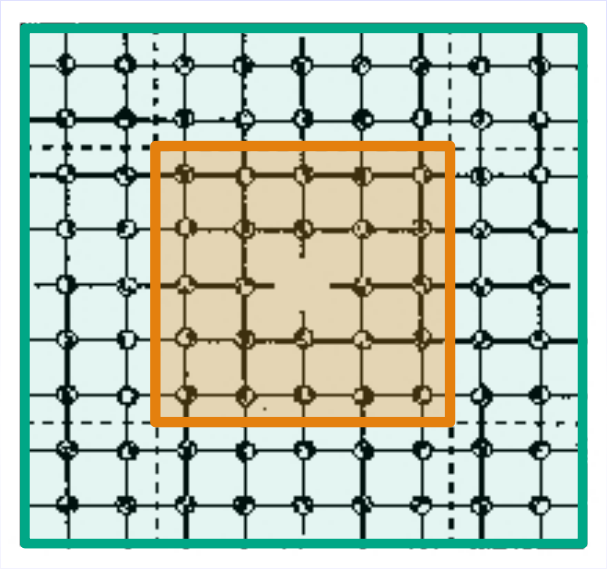
Self energy Σ_B

- Non-hermitian, energy dependent potential
- Accounts exactly for the effect of region B on A

Recap: Solving an Open System:

1. Split the system into:
   - Central region (where we are interested)
   - 'Embedding' or 'Electrodes' region
2. Solve the Green Function G_B of the 'embedding' region

$$G_{0,BB} = (z - H_B)^{-1}$$



3. Calculate the self-energy due to the embedding

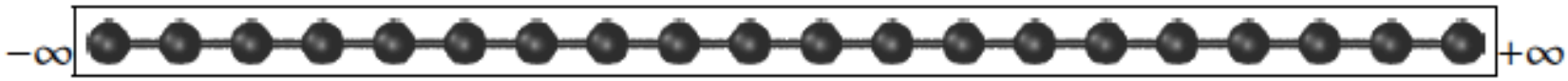
$$\Sigma_B(z) = V_{AB} G_{0,BB}(z) V_{BA}$$

Lopez-Sancho et al. J. Phys. F 14, 1205 (1984)

4. Solve the Green's Function of the central region

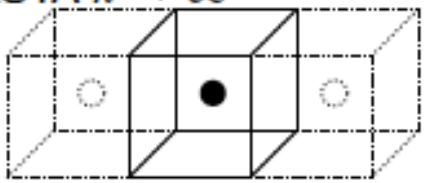
$$G_{AA}(z) = (z - H_A - \Sigma_B(z))^{-1}$$

A simple example: perfect linear 1D chain:

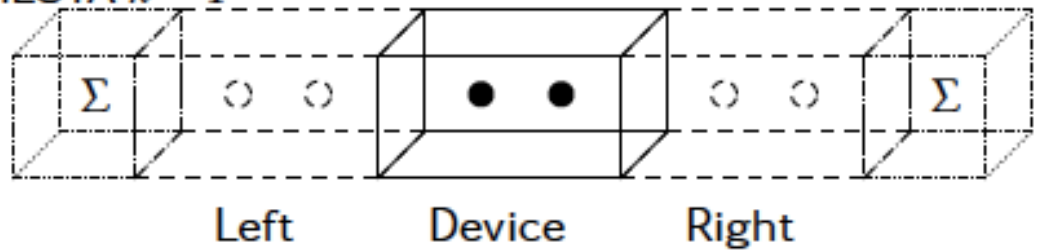


- Perfect systems can be handled equivalently, yet with different methods
- However, SIESTA is the best method for fully periodic systems when *not* applying a bias

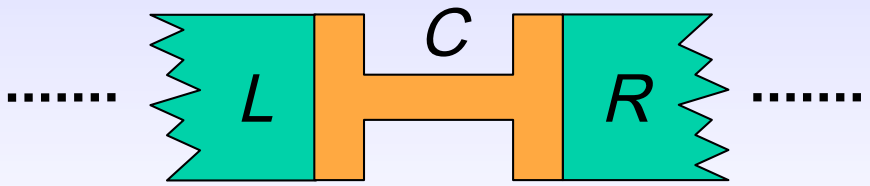
SIESTA $k \to \infty$



TranSIESTA $k = 1$



Nanocontacts: The problem at Equilibrium (Zero Bias)



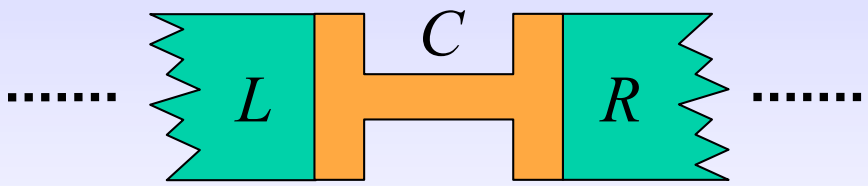
Coupling the finite contact to infinite electrodes

Greens Functions $G(\varepsilon + i\eta) = (\varepsilon + i\eta - H)^{-1}$

$$\rho(\varepsilon) = -\frac{1}{\pi} Im\, G(\varepsilon + i\eta)$$

$$\rho(r) = \sum_{\mu\nu} \underbrace{\left[\int_{-\infty}^{\infty} d\varepsilon\, \rho_{\mu\nu}(\varepsilon) n_F(\varepsilon - \mu_F) \right]}_{D_{\mu\nu}} \varphi_\mu(r) \varphi_\nu(r)$$

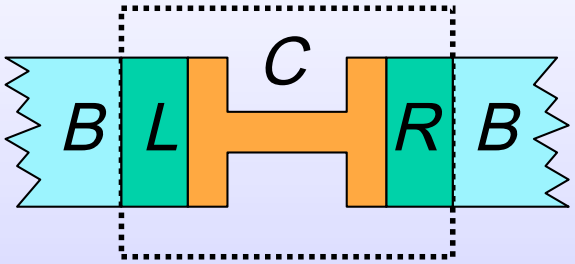
Setup (zero bias)



$$G(\varepsilon) = (\varepsilon - H)^{-1} = \begin{bmatrix} \ldots & -V_L^+ & & & \\ -V_L^- & \varepsilon - H_L & -V_{LC} & & \\ & -V_{CL} & \varepsilon - H_C & -V_{CR} & \\ & & -V_{RC} & \varepsilon - H_R & -V_R^+ \\ & & & -V_R^- & \ldots \end{bmatrix}^{-1}$$

Contact:

- Contains the molecule, and part of the Right and Left electrodes
- Sufficiently large to include the screening



Solution in finite system:

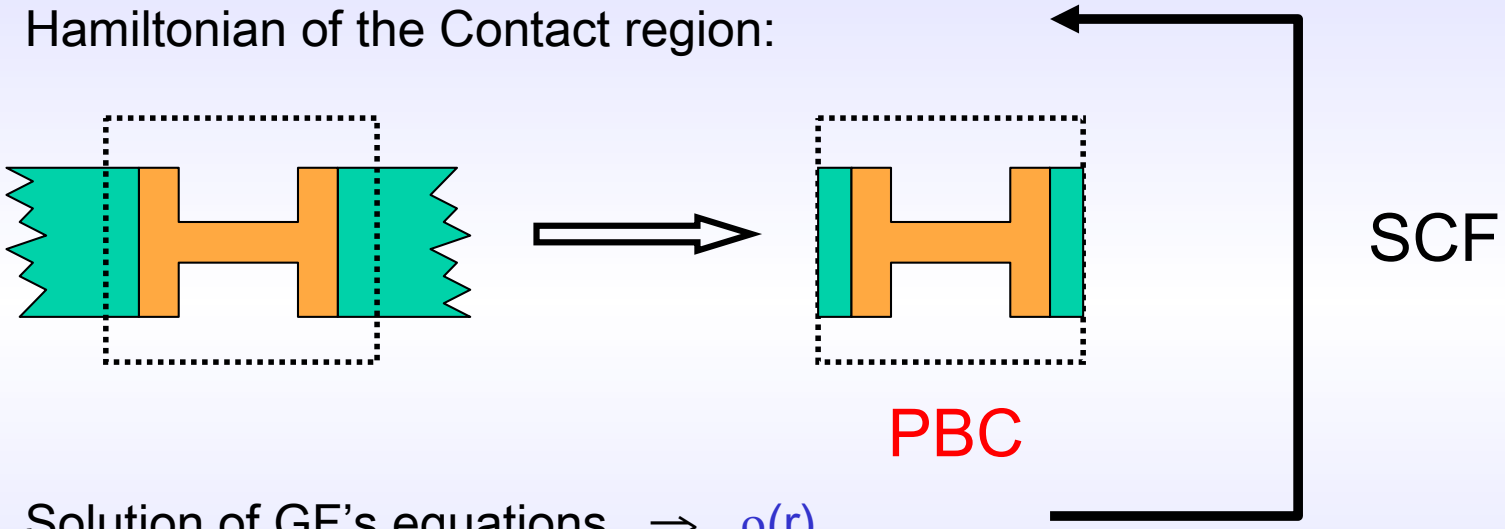
$$G(\varepsilon) = \begin{bmatrix} \varepsilon - H_L - \Sigma_L & -V_{LC} & \\ -V_{CL} & \varepsilon - H_C & -V_{CR} \\ & -V_{RC} & \varepsilon - H_R - \Sigma_R \end{bmatrix}^{-1}$$

$\Sigma(\varepsilon)$ = Selfenergies. Can be obtained from the bulk Greens functions

Lopez-Sancho et al. J. Phys. F 14, 1205 (1984)

Calculations (zero bias):

- Bulk Greens functions and self-energies (unit cell calculation)
- Hamiltonian of the Contact region:



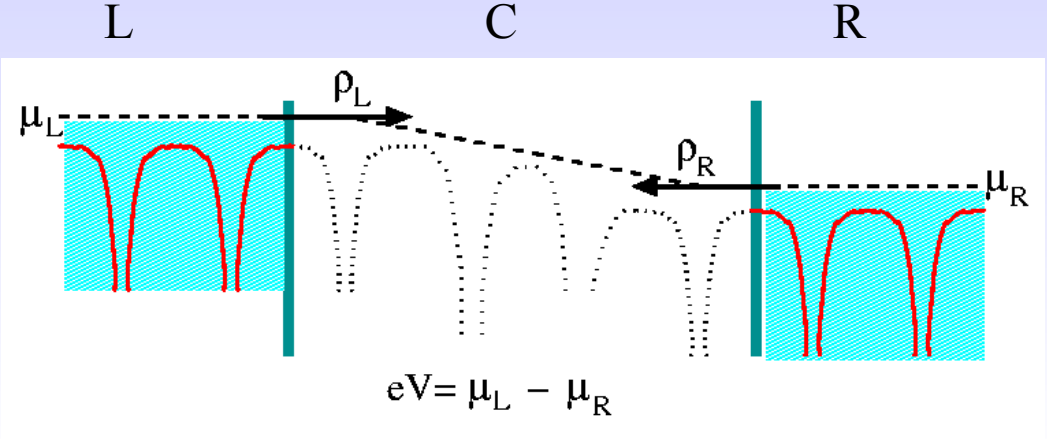
- Solution of GF's equations ⇒ ρ(r)
- Landauer conductance: transmission probability:

$$T(\varepsilon) = Tr\,[t^{+} t]\,(\varepsilon)$$

$$t(\varepsilon) = \left(Im\left[\Sigma_R(\varepsilon)\right]\right)^{1/2}\; G(\varepsilon)\; \left(Im\left[\Sigma_L(\varepsilon)\right]\right)^{1/2}$$

$$G = \frac{I}{V} = \frac{2e^2}{h} T(E_F) \;=\; G_0\, T(E_F)$$

Non-Equilibrium Green's Functions (NEGF)



- Keldysh-Kadanoff-Baym Non-equilibrium Green's Functions

Caroli, Combescot, Nozieres, Saint-James, J. Phys. C: Solid St. Phys., 1971

H. Haug and A.-P. Jauho, Quantum Kinetics in Transport and Optics of Semiconductors - Springer-Verlag, Berlin, (1996).

- Same equations can be derived using scattering states

Brandbyge, Mozos, Ordejón, Taylor, Stokbro, PRB 65, 165401 (2002)

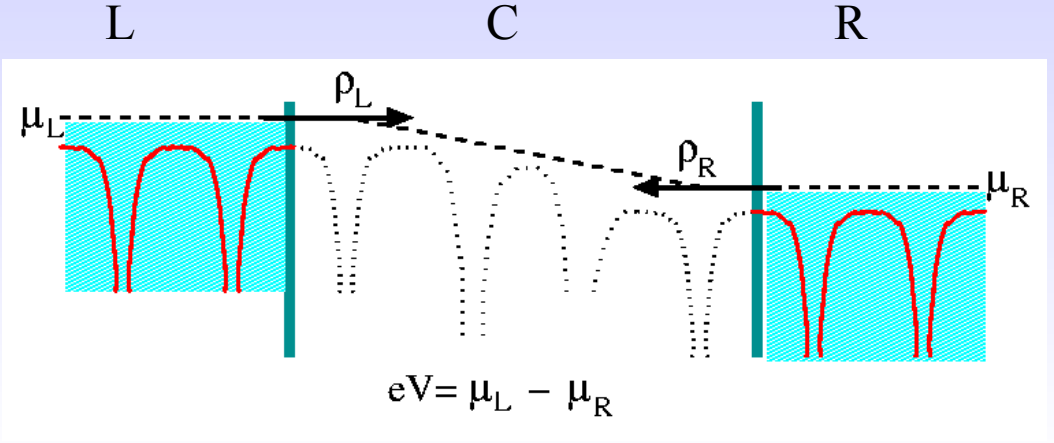
Density matrix from the incoming scattering states from left to right (with their corresponding chem. pot.)

$$D(\vec{x},\vec{y}) = \sum_l \psi_l(\vec{x})\psi_l^*(\vec{y})n_F(\varepsilon_l - \mu_L)$$

$$+ \sum_r \psi_r(\vec{x})\psi_r^*(\vec{y})n_F(\varepsilon_r - \mu_R)$$

Non-Equilibrium Green's Functions (NEGF)

$$\hat{H} = \begin{bmatrix} H_L & V_L & 0 \\ V_L^+ & H_C & V_R \\ 0 & V_R^+ & H_R \end{bmatrix}$$



$$\psi_l(\vec{x}) = \sum_\mu c_{l\mu}\phi_\mu(\vec{x})$$

Lippman-Schwinger Eq.:

$$\psi_l(\vec{x}) = \psi_l^0(\vec{x}) + \int d\vec{y}\, G(\vec{x},\vec{y})V_L(\vec{y})\psi_l^0(\vec{y})$$

$$c_{l\mu} = c_{l\mu}^0 + \sum_\nu [\mathbf{G}(z)\mathbf{V}]_{\mu\nu} c_{l\nu}^0, \quad z = \varepsilon_l + i\delta,$$

Density matrix:

$$\mathbf{D}_{\mu\nu} = \sum_l c_{l\mu}c_{l\nu}^* n_F(\varepsilon_l - \mu_L) + \sum_r c_{r\mu}c_{r\nu}^* n_F(\varepsilon_r - \mu_R)$$

After some algebra....

$$\mathbf{D}_{\mu\nu} = \int_{-\infty}^{\infty} d\varepsilon\, \rho^{L}_{\mu\nu}(\varepsilon) n_F(\varepsilon - \mu_L) + \rho^{R}_{\mu\nu}(\varepsilon) n_F(\varepsilon - \mu_R)$$

$$\rho^{L}_{\mu\nu}(\varepsilon) = \frac{1}{\pi}[\mathbf{G}(\varepsilon)\mathbf{\Gamma}_L(\varepsilon)\mathbf{G}^{\dagger}(\varepsilon)]_{\mu\nu}$$

$$\mathbf{\Sigma}_L(\varepsilon) \equiv [\mathbf{V}\mathbf{g}^{L}(\varepsilon)\mathbf{V}^{\dagger}],$$

$$\mathbf{\Gamma}_L(z) \equiv i[\mathbf{\Sigma}_L(\varepsilon) - \mathbf{\Sigma}_L(\varepsilon)^{\dagger}]/2,$$

Note that both the Density Matrix and the Spectral Density are more involved than in the equilibrium case (but reduce to them at equilibrium)

$$D_{\mu\nu} = \int_{-\infty}^{\infty} d\varepsilon\, \rho_{\mu\nu}(\varepsilon)\, n_F\left(\varepsilon - \varepsilon_F\right)$$

$$\rho(\varepsilon) = -\frac{1}{\pi} Im\, G(\varepsilon)$$

Conductance

$$G(V)=\frac{G_0}{V}\int_{-\infty}^{\infty} d\varepsilon[n_F(\varepsilon-\mu_L)-n_F(\varepsilon-\mu_R)]\,\mathrm{Tr}\,[\mathbf{t}^\dagger\mathbf{t}](\varepsilon)$$

$$\mathbf{t}(\varepsilon)=[\mathbf{\Gamma}_R(\varepsilon)]^{1/2}\mathbf{G}(\varepsilon)[\mathbf{\Gamma}_L(\varepsilon)]^{1/2}$$

We, then, recover a Landauer-Büttiker formula for the conductance!, with explicit formulas for the transmission matrix and the density matrix (and the density in real space).

Electrostatic Potential

Poisson's Eq: $\nabla^2 V(r) = -\rho(r)$

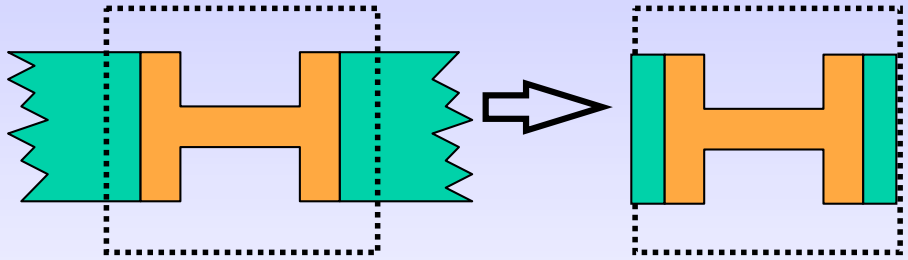
Given $\rho(r)$, $V_H(r)$ is determined except up to a linear term:

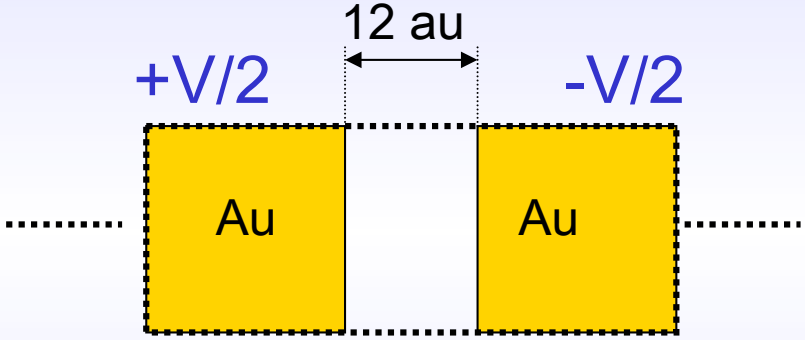
$$V_H(\mathbf{r}) = \phi(\mathbf{r}) + \mathbf{a}\cdot\mathbf{r} + \mathbf{b}$$

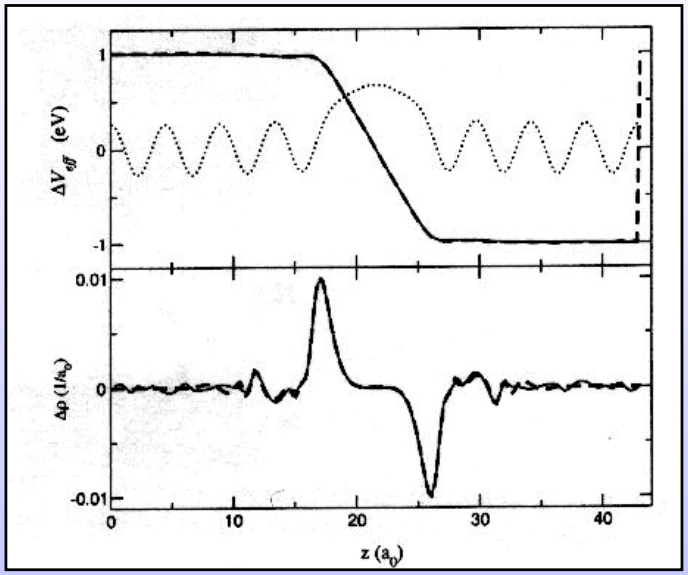
$\phi(r)$: particular solution of Poisson's equation

a and b: determined imposing BC: the shift V between electrodes

- ϕ (r) computed using FFT's
- Linear term: $-\frac{V}{L}\left(z - \frac{L}{2}\right)$

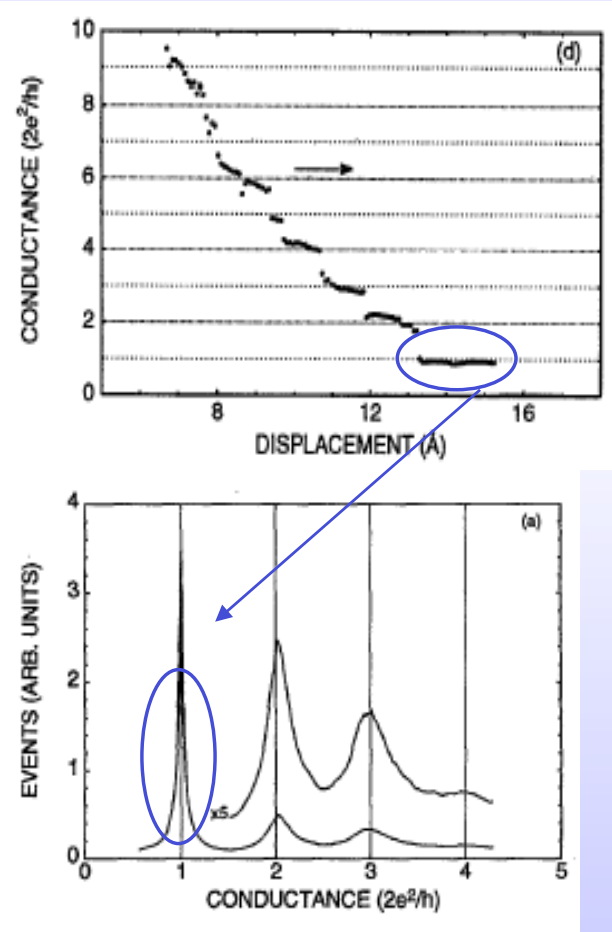






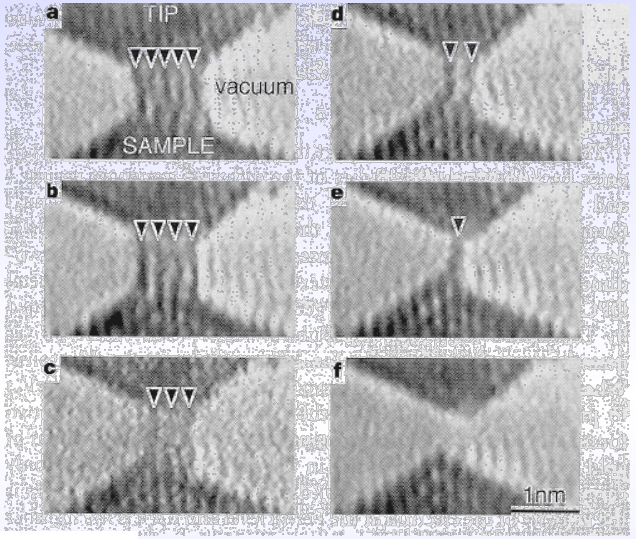
Monoatomic Gold Wires

Good statistics:
1 atom=1 conductance quantum

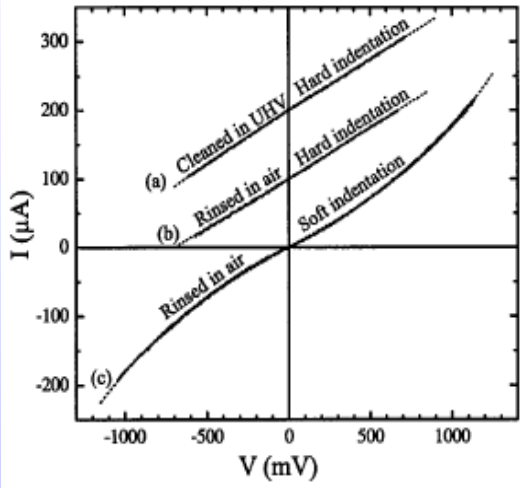


Brandbyge et al., PRB 52, 8499 (1995)

Onishi et al., Nature 395, 780 (1998)



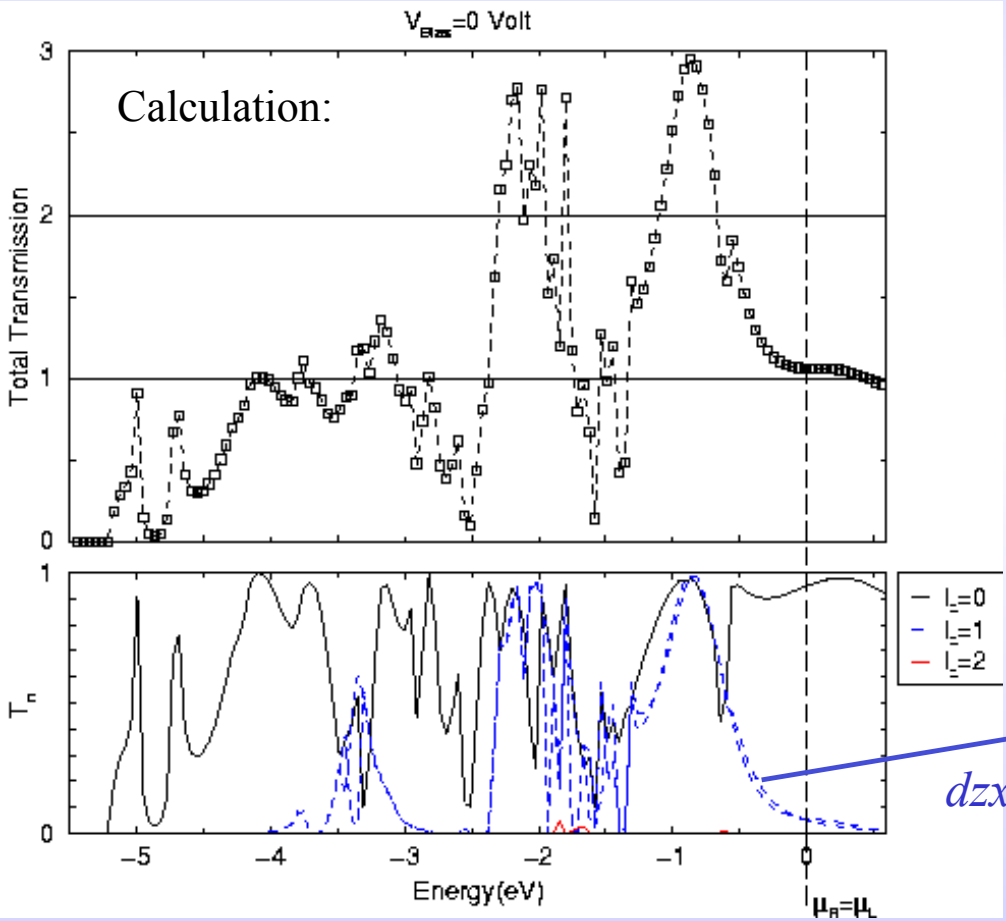
Linear I/V curves

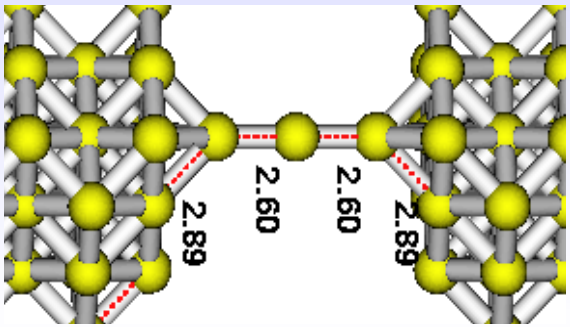


Hansen et al., APL 77, 708 (2000)

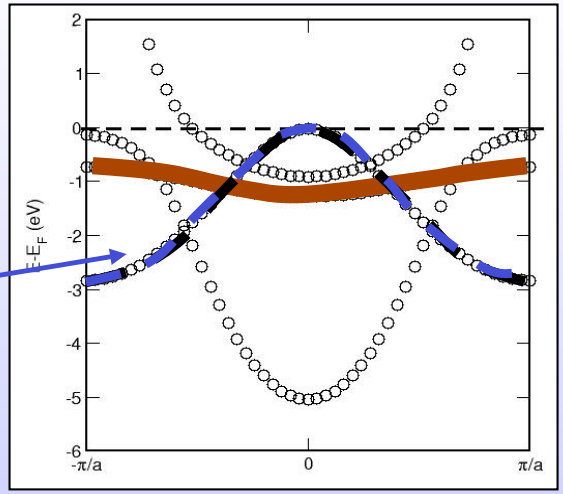
Monoatomic Gold Wires

Au chains - Au (001) electrodes; Zero bias





Bandstructure of infinite chain

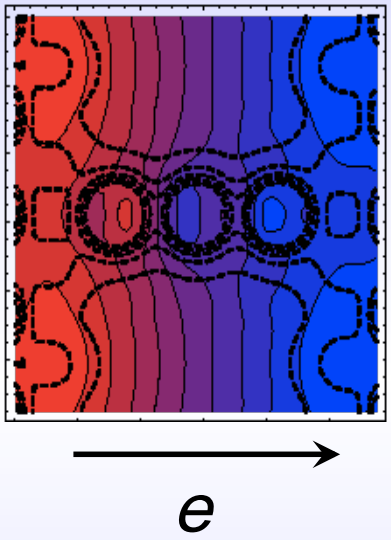


dzx,dyz

Same result (T≈1) obtained, irrespective of chain length, electrode surface, strain, etc., which explains the narrow peak at 1 G_o in the histograms

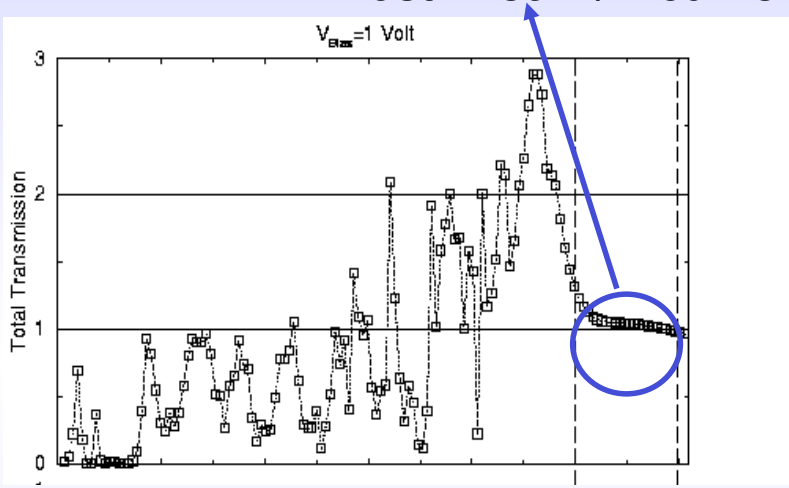
Monoatomic Gold Wires

Au chains - Au (001) electrodes; Finite bias

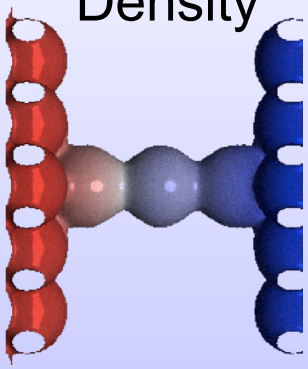


Voltage drop through the contact

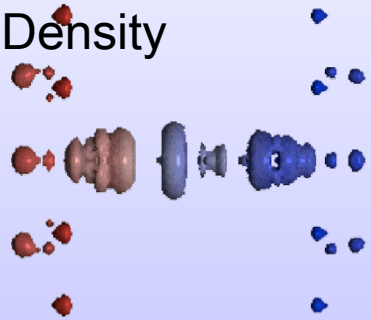
Almost linear I/V curve

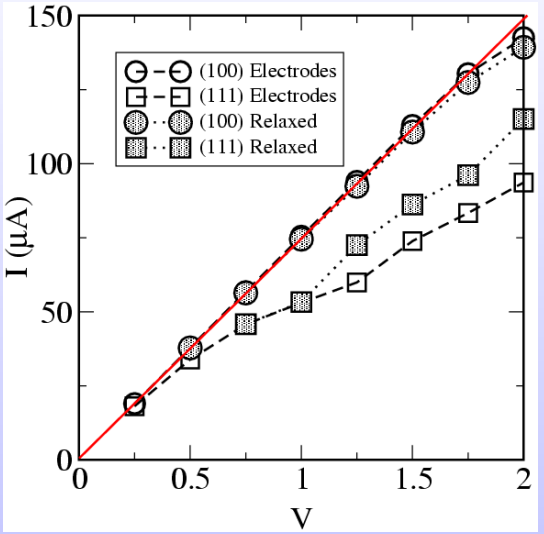


Density

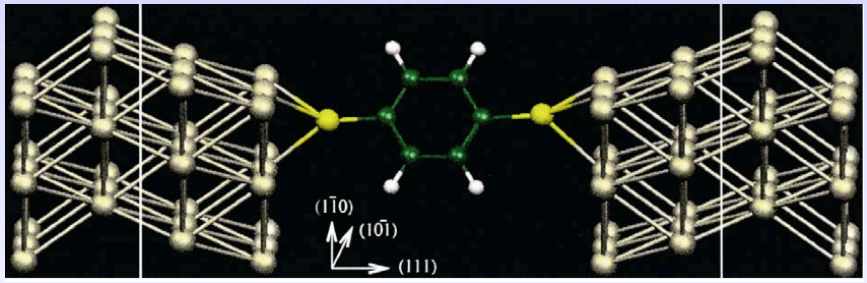


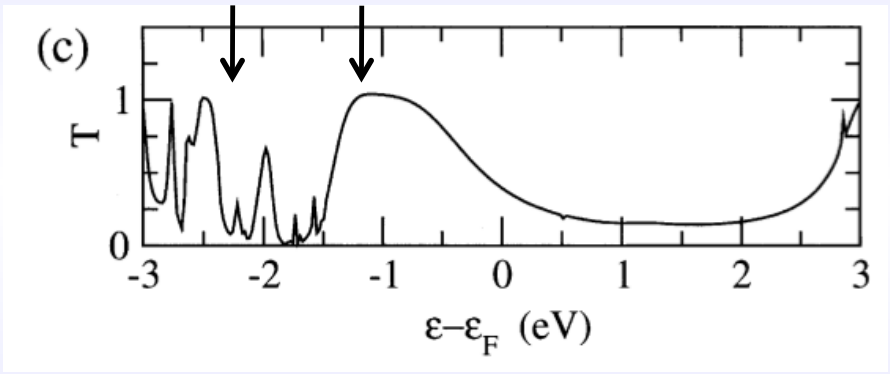
Change in Density

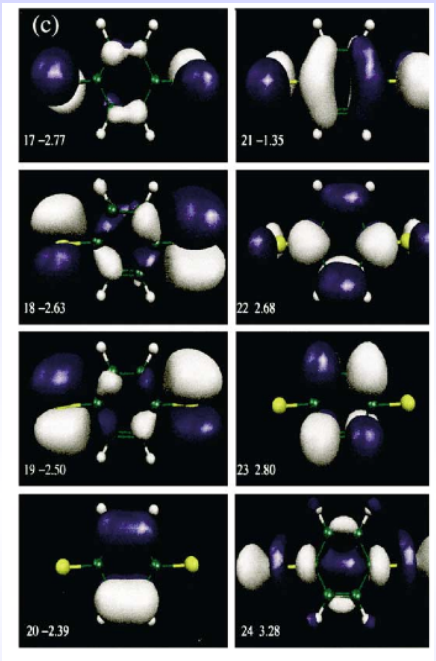


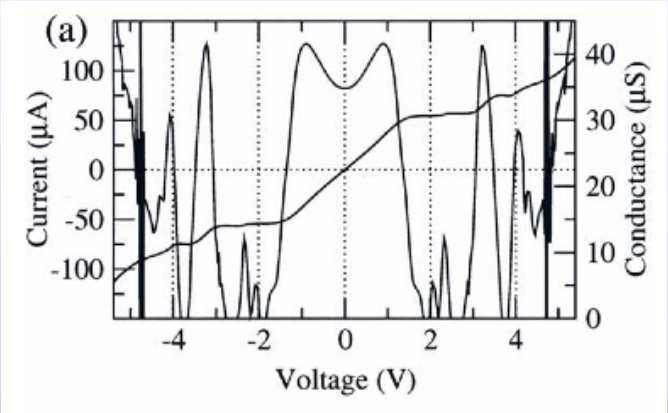


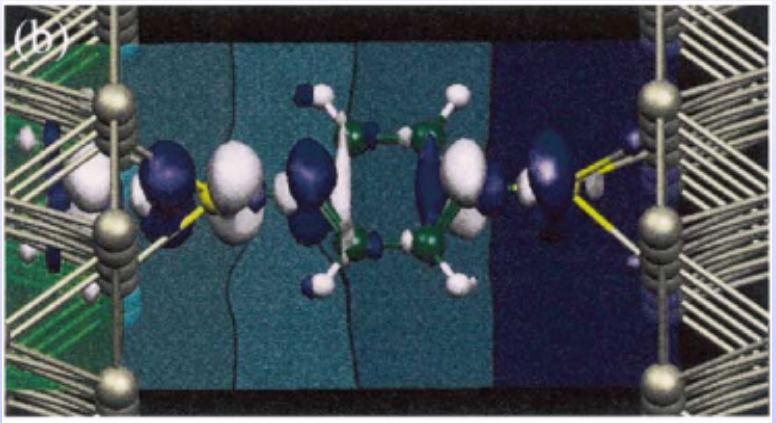
DTB (Di-thiol Benzene) on Au(111)





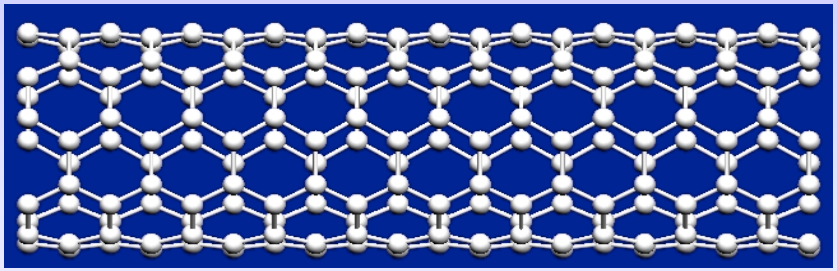


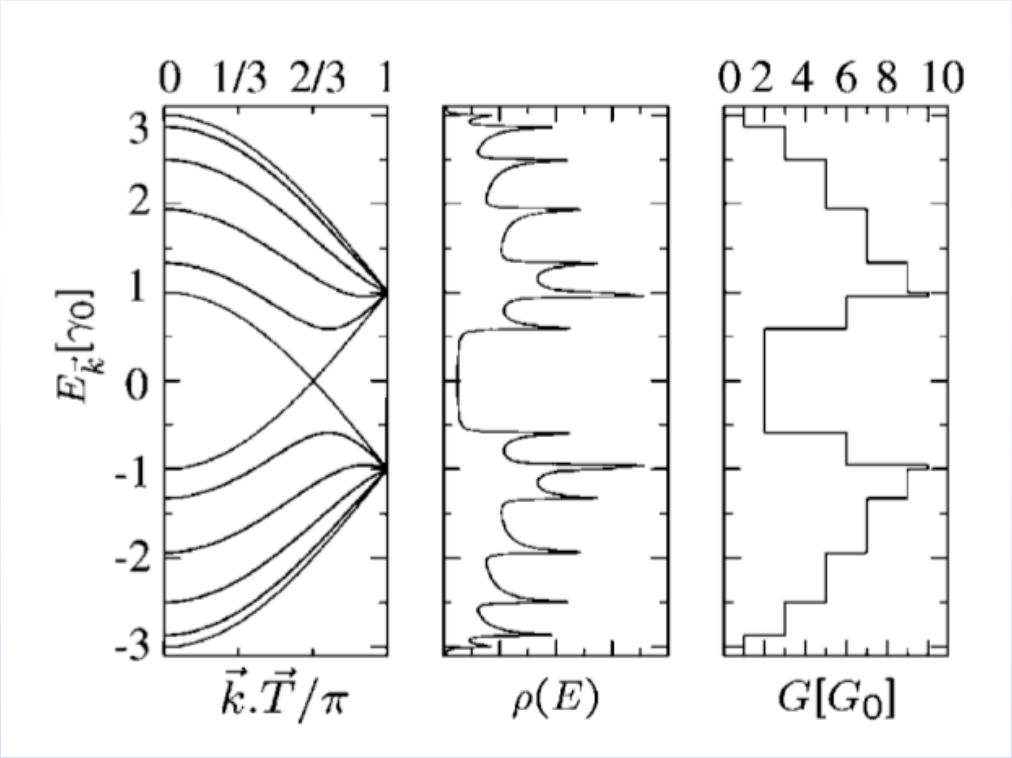




Stokbro, Taylor, Brandbyge, Mozos, Ordejón, Computational Materials Science 27 (2003) 151–160

Carbon Nanotubes





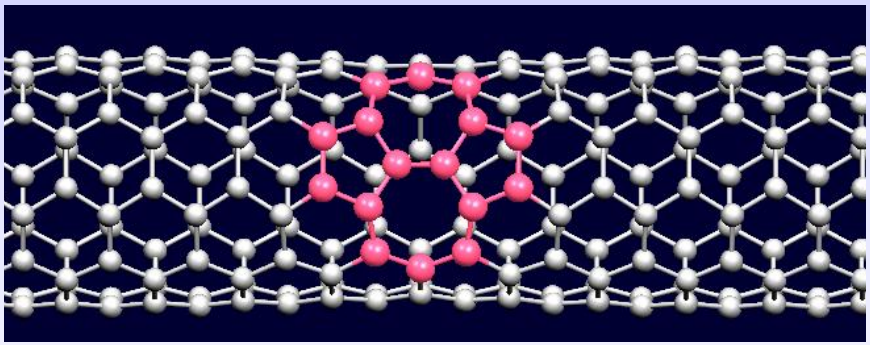
Defect-free, long (5,5) tube

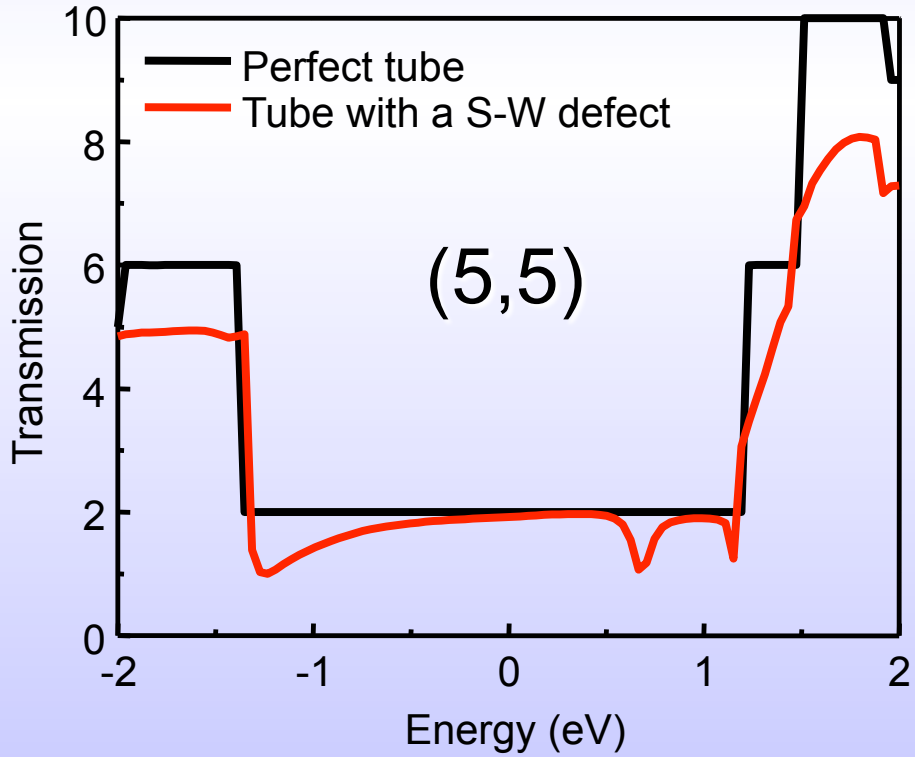
Conductance: $G = 2G_0$ (around E_F)

Charlier, Blase and Roche, RMP'07

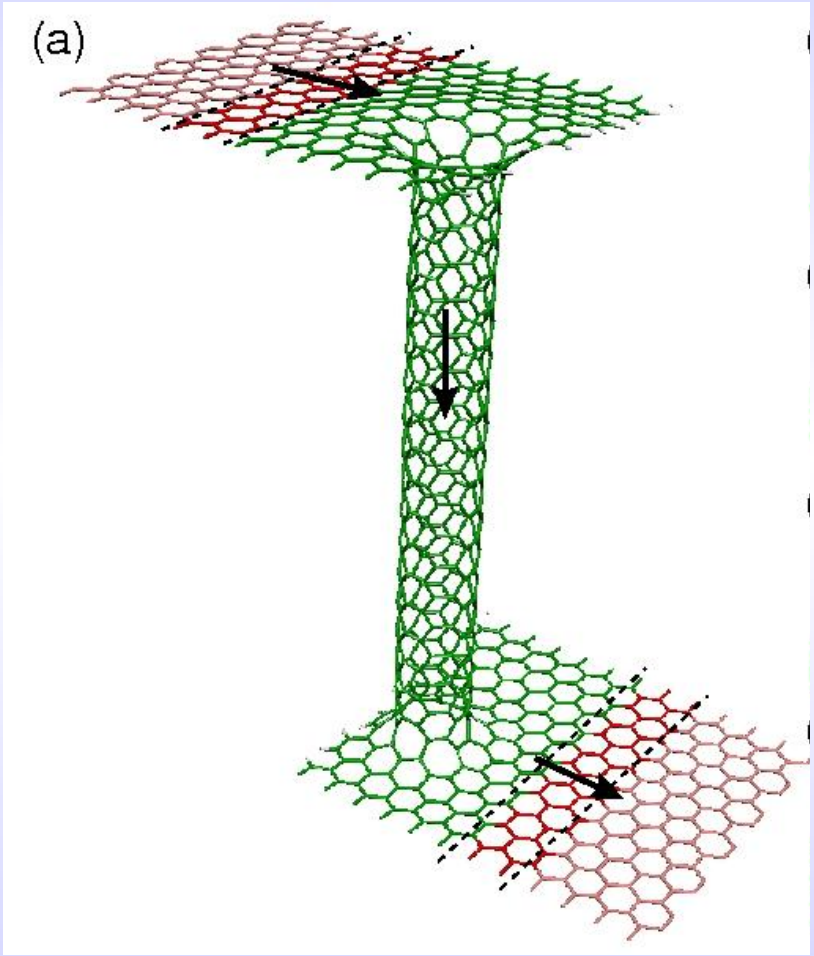
Carbon Nanotubes

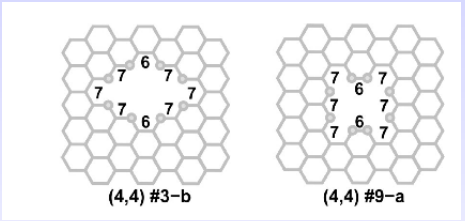
S-W defect in (5,5) CNT

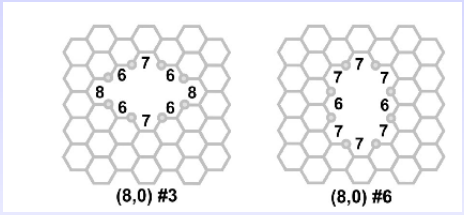


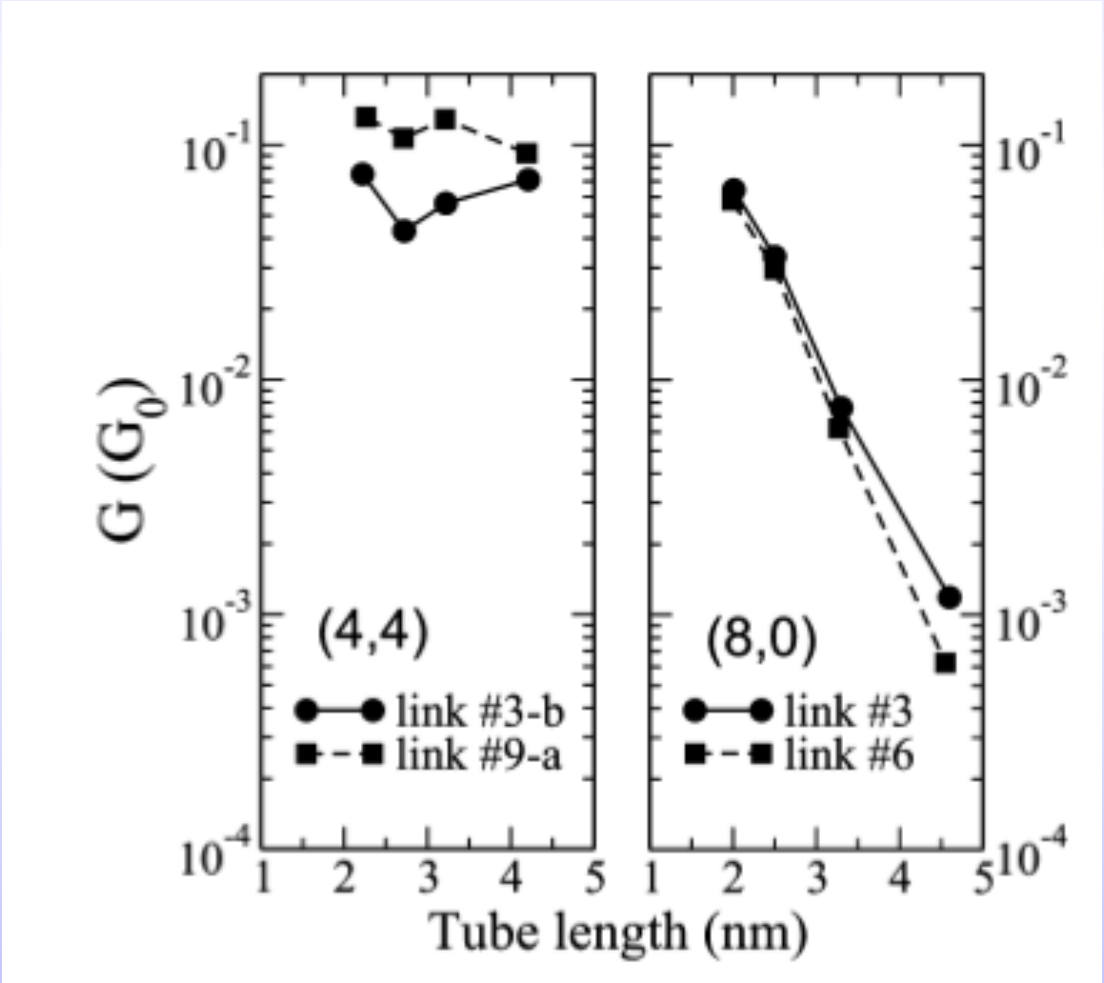


Carbon Nanotubes connected to Graphene









9. Beyond Elastic Scattering and Independent Electrons

NEQFs can be used to address inelastic effects (phonons, etc), and e-e interactions:

- General theory of contacts with e-e interactions (with non-interacting electrodes): Meir and Wingreen, PRL 2512, 68 (1992)
- GW Approximation (improvement on DFT excitation energies) - via self-energy

$$G(\omega) = (\omega - (H_{KS} - V_{xc}) - \Sigma_L - \Sigma_R - \Sigma_{GW}[G])^{-1}$$

- e-ph interactions: 1st order Born approximation

$$G_S(E) = (E - H_S - \Sigma_L(E) - \Sigma_R(E) - \Sigma_{1BA}(E))^{-1}$$

Code 'Inelastica' by Pausson and Fredriksen (http://sourceforge.net/projects/inelastica/)

- ....