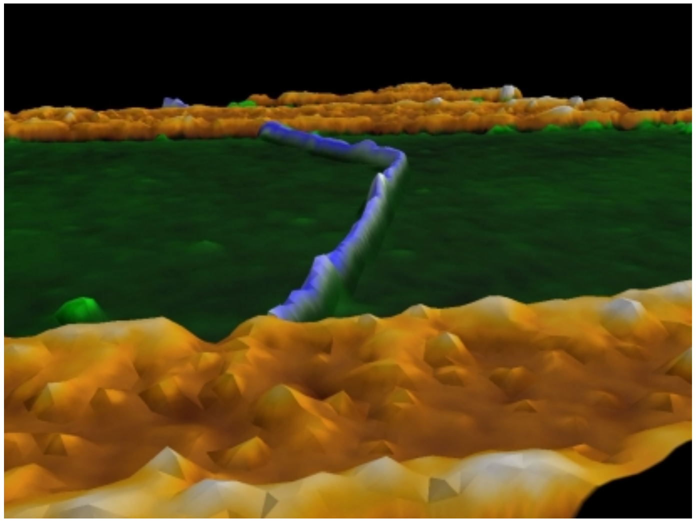
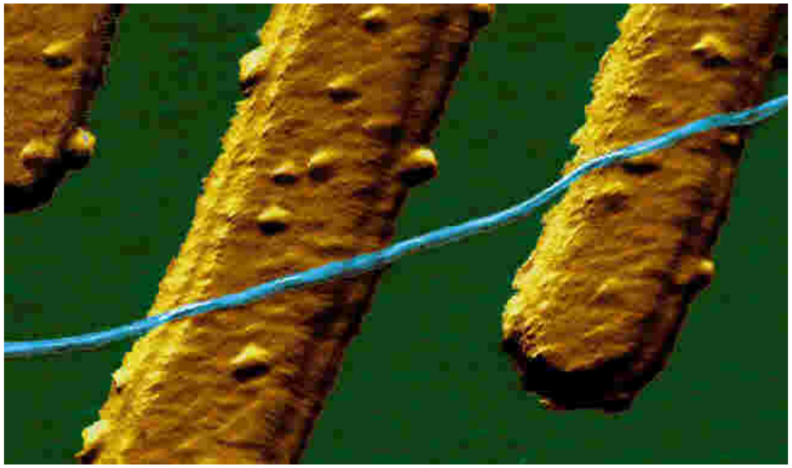
Nanotubes as electronic devices

Design of novel nanoscale electronic devices



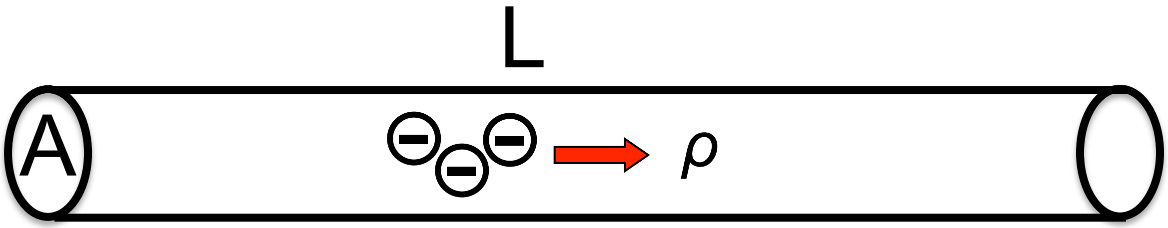
Manipulation and positioning of nanotubes as active circuit components imposes strong modifications on the physical properties of the nanotube

Strain, bending, substrate and doping will influence the electronic properties and tune the characteristics of the device



(C. Dekker, Delft)

Introduction to quantum conductance

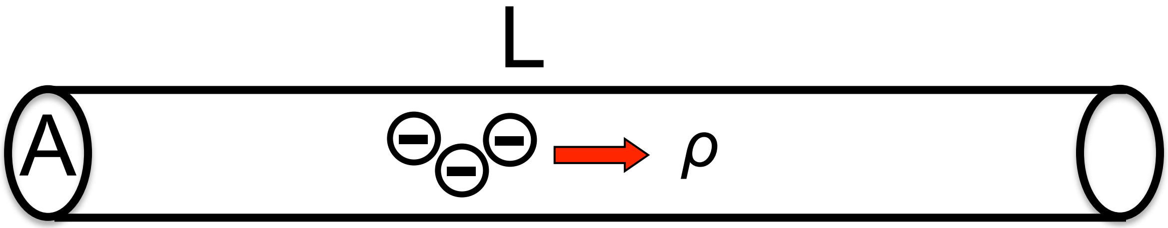


- Classical wire of area A and length L has a resistance (Ohm's law)

$$R = \frac{L}{A}\rho$$

- *ρ* in the resistivity, that is an intrinsic property of the material
- However, when the size becomes small quantum effects start to play a role and *ρ* will in general start to depend on *L* and *A*
- Three characteristic lengths:
  - mean free path L_m (depends on the density of scattering centers (defects etc.)
  - Fermi wavelength λ_F (de Broglie wavelength of the electrons at the Fermi energy – characterizes the electron wavefunctions)
  - phase relaxation length L_φ (length over which an electron retains its coherence as a wave)

Introduction to quantum conductance



- Classical transport

$$L_\varphi \ll L_m \ll L$$

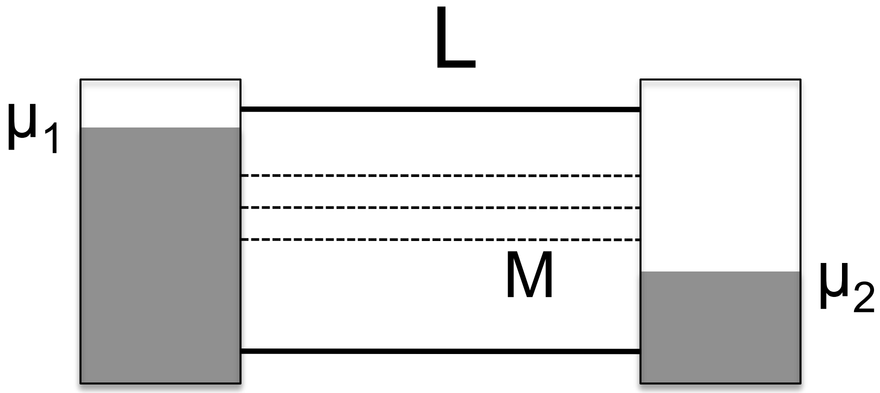
- multiple scattering events – phase recombination
- No single phase wavefunction can describe the electrons – no Schrödinger equation exists over the entire sample

- Ballistic conductor

$$L_\varphi , L_m \gg L$$

No electron scattering in the wire connected to the contacts

Introduction to quantum conductance

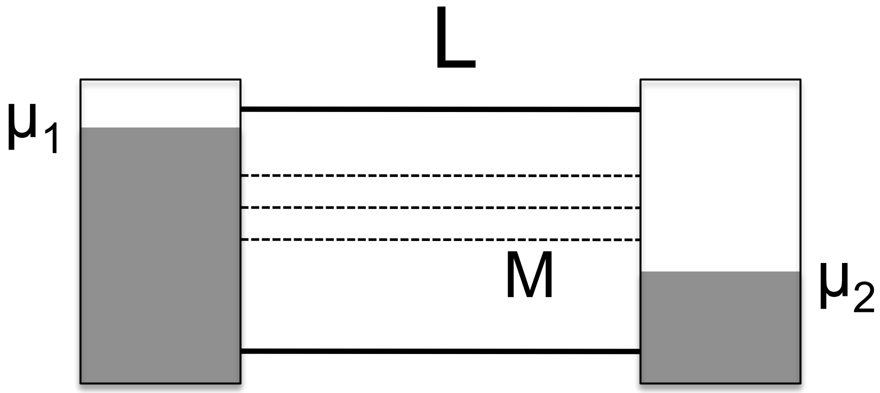


- Only the electrons that have energy between μ_1 and μ_2 can travel from contact 1 to contact 2 (assuming no scattering at the contacts
- In this energy electrons there are sub bands with same energy and k perpendicular to the transport direction – channels M(E)
- Total current can be written as

$$I = \frac{2e}{h}\int [f(E-\mu_1) - f(E-\mu_2)]M(E)dE =$$

$$\frac{2e^2}{h}\frac{(\mu_1 - \mu_{2)}}{e}M = \frac{2e^2}{h}VM \ \textbf{or}\ R_c = \frac{V}{I} = \frac{2e^2}{h}\frac{1}{M}$$

Introduction to quantum conductance

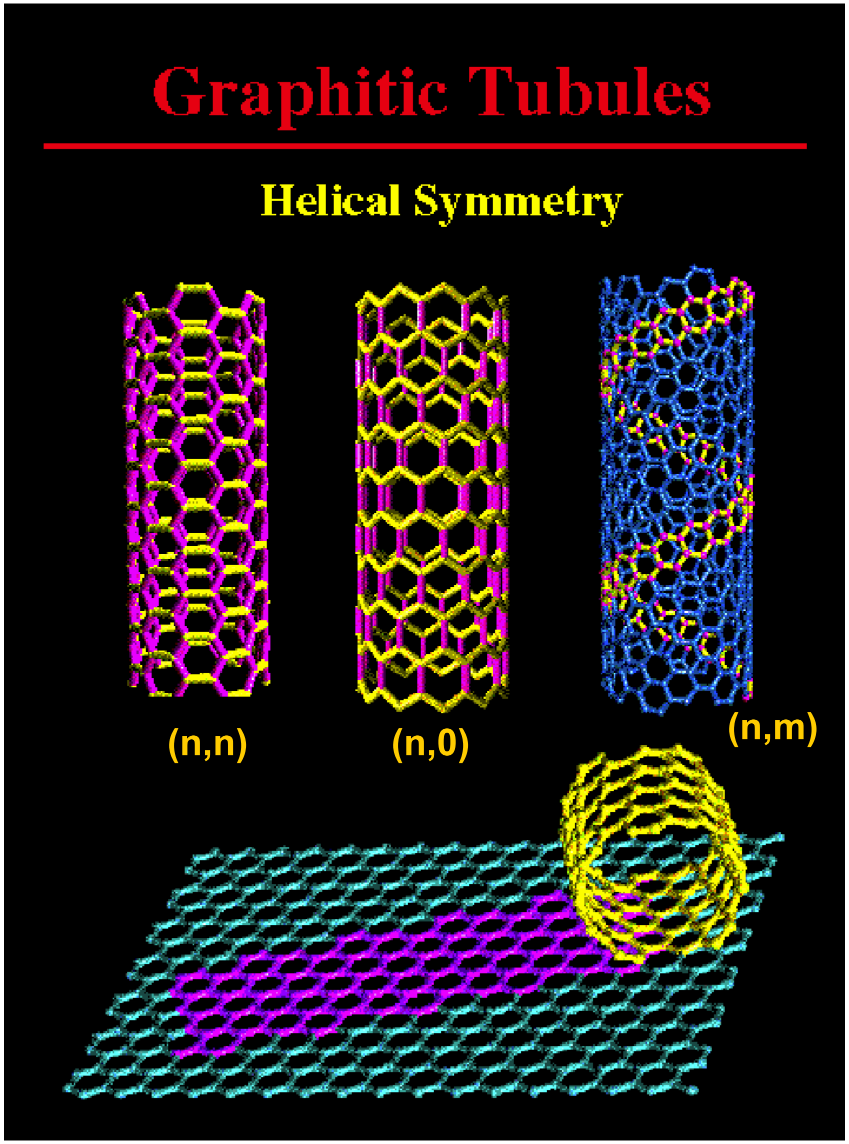


$$R_c = \frac{V}{I} = \frac{2e^2}{h}\frac{1}{M} \qquad G = \frac{h}{2e^2}M \qquad \frac{2e^2}{h} = 12.9\ \mathrm{k}\Omega$$

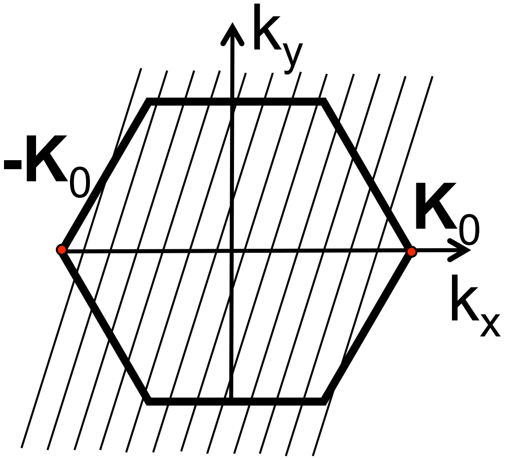
- The conductance is proportional to the number of channels and it is quantized
- In general one has to solve the scattering problem for the electrons at the contacts – one dimensional potential - square barrier
- Transmission probability T – probability for a channel to make it from 1 to 2:

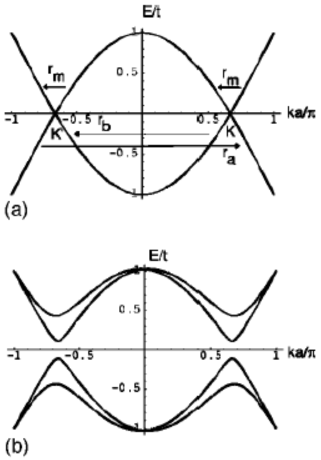
$$G = \frac{h}{2e^2}MT$$ Landauer formula

Graphitic nanotubes



- **Armchair** (n,n) – metals
- **Zig-Zag** (n,0) – mostly semiconductors
- **Chiral** (n,m) n≠m – mostly semiconductors and insulators





- **mod(3) rule**: if (n-m)=3l the tube might be metallic

Conductance of an ideal nanotube

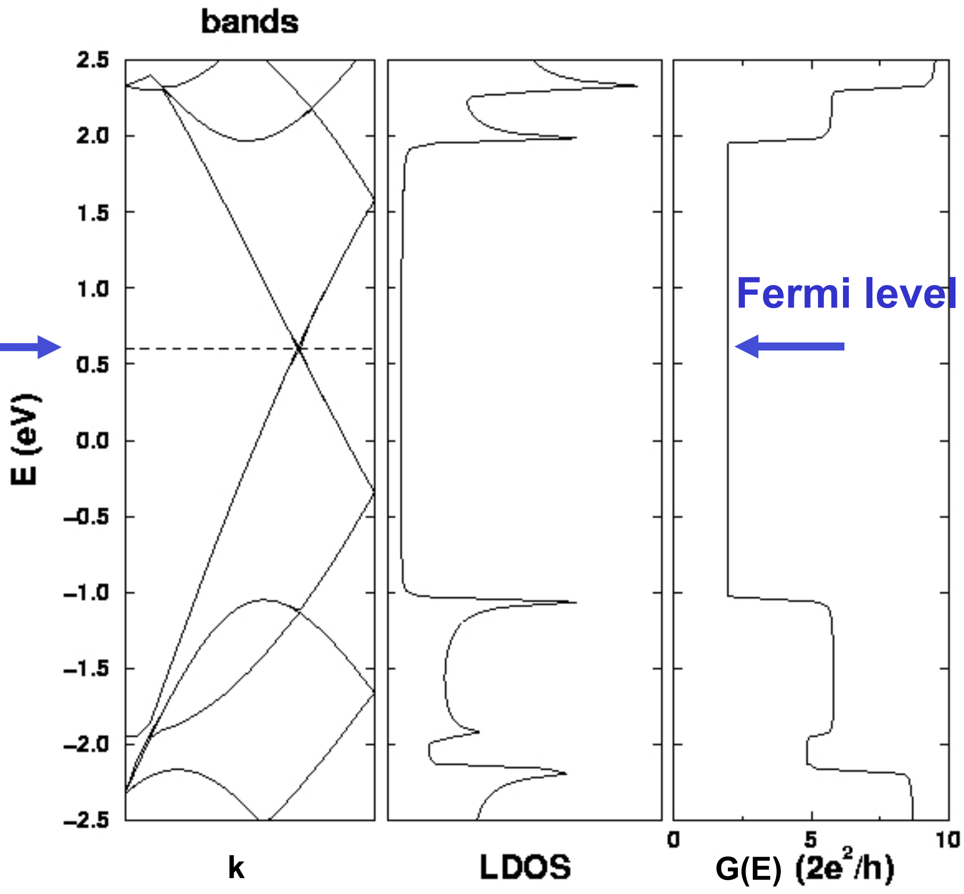
Two bands cross at the

Fermi level

Conductance $G(E_F) = 2$

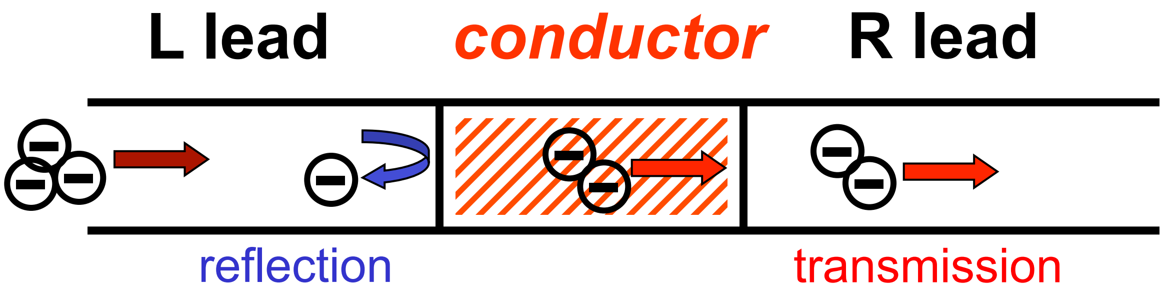
Units of $2e^2/h$

(5,5) nanotube



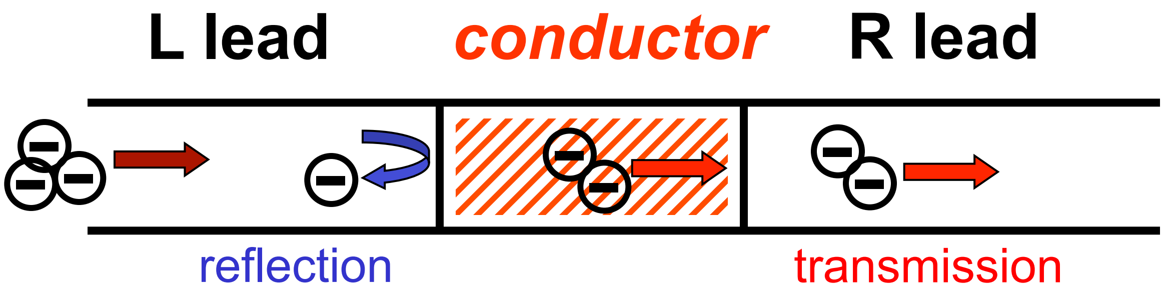
Fermi level

Introduction to quantum conductance



- Conductance as transmission through a nano-constriction ***(Landauer, 1957)***
  - Depends on the local properties of the conductor (transmission - scattering) and the distribution function of the reservoirs –> ***$G = (2e^2/h)\ T$***
  - Quantized – conduction quantum = ***$2e^2/h$*** **$= (12.9\ \mathrm{k\Omega})^{-1}$**
- Transmission function from Green's functions techniques ***(Fisher and Lee, 1982)***:
- Open (infinite) system effectively treated as closed (finite) in an exact fashion => No need for periodic boundary conditions
- Applicable to any system described by a localized orbital Hamiltonian: *TB, ab initio with localized orbitals* ***(MBN, PRB (1999); MBN,Fattebert and Bernholc, PRB (2001))***

Quantum transport in a local-orbital basis



$$G = \frac{2e^2}{h} T = \frac{2e^2}{h} Tr(\Gamma_L G_C^r \Gamma_R G_C^a)$$

$$G_C = (\varepsilon\, S_C - H_C - \Sigma_L - \Sigma_R)^{-1}$$

$$\Gamma_{\{L,R\}} = i[\Sigma^r_{\{L,R\}} - \Sigma^a_{\{L,R\}}]$$

- G_C -- Green's function of the conductor
- $\Gamma_{L,R}$ -- coupling functions between the conductor and the leads.
- H = Hamiltonian, S = overlap matrix
- Eigenvectors of the transmission matrix (***eigenchannels***) give direct information on the geometry of the transmission channels

- Self-energies are computed using Surface Green's function matching theory and the concept of layer orbitals:

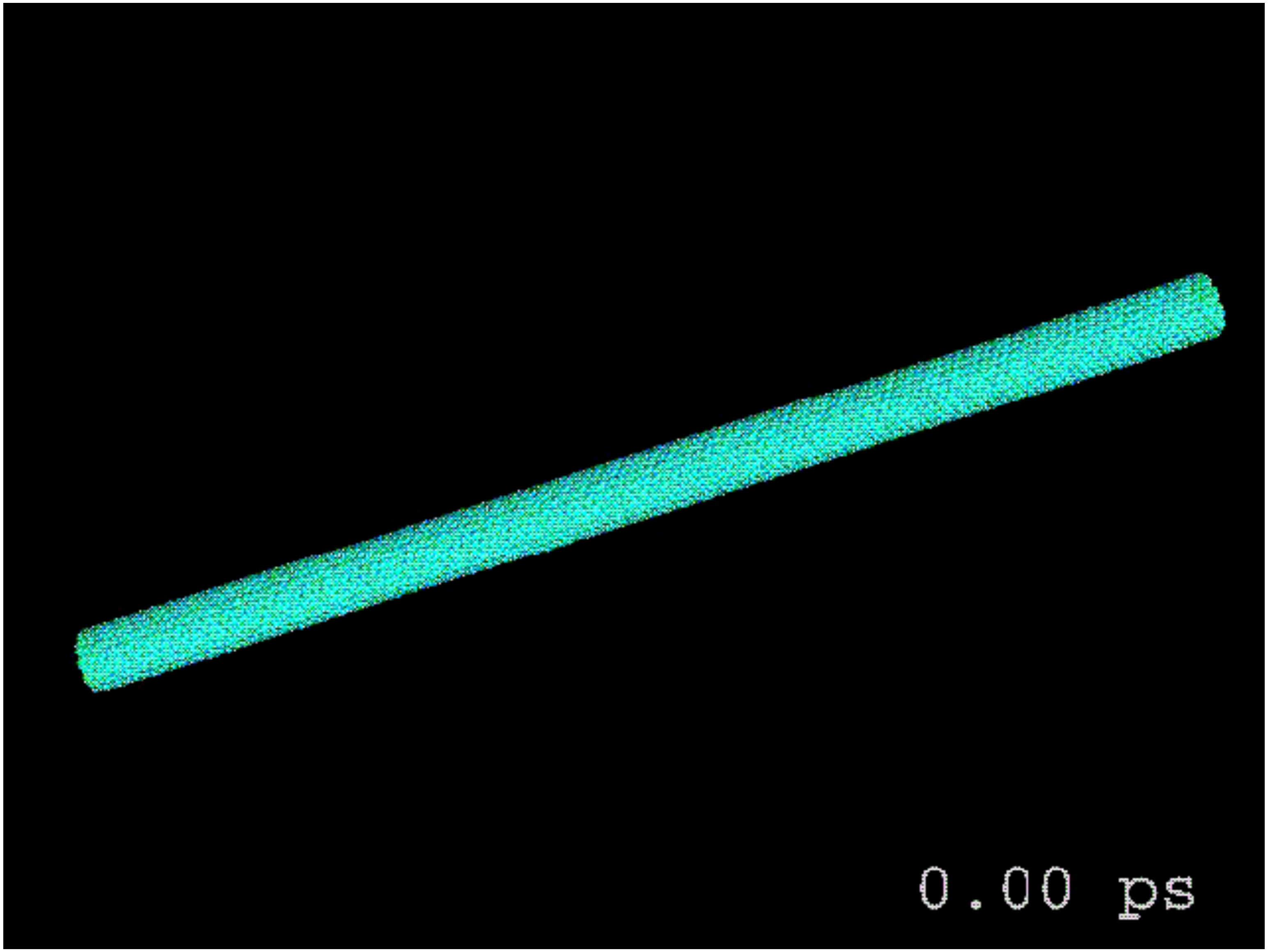
$$\Sigma_L = (\varepsilon\, S_{LC} - H_{LC})^+ (\varepsilon\, S_{00}^L - H_{00}^L + (\varepsilon\, S_{01}^L - H_{01}^L)^+ \overline{T}_L)^{-1} (\varepsilon\, S_{LC} - H_{LC})$$

$$\Sigma_R = (\varepsilon\, S_{RC} - H_{RC})\, (\varepsilon\, S_{00}^R - H_{00}^R + (\varepsilon\, S_{01}^R - H_{01}^R)^+ T_R)^{-1} (\varepsilon\, S_{CR} - H_{CR})^+$$

M. Buongiorno Nardelli, Phys. Rev. B 60, 7828 (1999)

Bending, straining, joining

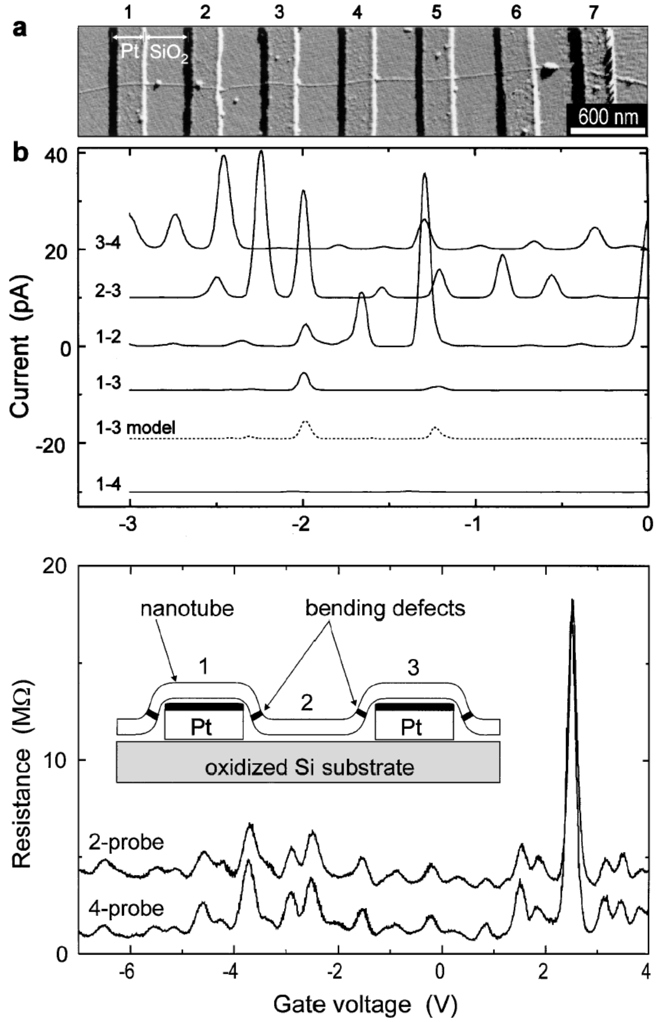
Bending



Bending tubes

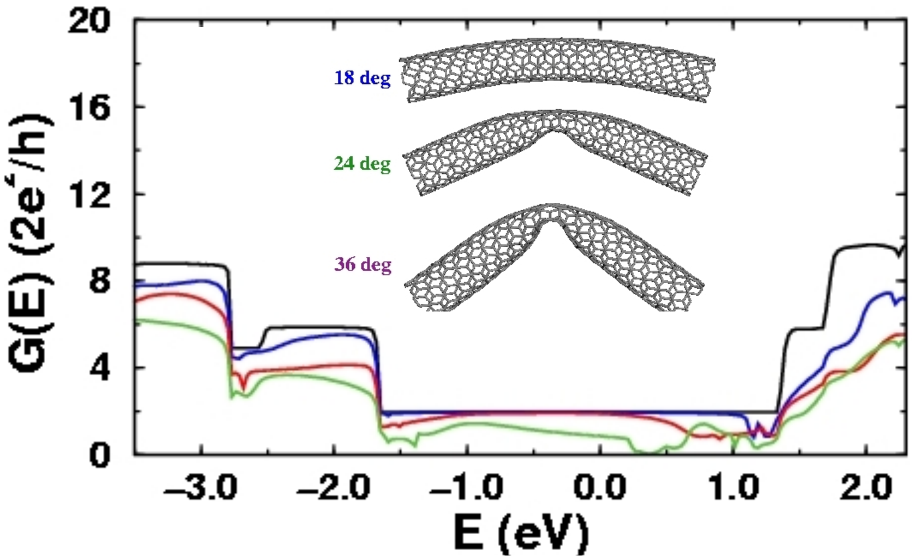
Bending can change the electrical response of nanotubes and can be used to distinguish between tubes of different symmetry

- Type I -> not conducting
- Type II -> conducting at all temperatures
- Type III -> conducting at high temperatures,
  non conducting at low temperatures

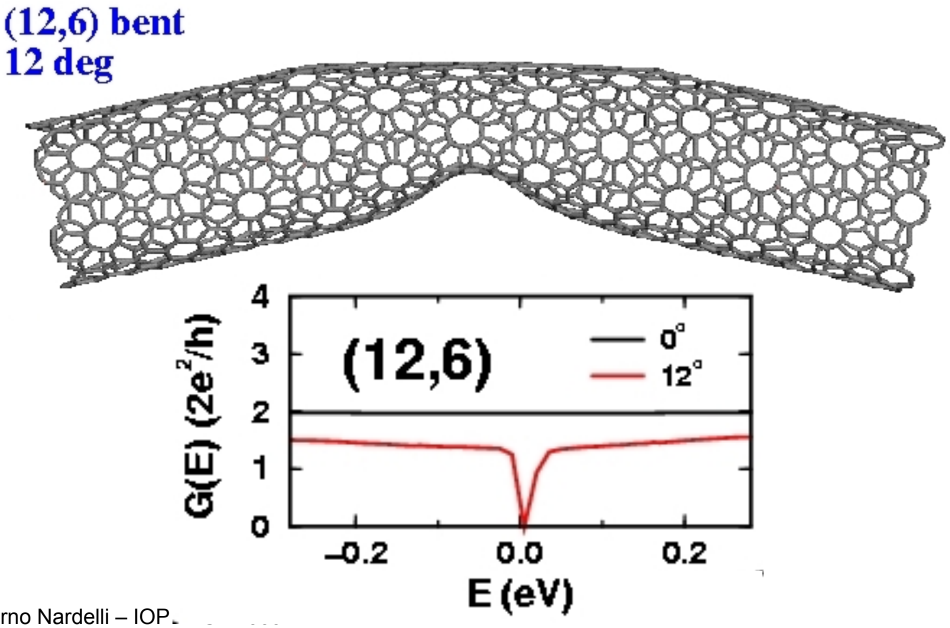


(Dekker et al., PRL 80, 4036 (1998))

Conductance of bent carbon nanotubes



- Armchair nanotubes remain conducting at fairly large bending angles (kinks). Only in very small diameter, asymmetrically bent nanotubes, a small pseudo-gap will occur.

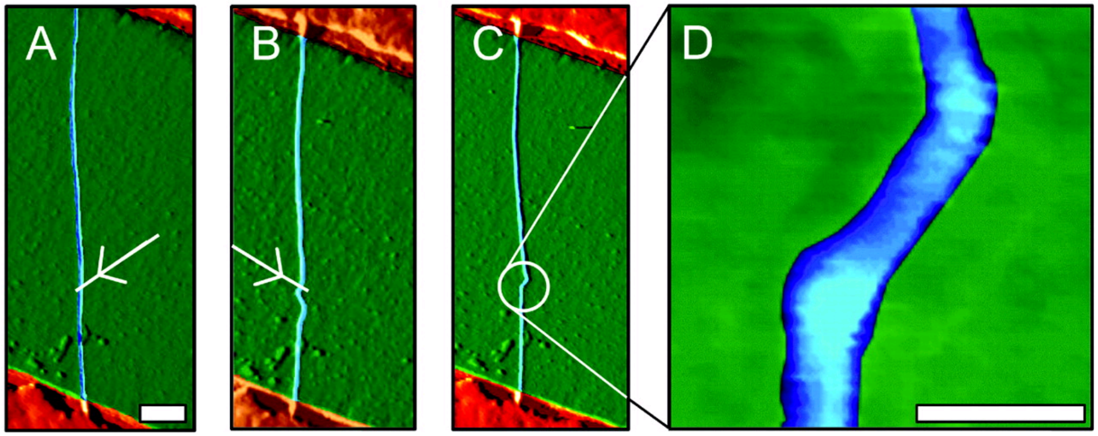


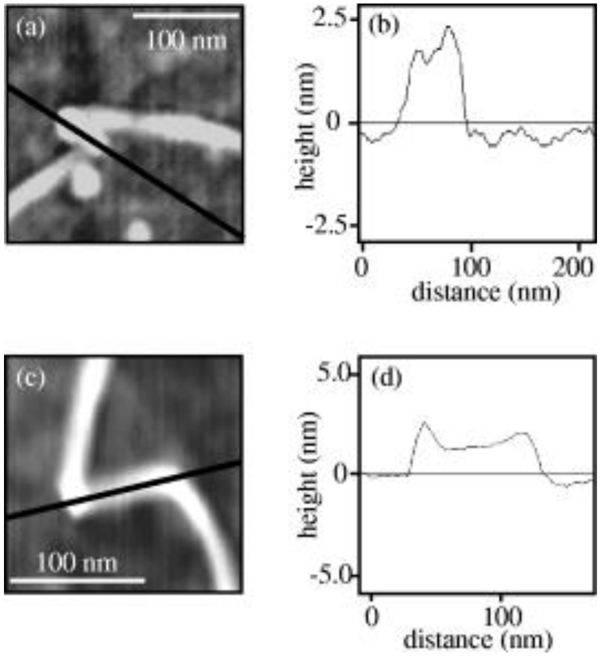
- Large diameter chiral nanotubes are metallic when *n-m=3k*, but bending opens a sizable pseudo-gap. This may explain the results of experiments

Single electron transistors from dots and kinks

- Single electron quantum dot-based transistor operating at room temperature

(Postma et al, Science 2001)



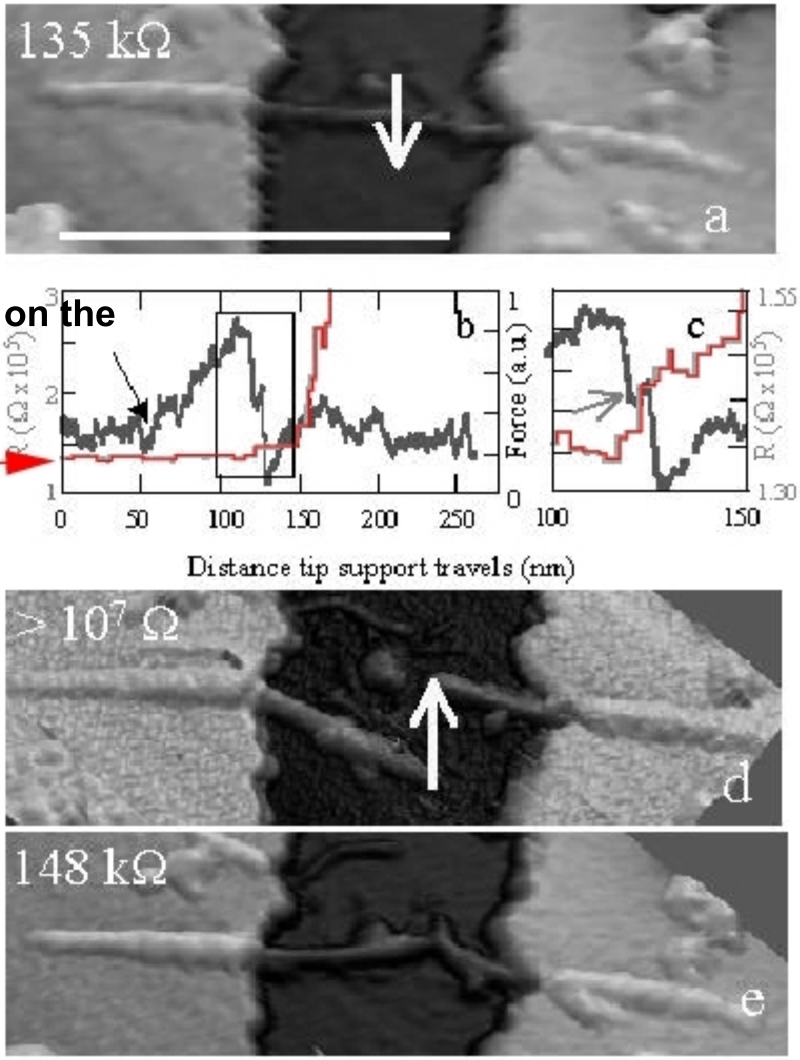


- Quantum dot operating up to 165K

(Bozovic et al, APL 2001)

AFM experiments with strained NT

Nanotube is pushed with an AFM tip



Force on the tip

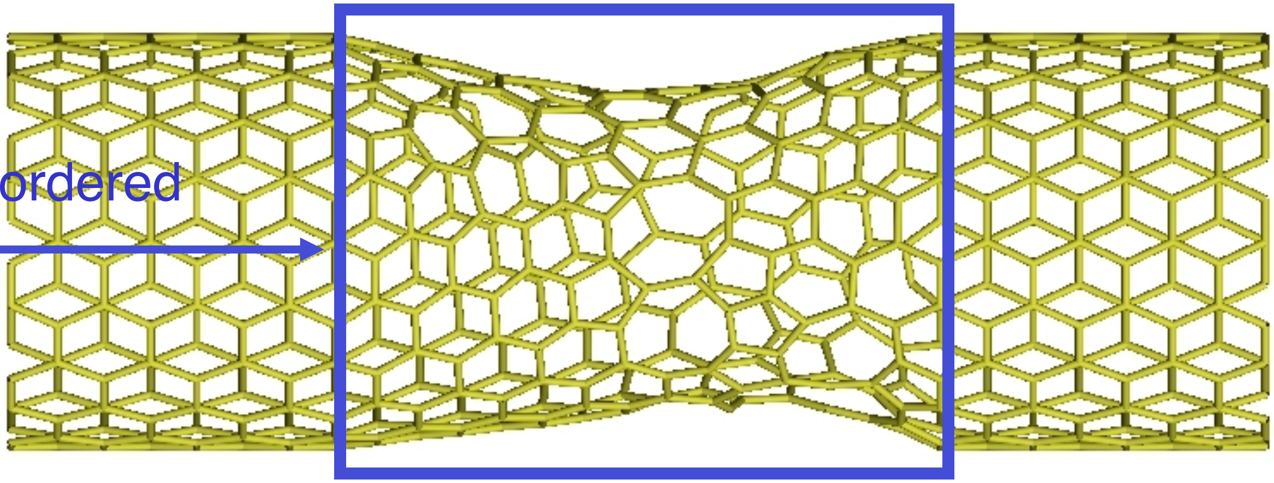
resistance

Nanotube is broken

The two ends are in contact

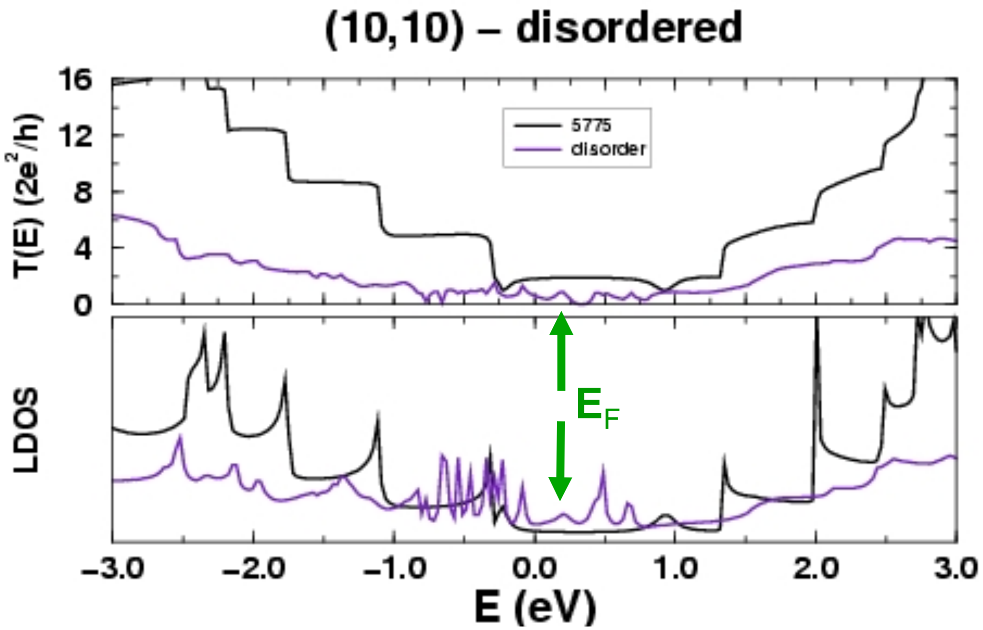
(Washburn et al., 1999)

AFM-induced large strains lead to defects and disorder

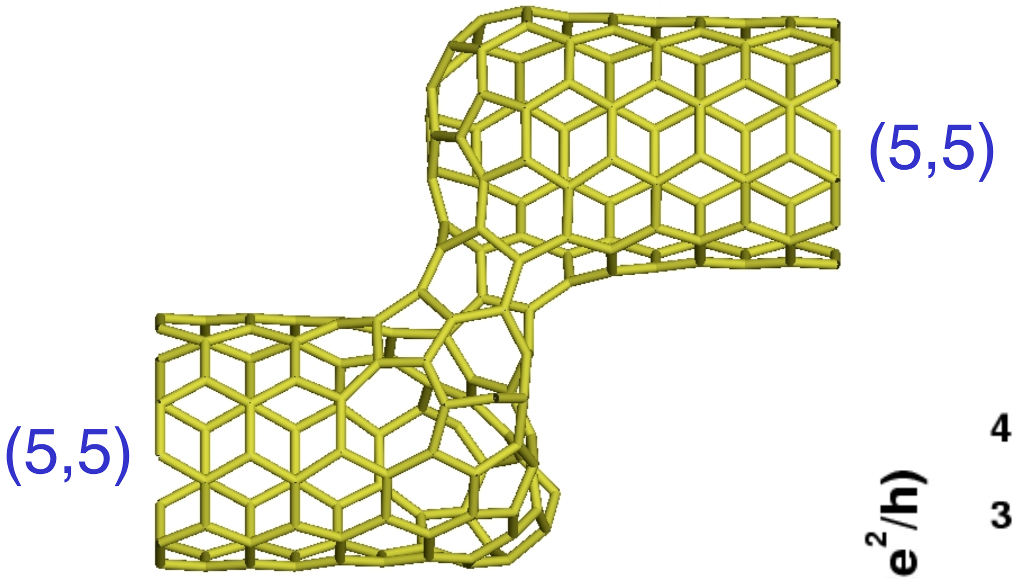


Highly disordered region

Disorder induces a drastic reduction in conductance: T(E) = 0.4 ($2e^2/h$)

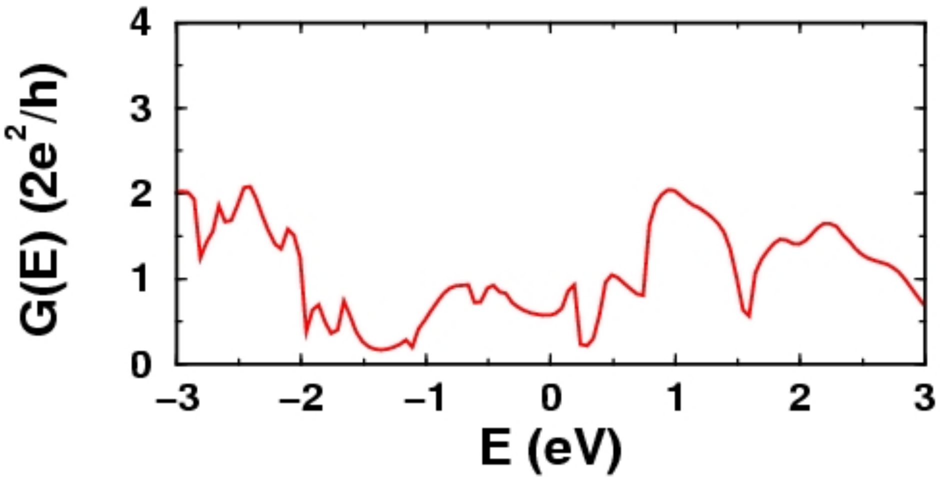


Device assembly



In the experiments tubes are reconnected using the AFM tip

Contact between tubes is sufficient to provide some degree of electronic transmission



(M. Buongiorno Nardelli and J. Bernholc, (1999))

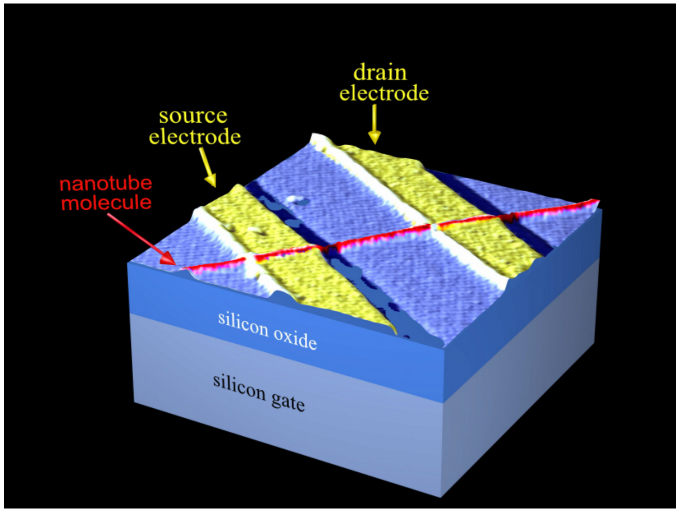
broken, reconnected tubes can conduct!

Substrates and contacts

Tubes on substrates

- Tube-substrate interaction changes the properties of the tube:
    - breaking wavefunction symmetry
    - Charge transfer (Fermi level shift)
    - Structural modifications

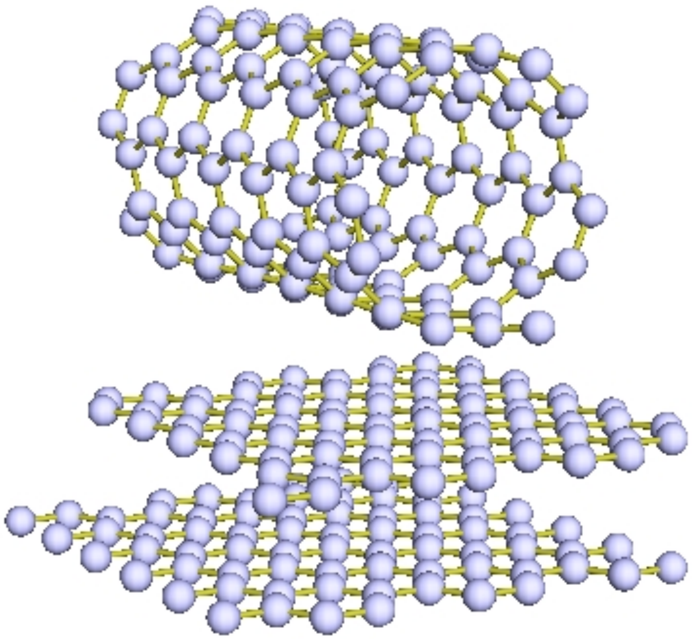
Substrate as a tuner of the response of the nanotube in a physical device



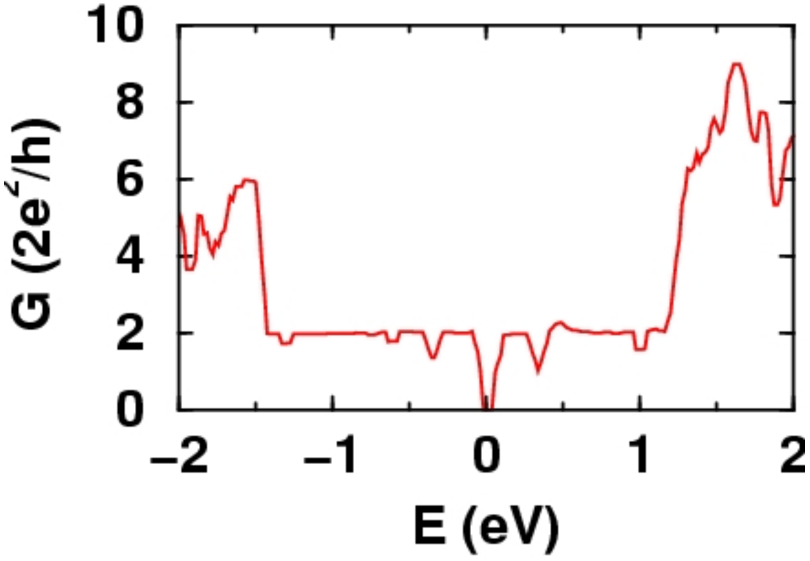
http://vortex.tn.tudelft.nl/~dekker

Need of the full power of *ab initio* calculations to describe correctly the microscopic interactions

Tube on graphite

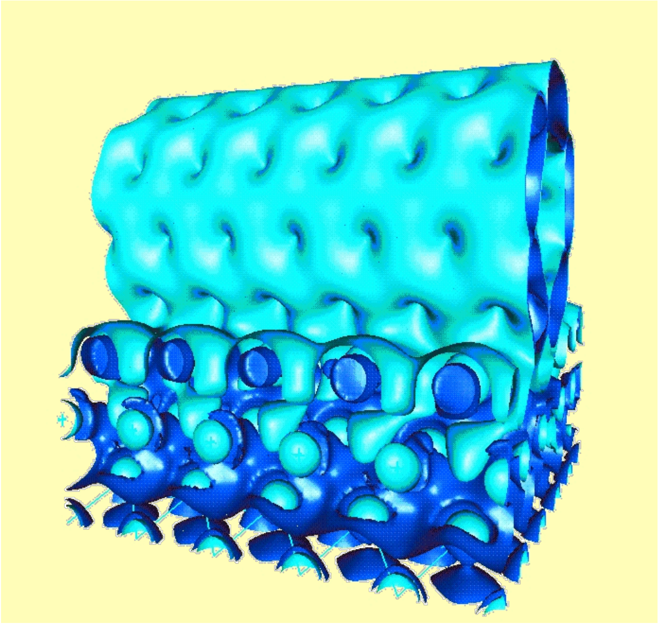


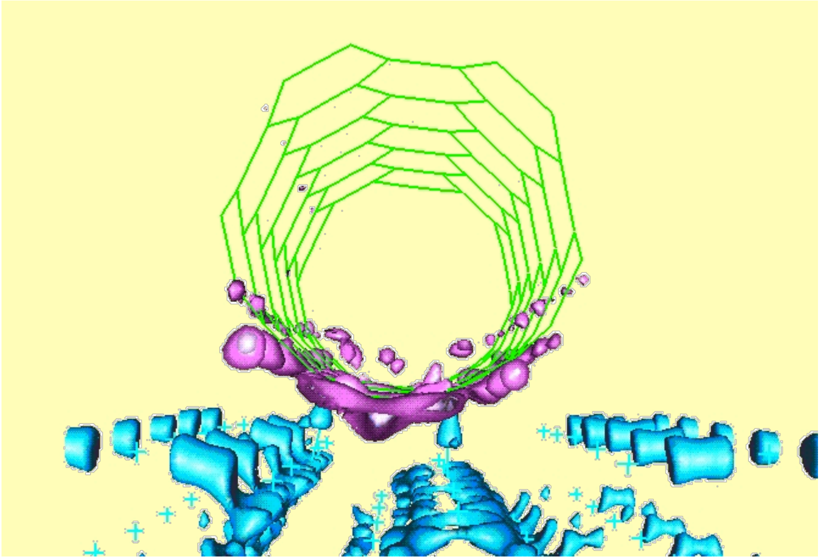
Symmetry breaking of the wavefunction induces a *metal-insulator transition*



- Very little structural relaxation
- Adsorption energy ~ 30 meV/atom

Nanotube-aluminum contact





Electron density

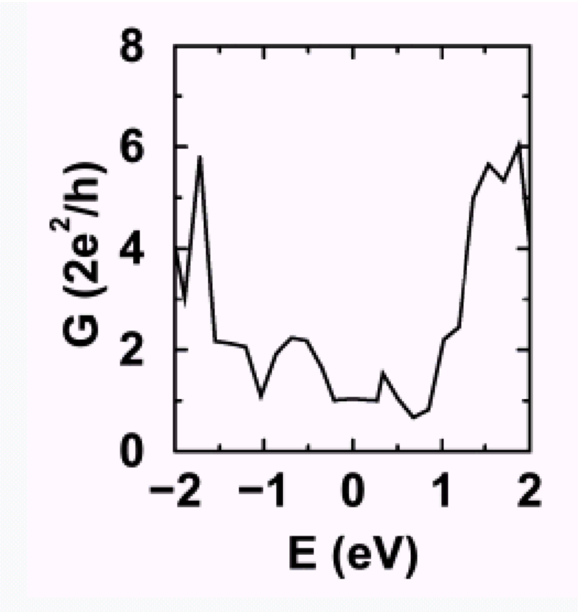
Charge transfer from nanotube to metal

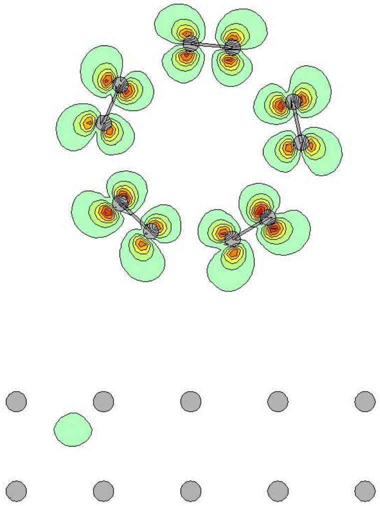
Electron depletion in the nanotube

Fermi-level shift → p-type conductivity

Experiments: very high contact resistance (MΩ vs. KΩ)

Conductance and electron transfer



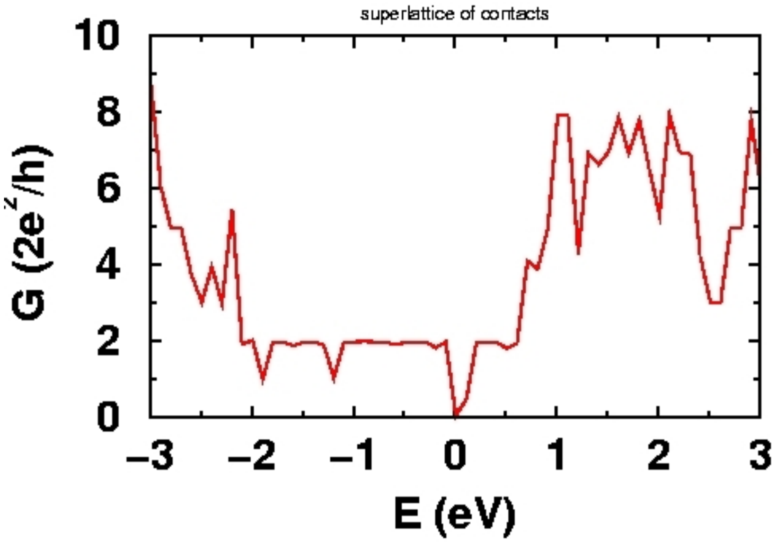


- Change in the conductance due to the tube-metal interaction
- Transmission *eigenchannel* highly localized on the nanotube

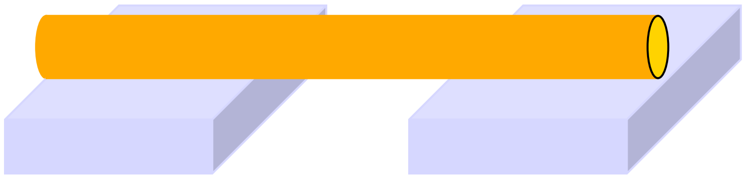
Very inefficient mechanism of electron transfer

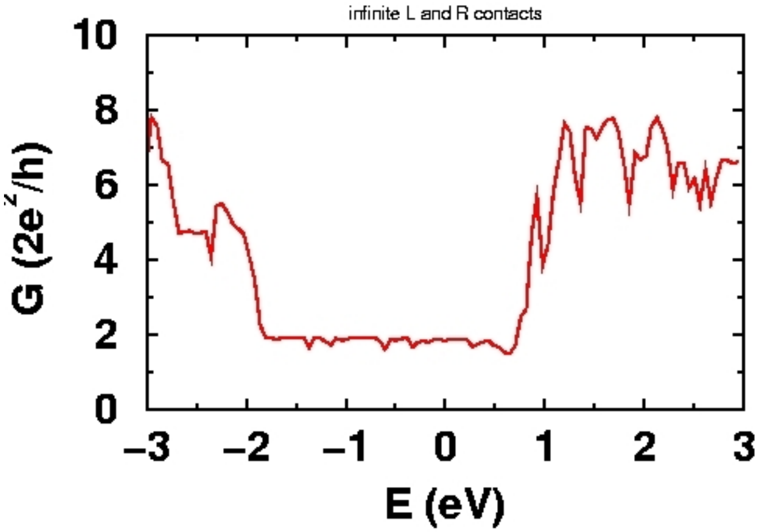
High contact resistance

Contact geometries



- An infinite tube deposited on a series of contacts develops a metal-semiconductor transition, due to breaking of the mirror symmetry induced by the localized perturbation of the nanocontact.

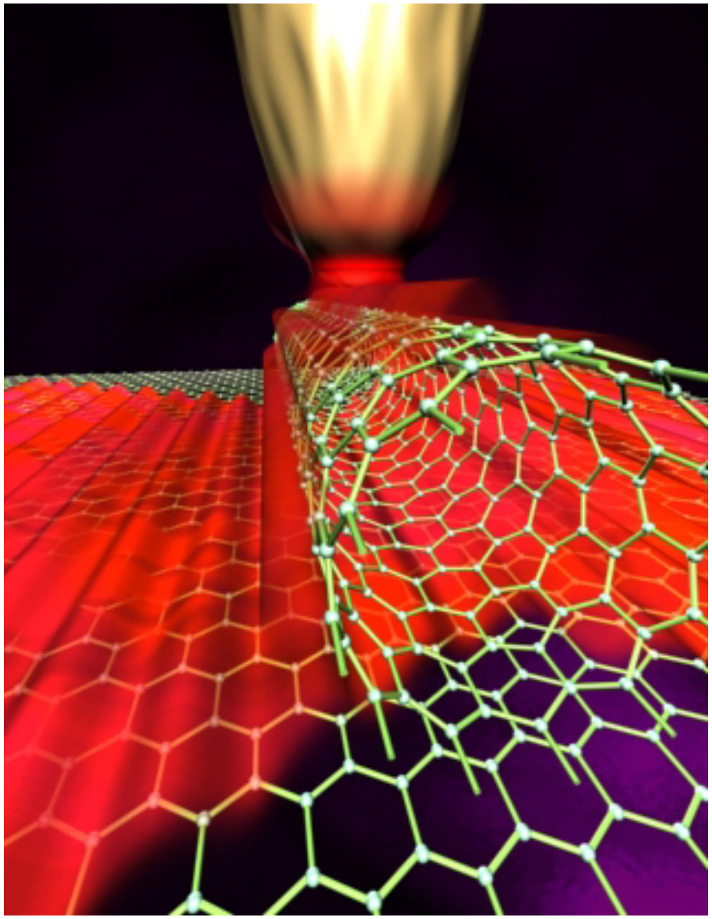




- An infinite tube deposited on infinite L and R contacts recovers the ideal conductance of the isolated tube, valence band edge aligns due to charge transfer.
- **High contact resistance: eigenchannels still localized on the nanotube.**

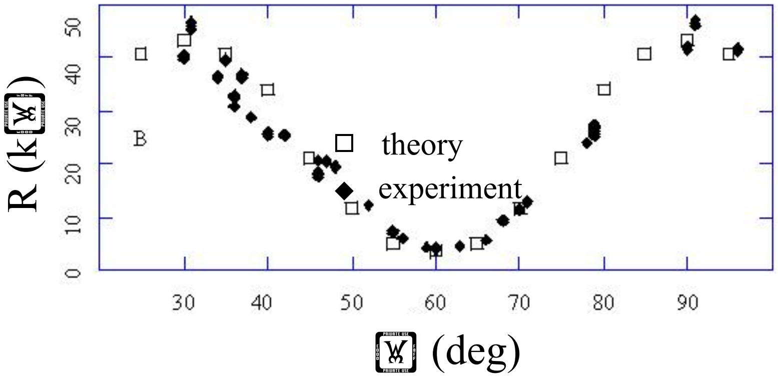
(M. Buongiorno Nardelli, J.-L. Fattebert and J. Bernholc, (2001))

Device prediction and design through computational materials science



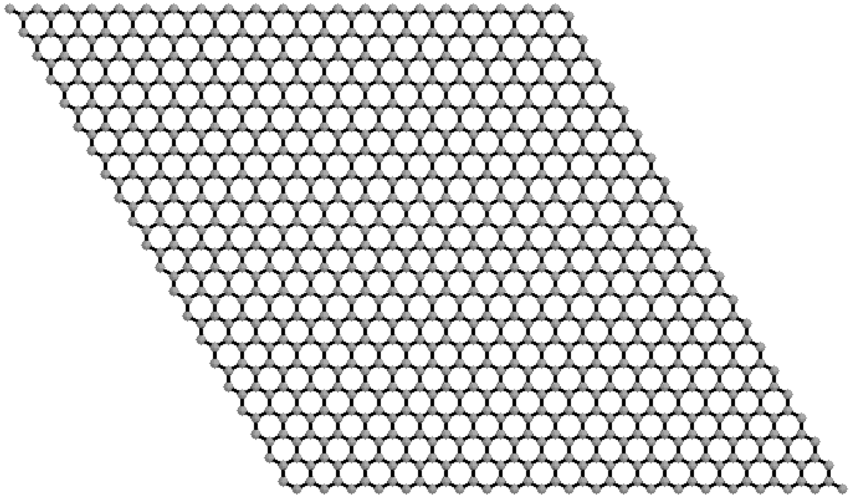
NANO-REHOSTAT: tunable resistance of a carbon nanotube-graphite interface

Transport through a "vertical" junction: angular dependence induced by momentum conservation

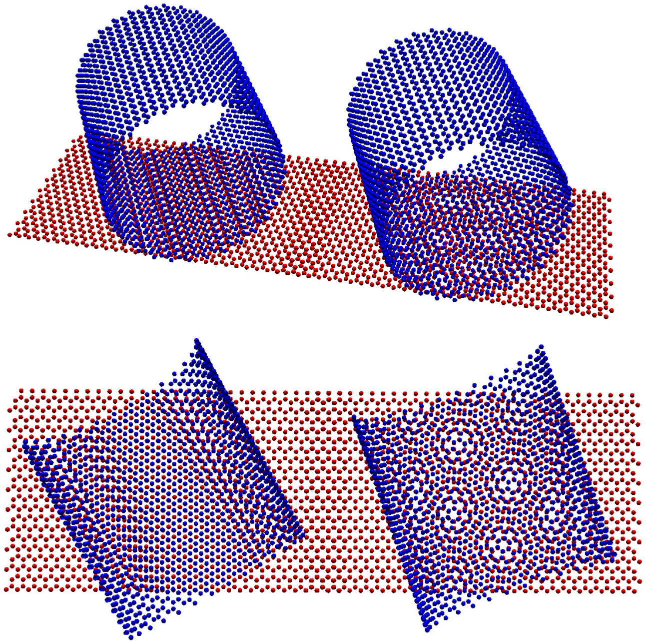


S. Paulson, A. Helser, M. Buongiorno Nardelli, R.M. Taylor II, M. Falvo, R. Superfine, S. Washburn, Science*, (2000).*

The nano-rehostat



Moiré patterns are formed when two images with a similar spatial repetition are held or moved over one another.



Variation of resistance in the nano-rehostat upon rotation of the nanotube on the substrate is the equivalent of the Moiré patterns for the electrons

Wannier functions

Maximally-localized Wannier functions

– From the Bloch orbitals $\psi_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}$ we can define Wannier functions through the transformation

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_{m} U_{mn}^{(\mathrm{k})} \, \Psi_{m\mathrm{k}}(\mathbf{r}) \, e^{-i\mathrm{k}\cdot\mathbf{R}} \, d\mathbf{k}$$

– Maximally localized Wannier functions (Marzari & Vanderbilt (1997)) – minimization of the spread functional exploiting the arbitrariness of the phase factors/unitary transformations between the Bloch orbitals

$$\Omega = \sum_n [\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2]$$

– ***``Exponential" decay in insulators, disentanglement in metals (Souza, Marzari, Vanderbilt (2002))***

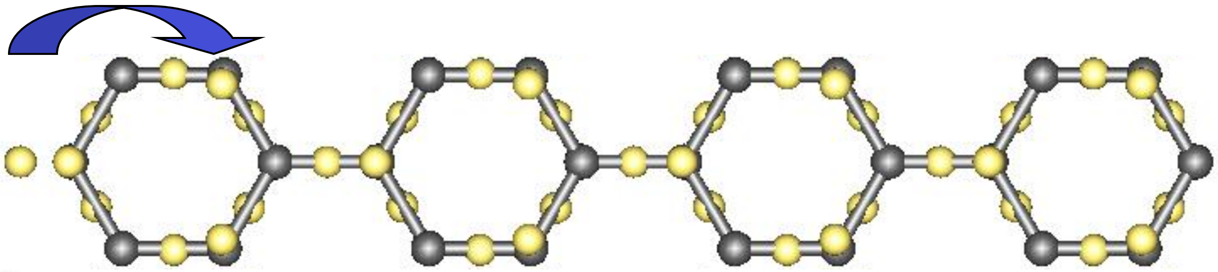
– On site $\mathbf{H}_{00}$ and coupling $\mathbf{H}_{01}$ Hamiltonian matrix elements can be easily computed either in reciprocal space or using real space integration techniques

– Simple post-processing step after a plain electronic structure calculation

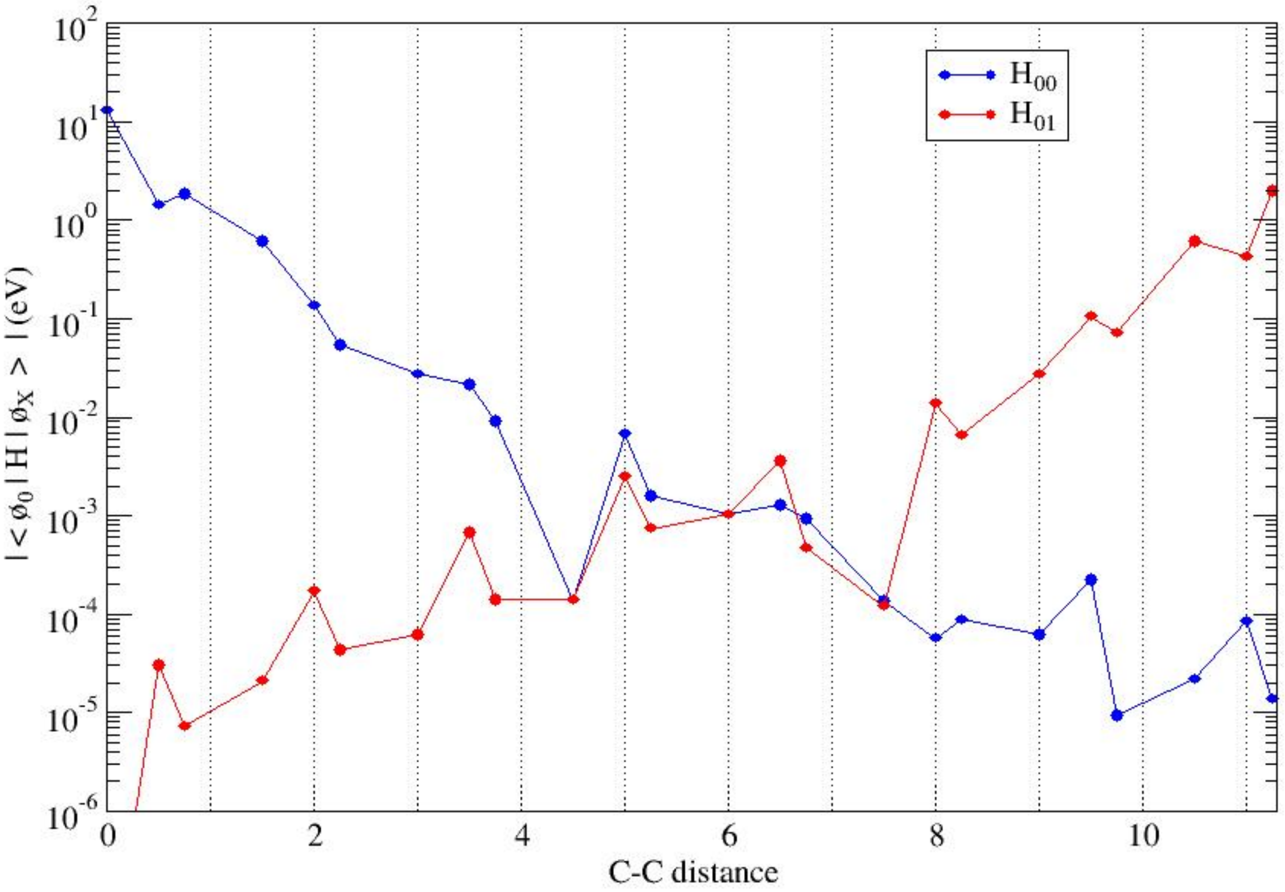
– Important information on the bonding properties of the system and how they influence electronic transport

Hamiltonian in a localized basis

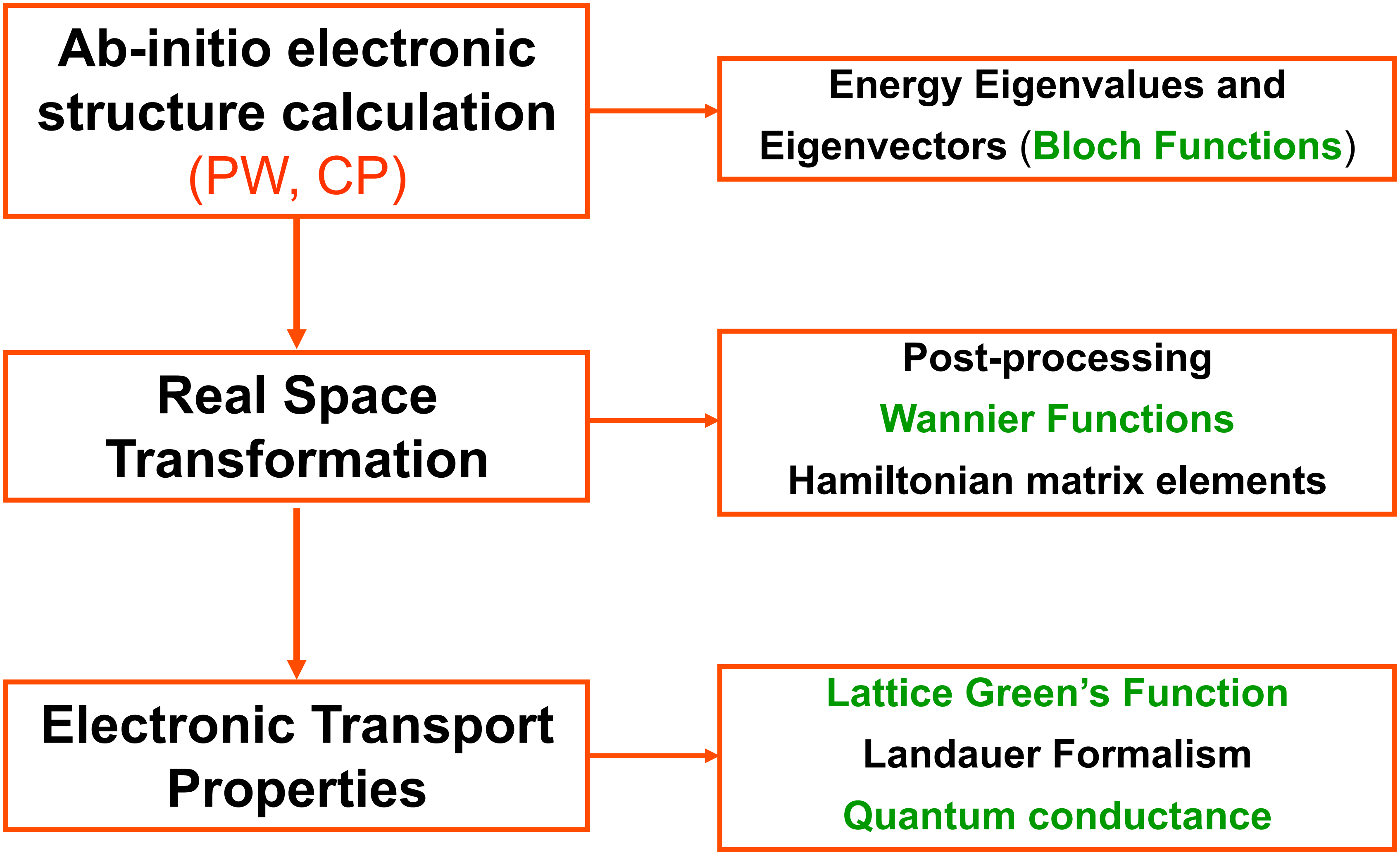
(8,0) Nanotube



Decay of the hamiltonian matrix elements as indication of the localization properties of Wannier functions



Scheme of the method



Ab-initio electronic structure calculation (PW, CP)

Energy Eigenvalues and Eigenvectors (Bloch Functions)

Real Space Transformation

Post-processing

Wannier Functions

Hamiltonian matrix elements

Electronic Transport Properties

Lattice Green’s Function

Landauer Formalism

Quantum conductance

Quantum conductance from Wannier functions

- Conductance as transmission through a nano-constriction ***(Landauer, 1957)***
- Green's functions techniques

$$G = \frac{2e^2}{h}T = \frac{2e^2}{h}Tr(\Gamma_L G_C^r \Gamma_R G_C^a)$$

- Local orbital formulation in terms of <u>maximally localized Wannier functions</u> ***(Marzari & Vanderbilt, 1997)***:

Bloch orbitals

Wannier functions

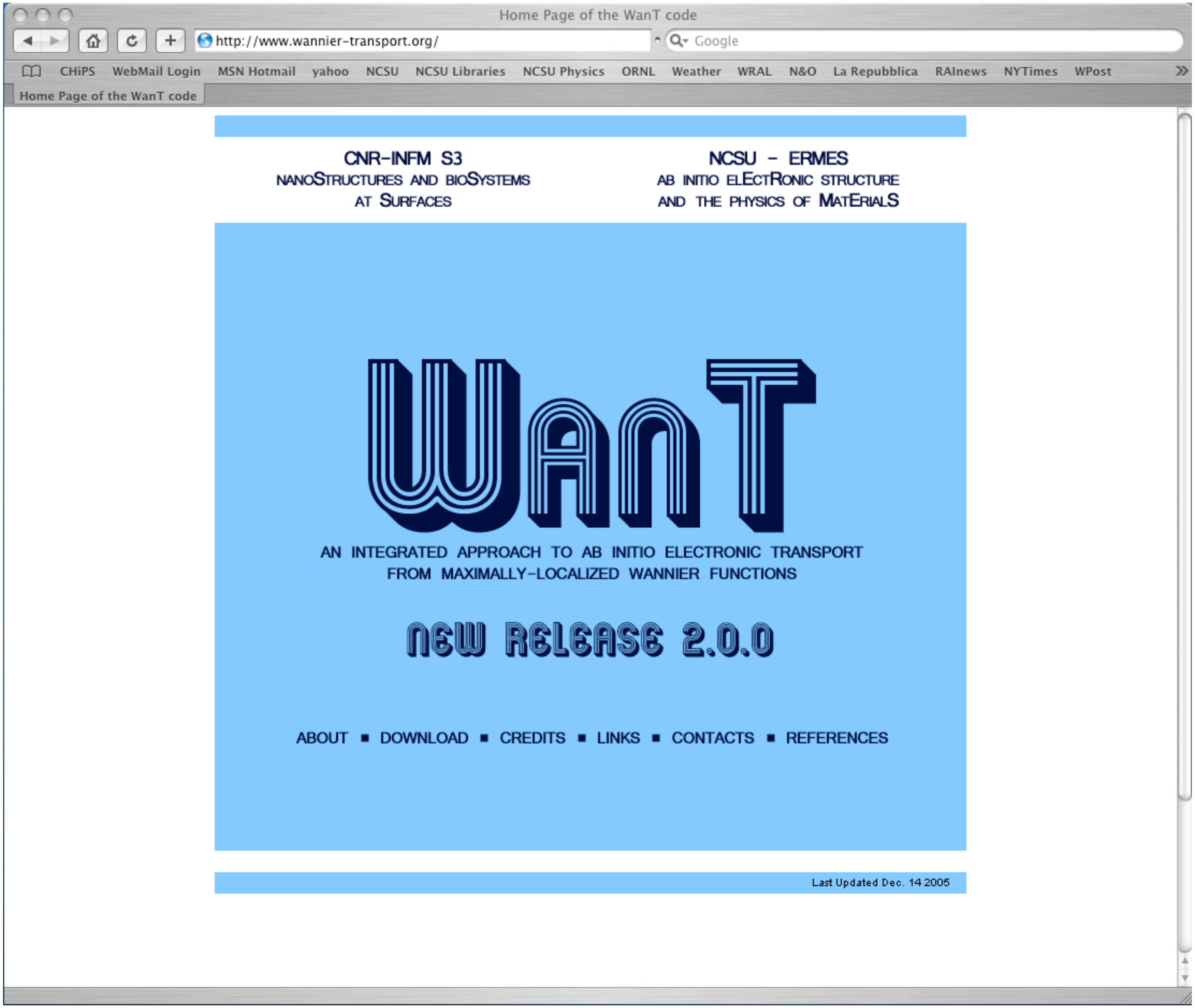
Spread functional for maximal localization

$$\psi_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}} \longrightarrow \left|\mathbf{R}n\right\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \psi_{m\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

$$\Omega = \sum_n \left[\left\langle r^2 \right\rangle_n - \left\langle \mathbf{r} \right\rangle_n^2 \right]$$

- Span same Hilbert space of original Bloch wave functions
- Lead to **exact tight-binding** orthonormal basis functions
- Center and spread of MLWFs : intuition for chemical effects
- From traditional PW or Car-Parrinello
- Ultrasoft pseudopotentials
- Disentanglement**:** maximally-localized Wannier-like functions for conduction subspaces
- Non-equilibrium transport through NEGF and self-consistent tight-binding

(Calzolari, Marzari, Souza and MBN, PRB 2004)



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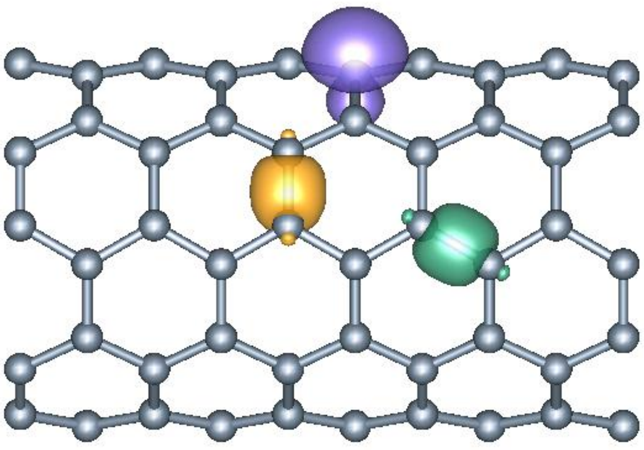
Conductance of an ideal nanotube

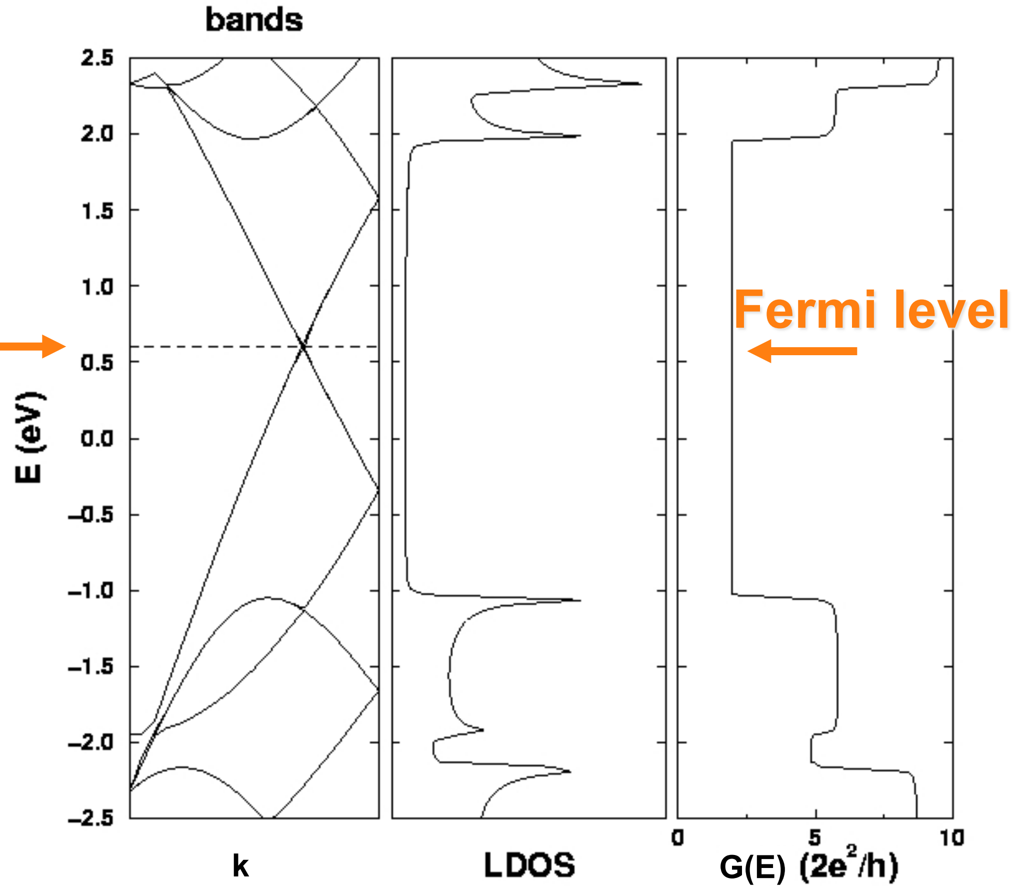
Two bands cross at the Fermi level ⇒ Conductance ⇒ $G(E_F) = 2$

Units of $2e^2/h$ $(12.9\ k\Omega)^{-1}$



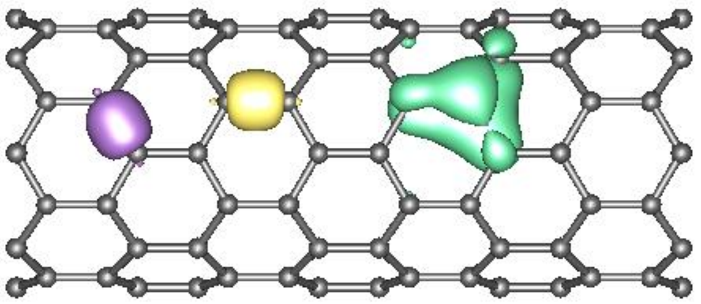
σ and π Wannier functions of the CNT

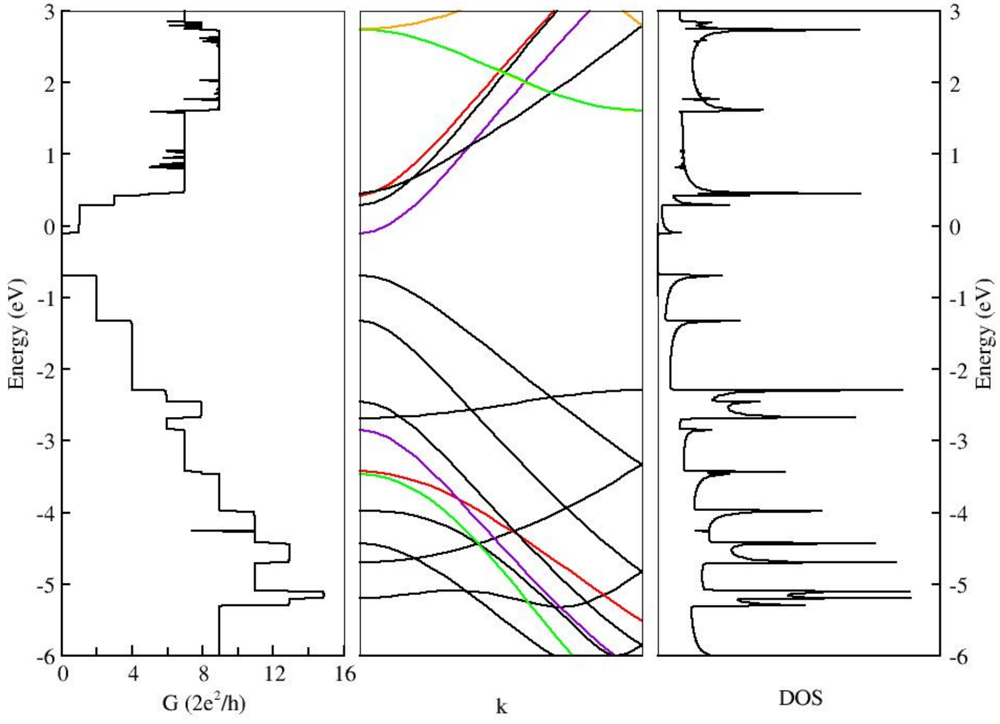
(5,5) nanotube



Fermi level

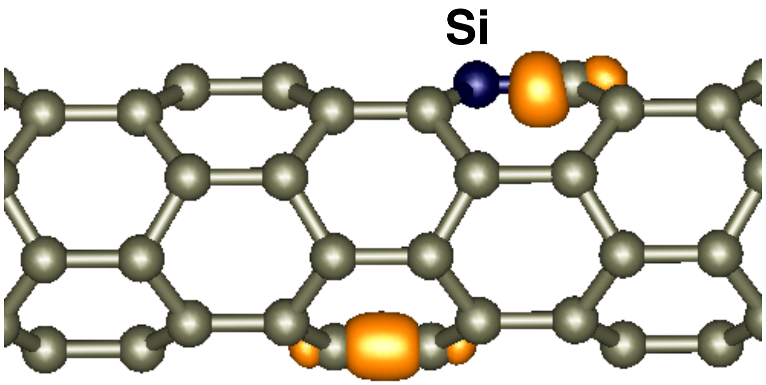
(8,0) C-nanotube

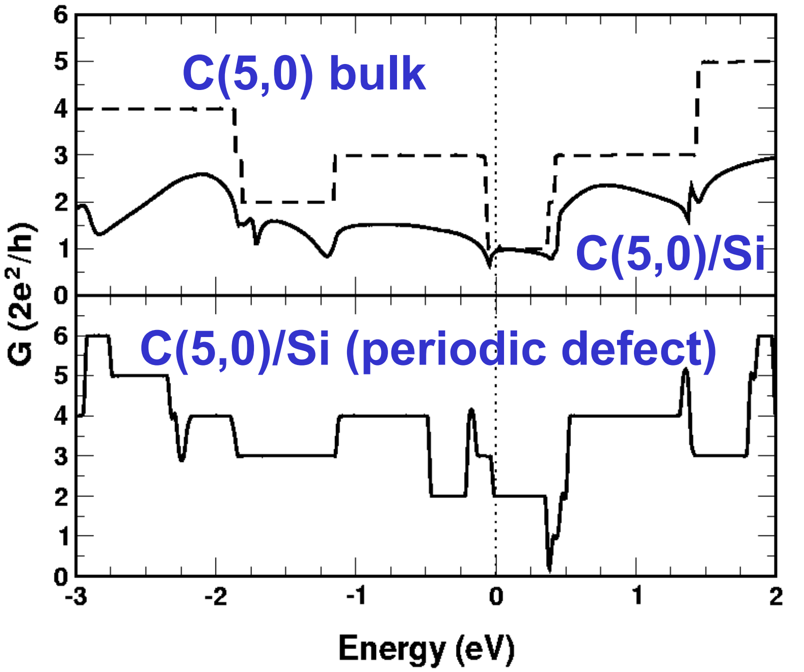




- Large scale calculation (Car-Parrinello), Gamma-sampling only (4 repeated unit cells along tube direction)
- LDOS peaks in perfect agreement with band-structure calculated with a regular plane-wave code
- **Opens the possibility of modeling large nanostructures at finite temperature !!**

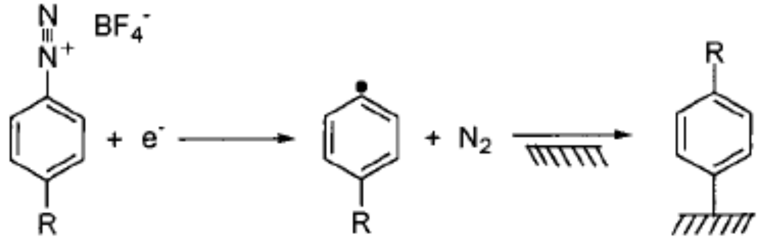
(5,0) C-nanotube + Si defect



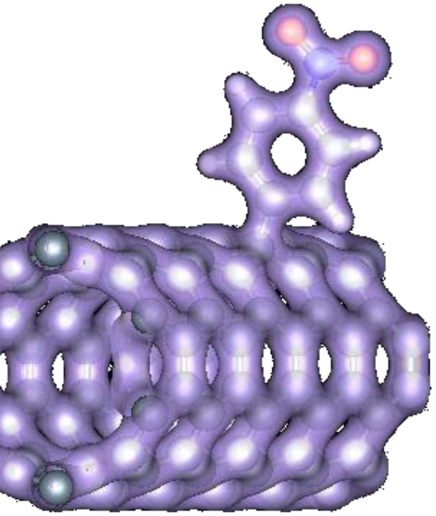


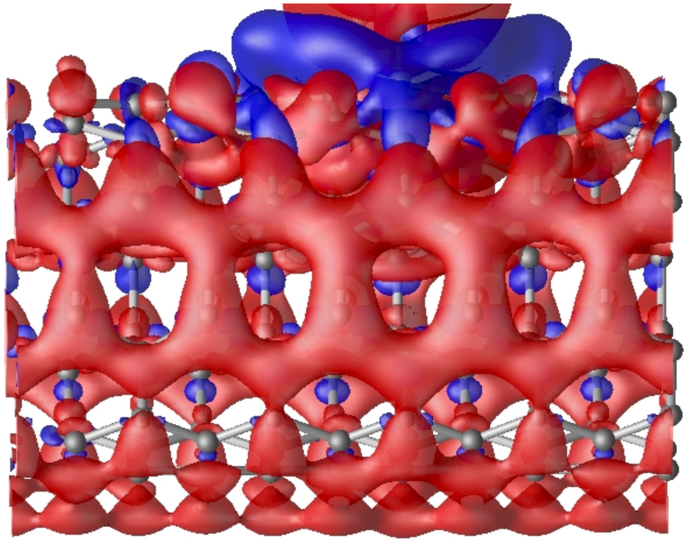
- Example of two-terminal conductance calculation: leads = ideal nanotube, conductor = defective region
- Si polarized the WF's in its vicinity = affects the electronic and transport properties of the system
- General reduction of conductance due to the backscattering at the defective site
- Characteristic features of conductance of nanotubes with defects
- Periodically repeated defect shows completely different conductance properties – importance of the proper inclusion of the leads in transport calculations

Functionalized nanotubes and disorder effects



- Effect of covalent functionalization can be systematically investigated by binding of different chemical groups to the nanotube walls
- System : (5,5) SWCNT (100 carbon atoms) + one phenyl moiety
- R = NO2 ,COOH, H, NH2 ,COO-, NH3+

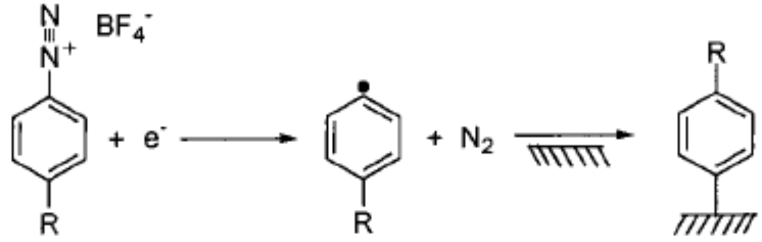


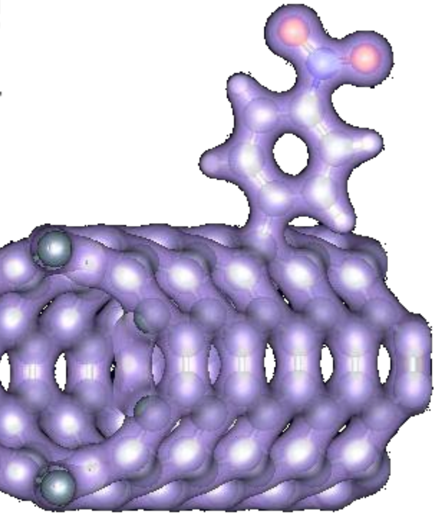


Charge transfer induced by functionalization

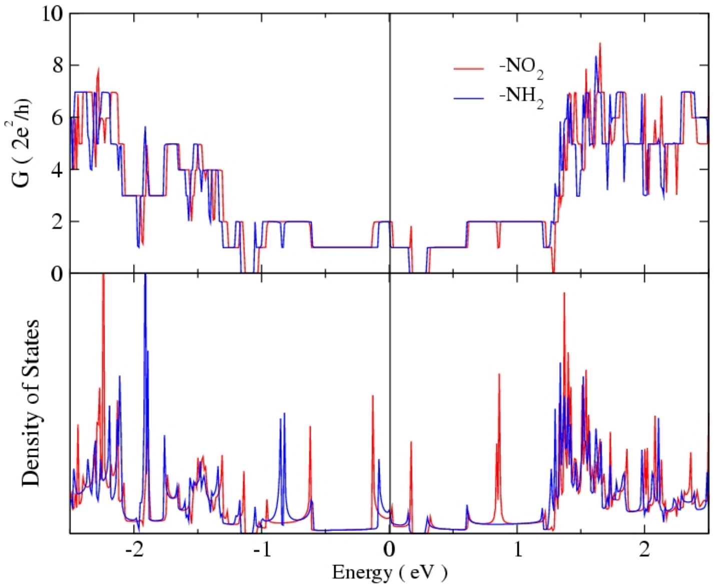
(Li, MBN, Marzari, PRL, 2005)

Functionalized nanotubes and disorder effects





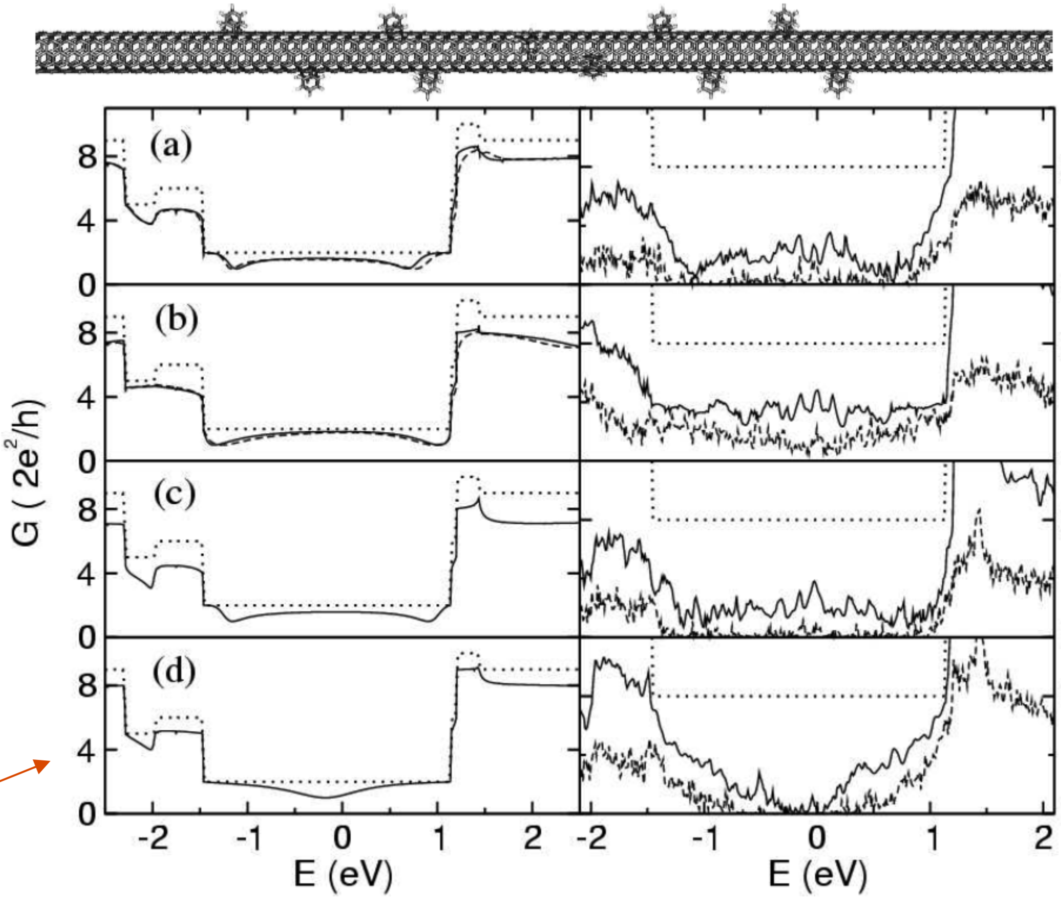
- Effect of covalent functionalization can be systematically investigated by binding of different chemical groups to sidewall legands
- System : (5,5) SWCNT (100 carbon atoms) + one phenyl moiety
- R = NO2 ,COOH, H, NH2 ,COO-, NH3+



A single functional molecule does not change dramatically the transport properties

(Lee, MBN, Marzari, PRL, 2005)

Functionalized nanotubes and disorder effects



Ligand pairs

Single ligand or isolated ligand pairs

Random distribution of ligands or ligands pairs

Single ligand

- (5,5) metallic nanotube functionalized with phenyl ligands
- conductance changes as function of the density of ligands and their distribution (single or pair)
- very large-scale simulation (>1000 atoms, Car-Parrinello) demonstrates the high computational efficiency of the method

(Lee, MBN, Marzari, PRL, 2005)