Transport Properties of Carbon Nanotube Links Connecting Graphene Layers

Pablo Ordejón

Theory and Simulation Group @

CSIC

ICN2 Institut Català de Nanotecnologia

CIN2

CENTRE D'INVESTIGACIÓ EN NANOCIÈNCIA I NANOTECNOLOGIA

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1. INTRODUCTION AND MOTIVATION

2. STRUCTURAL MODEL AND METHODOLOGY

3. ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES

4. CONCLUDING REMARKS

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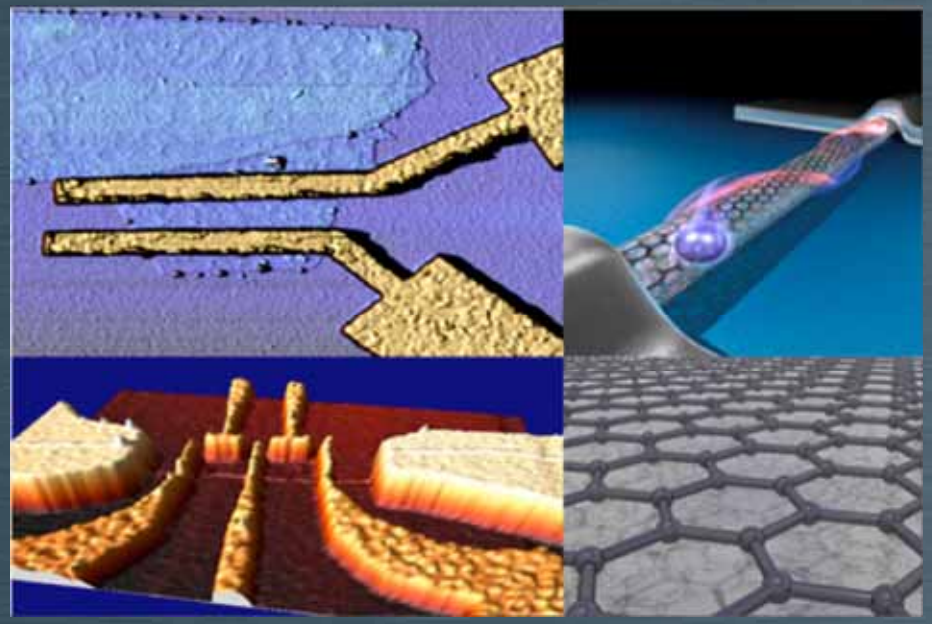
1. INTRODUCTION AND MOTIVATION

CIN2

CARBON NANOELECTRONICS: NANOTUBES & GRAPHENE



From P. Jarillo-Herrero's (MIT) Web Page

REVIEWS OF MODERN PHYSICS, VOLUME 79, APRIL–JUNE 2007

Electronic and transport properties of nanotubes

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REVIEWS OF MODERN PHYSICS, VOLUME 81, JANUARY–MARCH 2009

The electronic properties of graphene

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N. M. R. Peres

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K. S. Novoselov and A. K. Geim

Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, United Kingdom

INTERCONNECTS: "GOING VERTICAL"

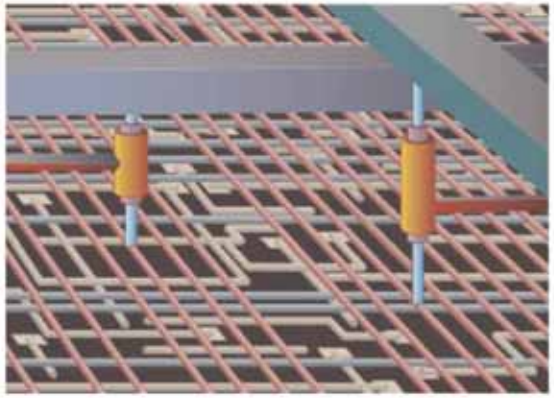
MATERIALS SCIENCE

Nanowires in Nanoelectronics

Connecting circuit layers with nanowires and nanotransistors may bring about a paradigm shift in microchip design.

David K. Ferry

For almost four decades, progress in microchips has followed Moore's (*1*) famous dictum that the transistor density would double roughly every 18 months. This steady progress has brought us to the point today where leading-edge chips have transistors whose critical dimension is only about 100 atoms long. Clearly, this evolution cannot continue down this same path much longer. Recognition of the impending "end of the road" has led many to seek an alternative to the ubiquitous silicon transistor, hoping thereby to revolutionize the industry that has fueled the massive information revolution since World War II (*2*, *3*). Among the promising candidates are nanowires and transistors made from them (*4*–*7*). These nanowires have been grown as carbon nanotubes or from silicon, as well as a variety of other semiconductors. As with most new technologies, there are remarkable expectations for the usefulness of these nanowires. In reality, they are not likely to replace the silicon transistor, but they may well provide the paradigm shift that will extend Moore's "law."



CREDIT: MICROCIRCUIT LAYOUT DIAGRAM ADAPTED FROM L. T. CLARK/ARIZONA STATE UNIVERSITY

Going vertical. A schematic, conceptual view of the introduction of vertical nanowires on a microchip. The bottom layer is a chip layout drawing; the various colors represent interconnection levels on the chip. The nanowires can reach from the chip level to higher-lying interconnects or they can reach between various metal layers.

To understand how this paradigm shift must occur, we need to understand the driving force for Moore's Law. It is a trend that does not derive from physical science but from economics. Transistors are laid out on the microchip in a planar fashion, much like houses in a modern southwestern city. According to Intel, the latest 45-nm microprocessor (with a gate length—the critical dimension in the direction of current flow—of ~22 nm) has about 410 million transistors in 107 mm^2, or each transistor occupies a square of silicon real estate that is roughly 500 nm on a side.

Originally, Moore's Law was driven by three factors: (i) reducing the transistor size (and therefore the square of silicon upon which it sits), (ii) increasing the size of the microchip itself, and (iii) circuit cleverness (by which the number of transistors needed to perform a function could be reduced with consequent savings in silicon real estate). As the number of transistors increased, the number of functional units in each chip could be

The author is in the Department of Electrical Engineering, Arizona State University, Tempe, AZ 85287, USA. E-mail: ferry@asu.edu

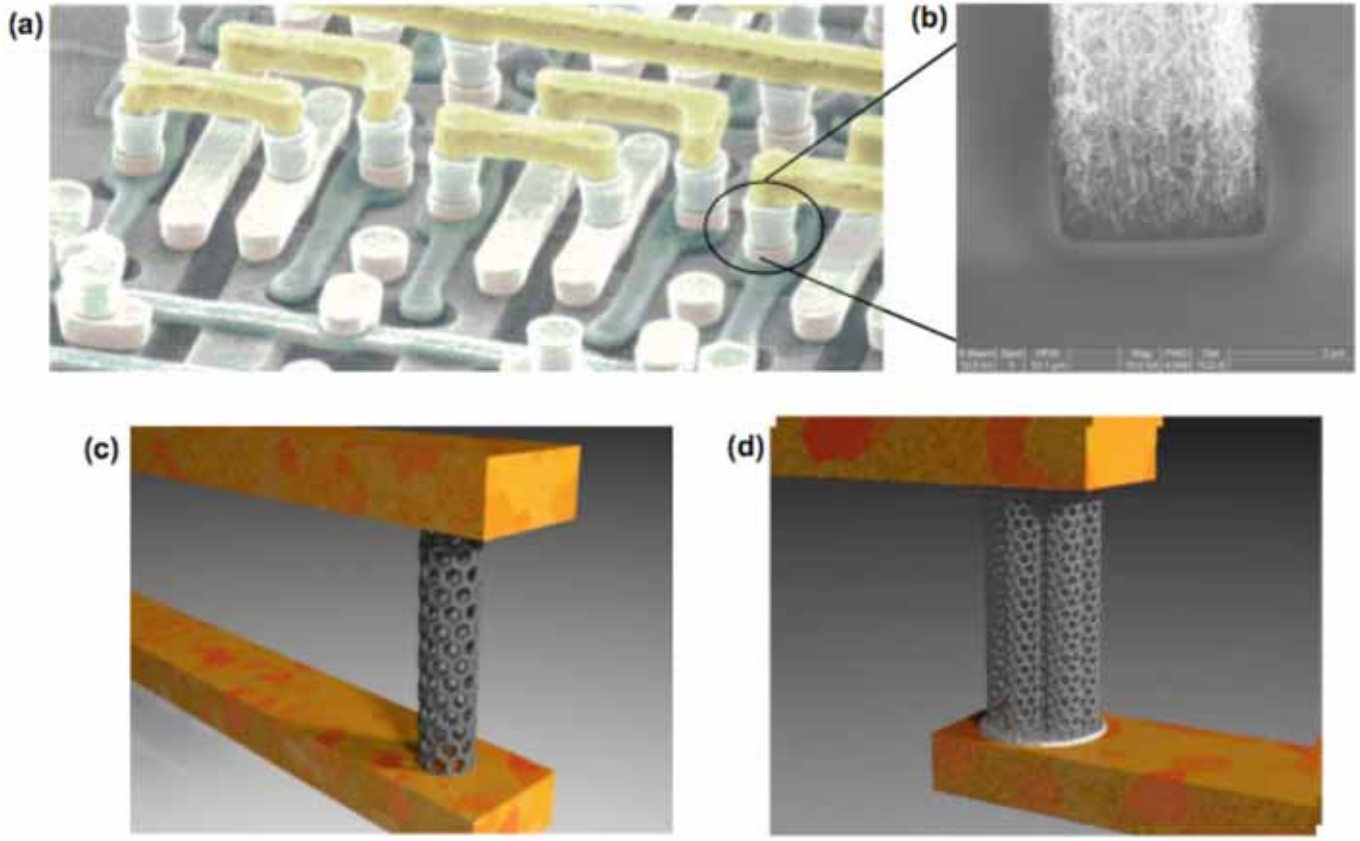
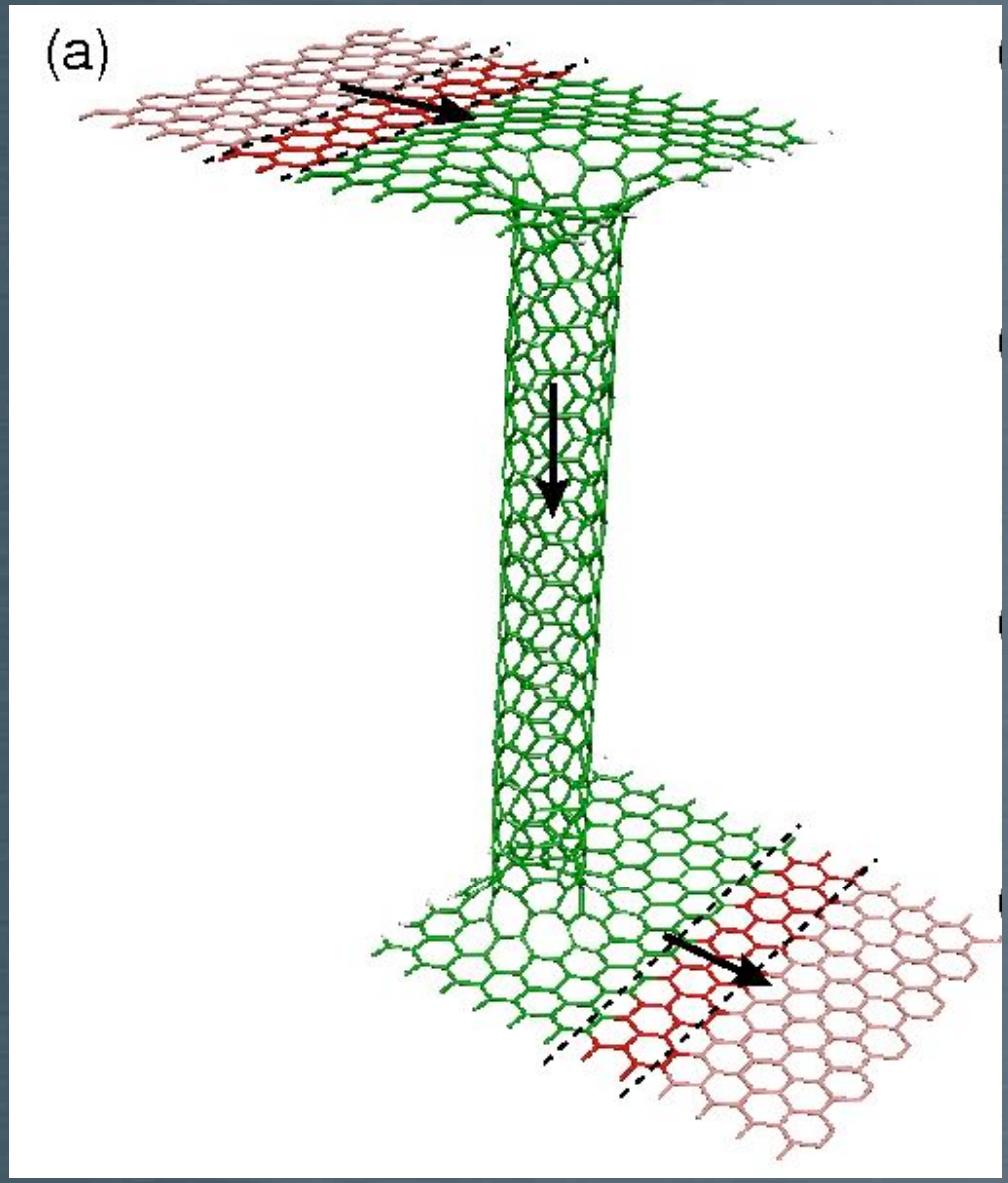
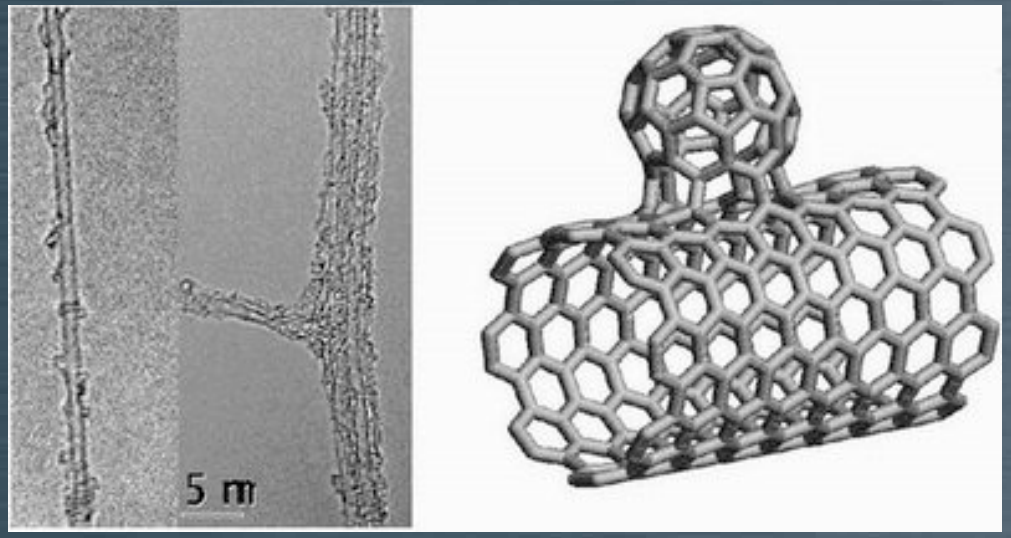


Figure 8. (*a*) A pictorial representation of the wiring in an integrated circuit. The horizontal interconnects are shown in yellow and the vertical interconnects are shown in grey. (*b*) An example of a MWNT array grown in a silicon oxide via, which can potentially be used as a vertical interconnect provided excellent electrical contacts can be made to both the top and bottom of the nanotube array. (*c*) A pictorial representation of the limit where a SWNT is used as a vertical interconnect in what may eventually become a molecular circuit. (*d*) An interconnect based on a bundle of SWNTs will have a low bias resistance of 6.5 kΩ divided by the number of nanotubes. (Source: (*a*) IBM Journal of Research and Development, (*b*) from [Kre02], (*c*) and (*d*) courtesy of Infineon Technologies.)

OUR WORK:
CNT's AS WIRES TO CONNECT GRAPHENE DEVICES



RELATED STRUCTURES (obtained by CVD):

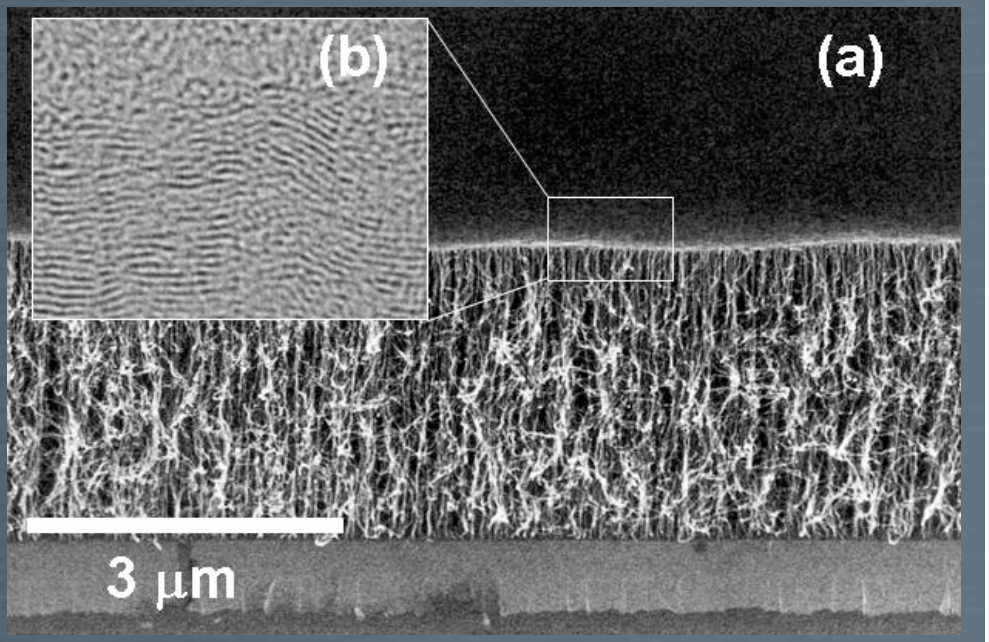


Carbon "Nanobuds" (nanotubes with fullerenes covalently attached)

Nanotube/Graphite composite

FUJITSU THE POSSIBILITIES ARE INFINITE

Atsugi, Japan, March 3, 2008 — The newly-discovered composite structure is synthesized at a temperature of **510 °C,** cooler than for conventional graphene formed at temperatures too high for electronic device applications, thereby paving the way for the feasible use of graphene as a material suitable for future practical use in electronic devices which are vulnerable to heat.



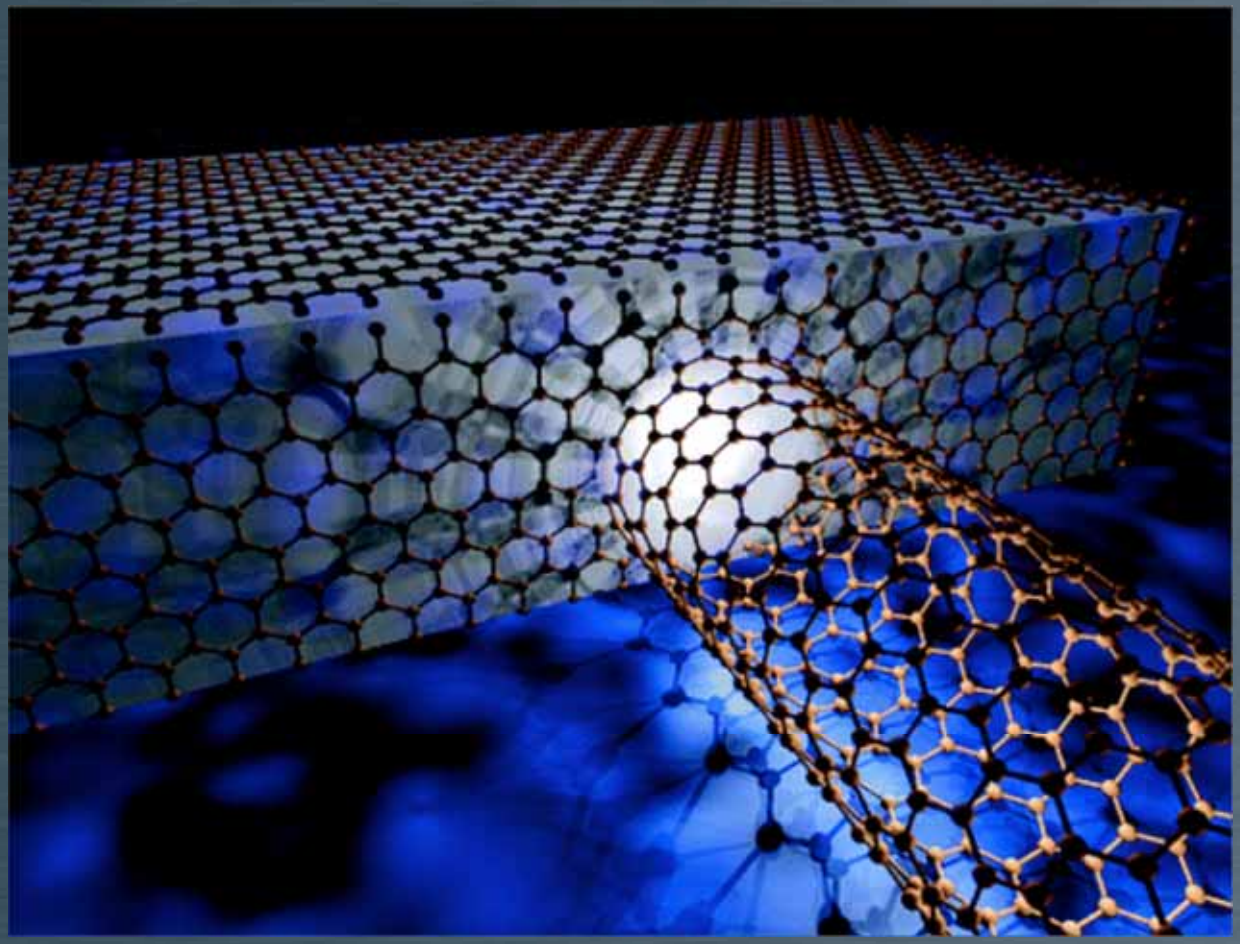
EXPERIMENTAL REALIZATION?

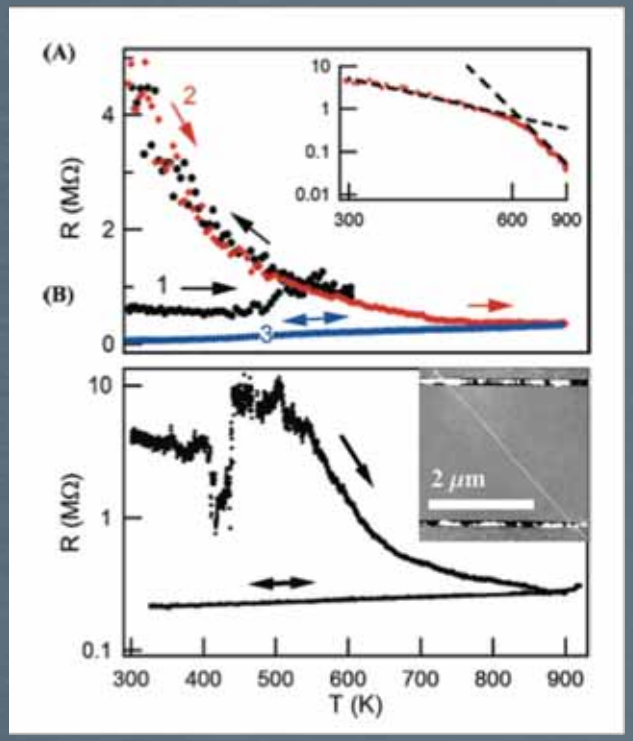
Graphitic Electrical Contacts to Metallic Single-Walled Carbon Nanotubes Using Pt Electrodes

Alexander A. Kane,† Tatyana Sheps,† Edward T. Branigan,‡ V. Ara Apkarian,‡ Ming H. Cheng,‡ John C. Hemminger,‡ Steven R. Hunt,† and Philip G. Collins*,†

NANO LETTERS

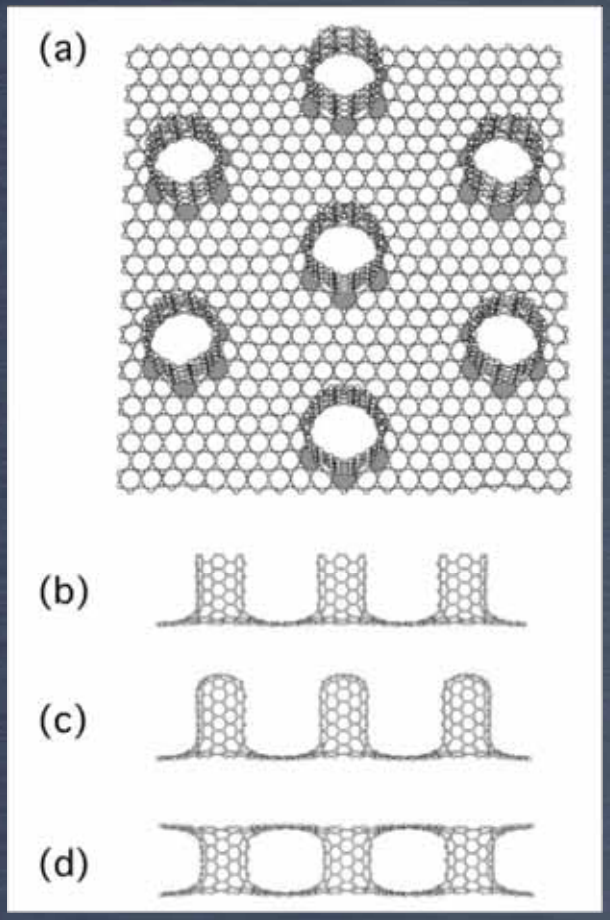
2009
Vol. 9, No. 10
3586-3591



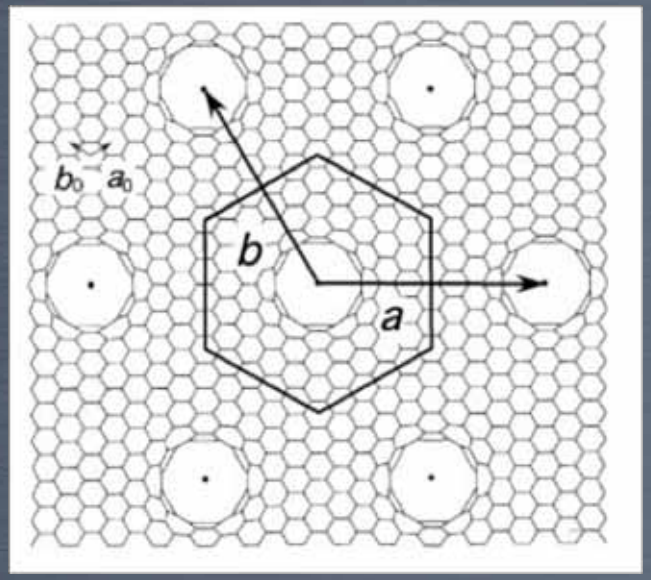


2. STRUCTURAL MODEL AND METHODOLOGY

PREVIOUS WORK (I)



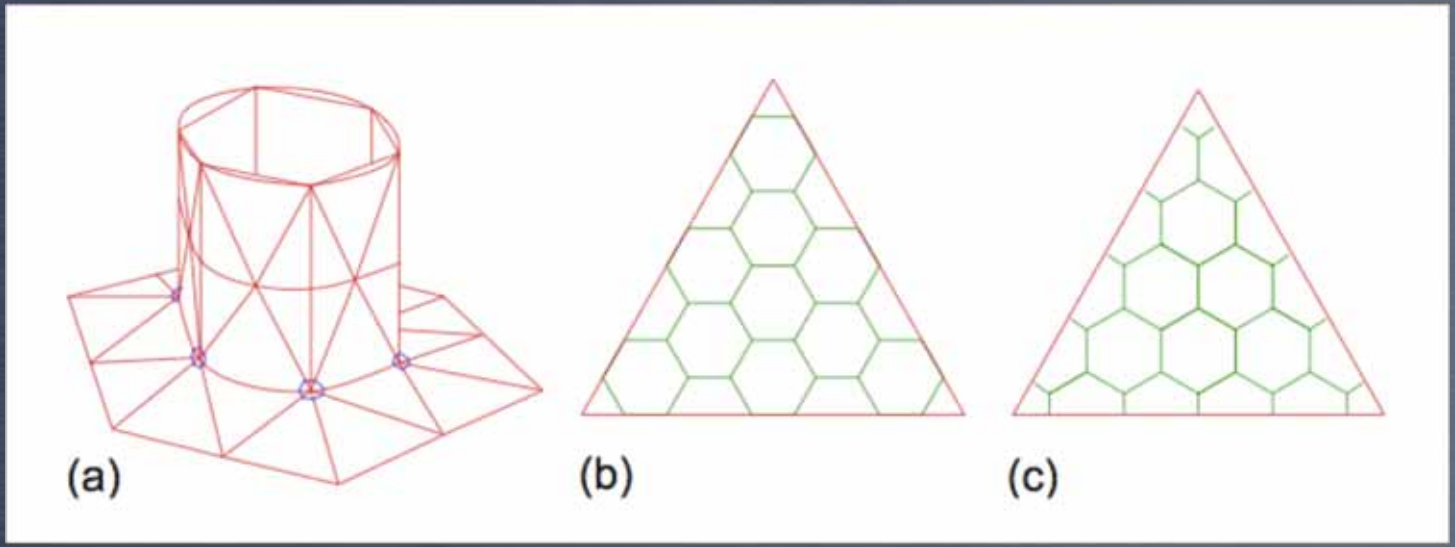
Matsumoto and Saito,
J.Phys. Soc. Jpn. **71**, 2765 (2002)



- (6,6) tubes
- C_{6v} symmetry preserved
- DFT calculations (relaxations + electronic structure)

PREVIOUS WORK (II)

Gonzalez, Guinea and Herrero
PRB **79**, 165434(2009)



- Metallic (6n,6n) and (6n,0) tubes
- C_{6v} symmetry preserved
- Both Single links and hexagonal arrays
- TB and continuum theory (Dirac eq.) approaches

- Existence of propagating, evanescent and localized states, depending on the nanotube chirality and size.
- Estimate of transmission properties

COVALENT sp2 LINK OF NANOTUBES TO GRAPHENE

Baowan, Cox and Hill, Carbon **45**, 2972 (2007)

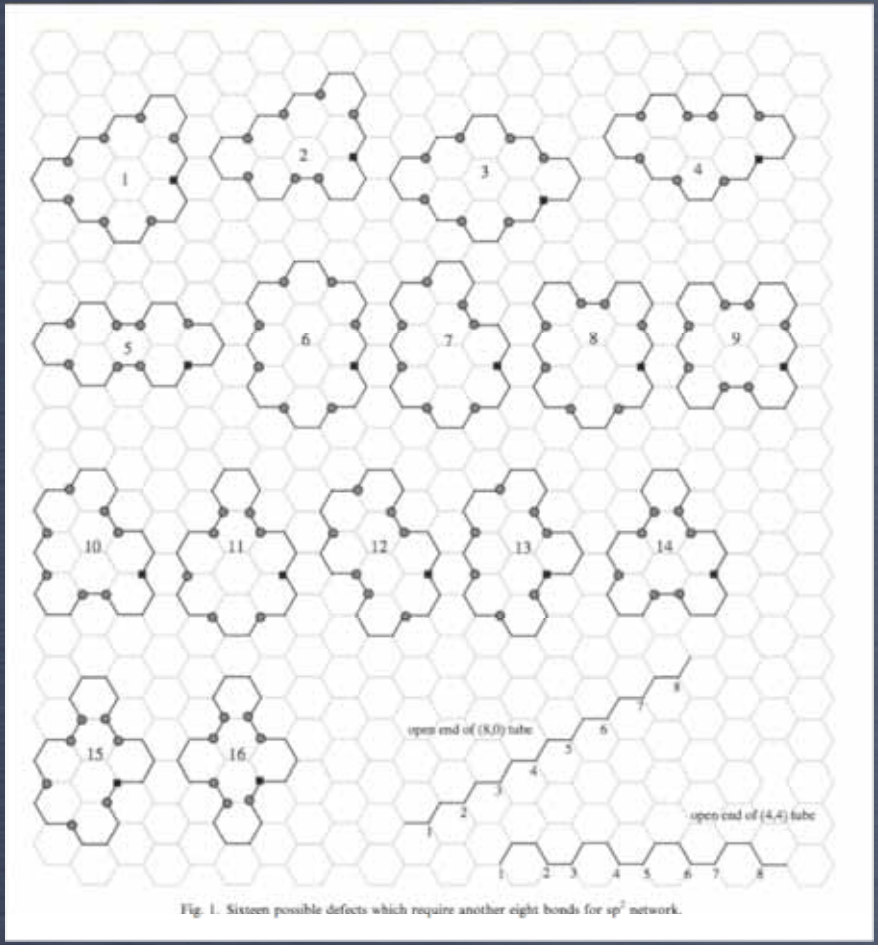
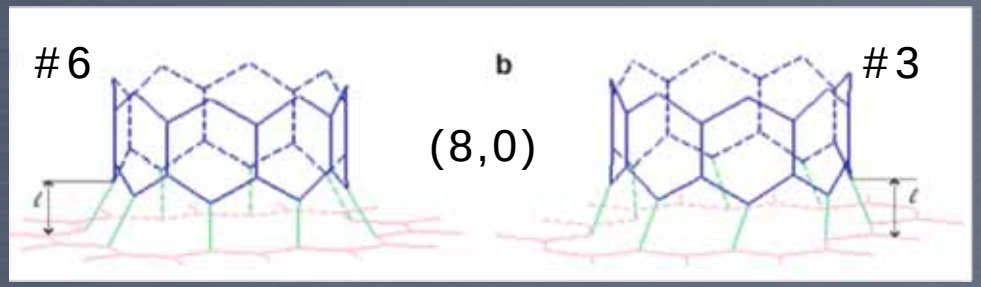
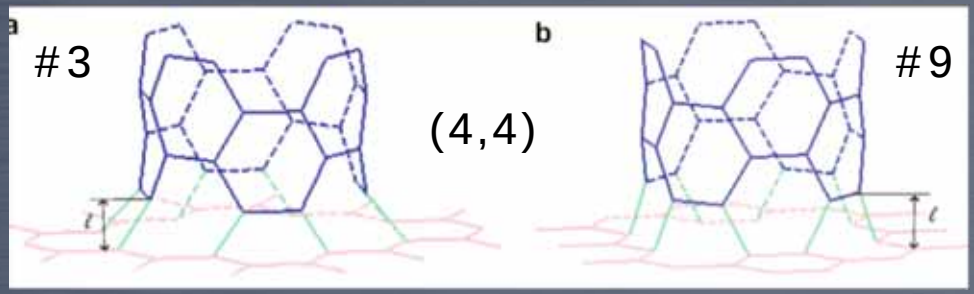


Fig. 1. Sixteen possible defects which require another eight bonds for sp^2 network.





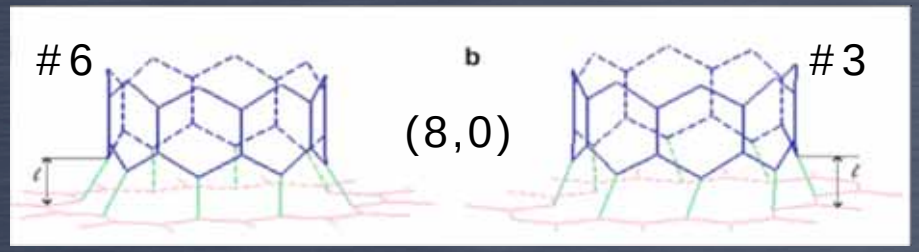
Geometrical ‘least-squares’ optimization

$$f(X, Y, \ell, \theta) = \sum_{i=1}^{8} (|\mathbf{a}_i - \mathbf{b}_i| - \sigma)^2.$$

COVALENT sp2 LINK OF NANOTUBES TO GRAPHENE

Table 1
Values of least square function f (Å^2) and distance ℓ (Å) for 16 configurations of (8,0) tube and corresponding polygons P_n where n is number of sides

Configurations #	f	ℓ	P_5	P_6	P_7	P_8	P_9
1	0.0239	1.3243	–	4	2	2	–
2	0.2092	1.1663	1	3	1	3	–
3	0.0018	1.3027	–	4	2	2	–
4	0.0676	0.9471	1	2	3	2	–
5	1.2631	0.0010	2	–	4	2	–
6	0.0817	1.3218	–	2	6	–	–
7	0.0729	1.1823	1	1	5	1	–
8	0.0020	1.3500	1	2	3	2	–
9	0.0592	1.3349	2	2	–	4	–
10	0.0793	1.2210	2	1	2	3	–
11	0.5513	0.9560	2	–	5	–	1
12	0.2498	0.9191	2	–	4	2	–
13	0.0404	1.1951	2	1	2	3	–
14	0.6005	0.9841	3	–	2	2	1
15	0.5262	0.9482	3	–	2	2	1
16	0.5284	0.9227	4	–	–	2	2



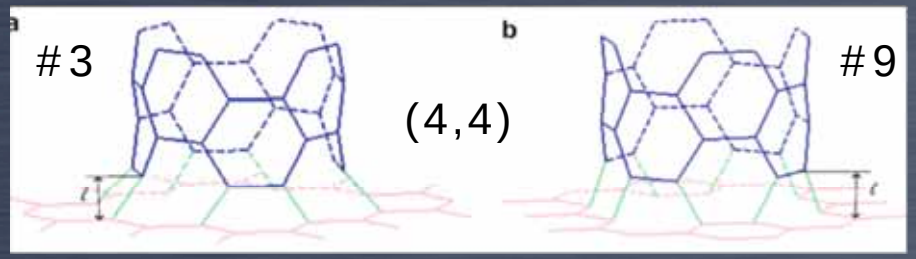


Table 2
Values of least square function f (Å^2) and distance ℓ (Å) for 32 configurations of (4,4) tube and corresponding polygons P_n where n is the number of sides. By symmetry 1-a and 1-b are equivalent

Configurations #	f	ℓ	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}
1-a	0.0526	1.1548	–	2	1	3	1	1	–
1-b	0.0526	1.1548	–	2	1	3	1	1	–
2-a	0.0638	1.1501	–	1	2	4	–	1	–
2-b	0.0528	1.1798	1	2	–	2	1	2	–
3-a	0.4494	1.2208	–	4	–	–	2	2	–
3-b	0.0643	1.1157	–	–	2	6	–	–	–
4-a	0.3751	1.0544	–	2	3	–	1	2	–
4-b	0.0847	0.9834	1	–	1	4	2	–	–
5-a	0.0435	0.6723	–	–	6	–	–	2	–
5-b	0.2458	0.6746	2	–	–	2	4	–	–
6-a	0.5177	1.1151	–	–	4	2	2	–	–
6-b	0.3802	1.1098	–	2	2	–	4	–	–
7-a	0.3132	1.0767	1	–	3	1	2	1	–
7-b	0.2498	1.1093	–	1	3	1	3	–	–
8-a	0.0273	1.1968	–	–	3	4	1	–	–
8-b	0.1637	1.2151	1	2	1	–	2	2	–
9-a	0.0127	1.2968	–	–	2	6	–	–	–
9-b	0.0161	1.3612	2	2	–	–	–	4	–
10-a	0.0687	1.1979	1	–	2	3	1	1	–
10-b	0.0393	1.1624	1	1	2	1	1	2	–
11-a	0.0272	1.1240	2	–	2	–	3	–	1
11-b	0.5537	1.0920	–	–	5	–	3	–	–
12-a	0.0430	0.6309	2	–	2	–	2	2	–
12-b	0.1764	1.0026	–	–	4	2	2	–	–
13-a	0.2451	0.8439	2	–	2	1	–	3	–
13-b	0.0425	1.1583	–	1	2	3	2	–	–
14-a	0.0176	0.7303	2	–	1	2	2	–	1
14-b	0.2985	1.1284	1	–	4	–	1	2	–
15-a	0.0494	1.0936	3	–	1	–	1	2	1
15-b	0.4425	1.1057	–	–	4	2	2	–	–
16-a	0.0561	1.0353	4	–	–	–	–	2	2
16-b	0.3448	1.1007	–	–	4	2	2	–	–

METHODOLOGY: siesta http://www.uam.es/siesta

Soler, Artacho, Gale, García, Junquera, Ordejón and Sánchez-Portal
J. Phys.: Cond. Matt. **14**, 2745 (2002)

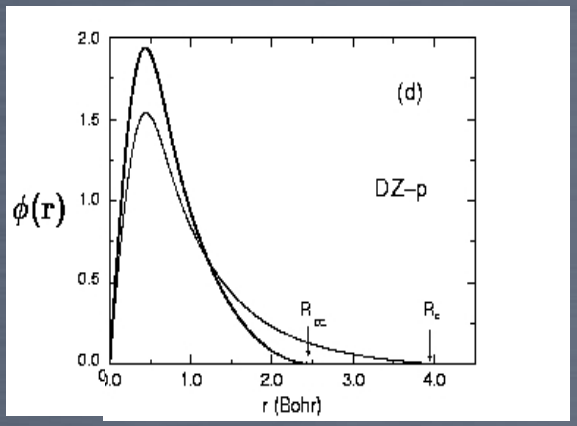
- Self-consistent DFT code (LDA, GGA)
- Pseudopotentials (Kleinman-Bylander)
- LCAO approximation:

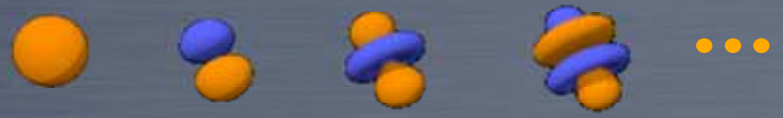
  Basis set:

  Confined Numerical Atomic Orbitals

  (Sankey's "fireballs")

  As complete as needed



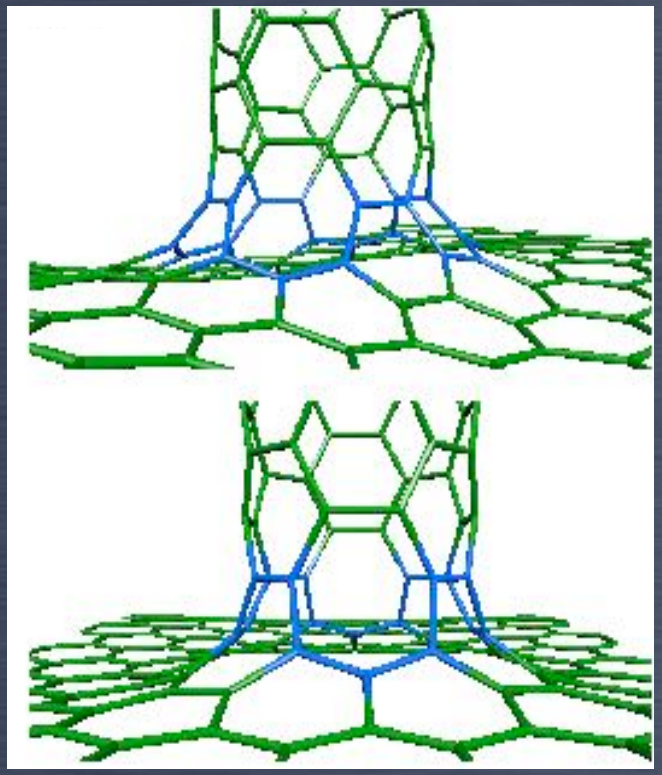


- Order-N methodology (in the calculation of the DFT Hamiltonian and (if required) in the solution of the eigenvalue equation to obtain the WFs)

STRUCTURAL RELAXATIONS (DFT)

GGA (PBE); DZP Basis set

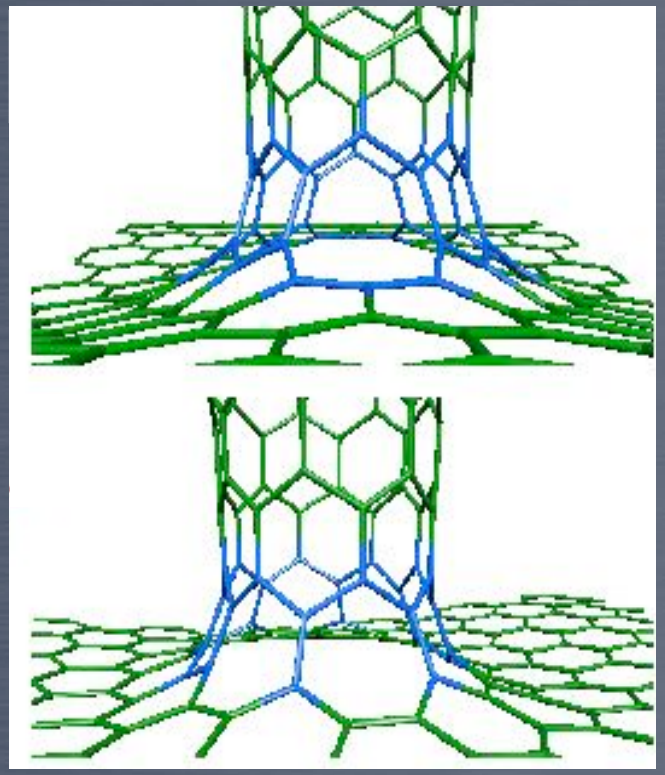
(4,4)



#3
8.13 eV

#9
9.77 eV

(8,0)

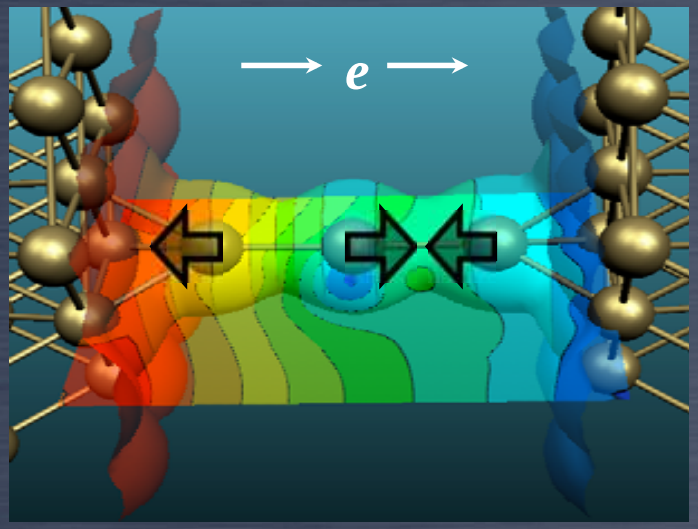


#3
10.68 eV

#6
11.05 eV

$$\Phi = E_T^{junct} - n_C^g \mu_C^g - n_C^t \mu_C^t$$

METHODOLOGY: TranSIESTA (I)



(in colaboración con M. Brandbyge, K. Stokbro, TU-Denmark)

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

(Other similar packages can also be linked to SIESTA)

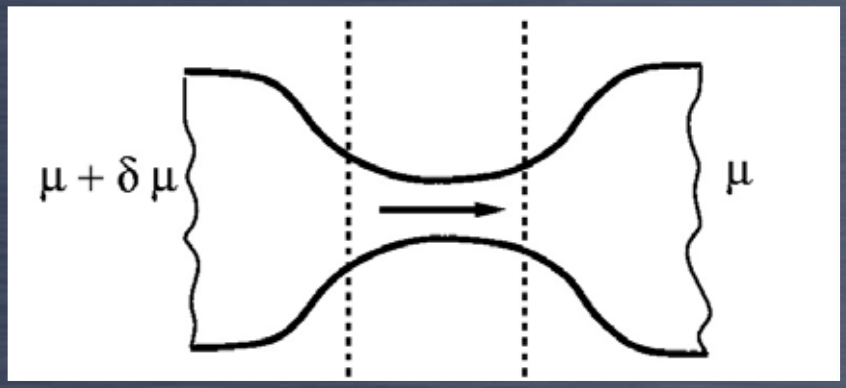
Model the nanocontact-electrode system from ***first principles:***

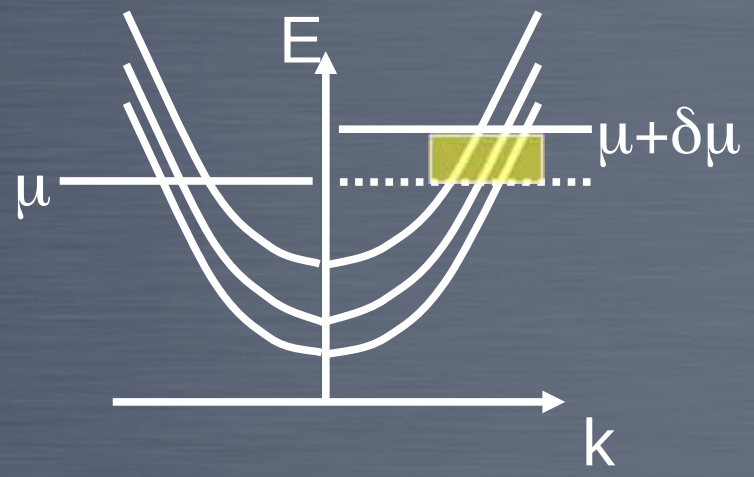
Atomistic level --- No adjustable parameters

- Model a **molecule** coupled to **bulk (semi-infinite) electrodes**
- Include **finite bias** voltage/current and determine the **potential profile**
- Electrons **out of equilibrium** (do not follow the thermal Fermi occupation)
- Calculate the **conductance** (quantum transmission through the molecule)
- Determine **geometry**: Relax the atomic positions to an energy minimum

METHODOLOGY: TranSIESTA (II)

Narrow, refletionless constriction





$$\delta\mu = -eV$$

$$I = -2e \sum_{i}^{bands} \int_{\square} dk\, f(k) v_g(k,i) \approx \frac{2e^2}{h} V N_{channels}$$

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

QUANTUM OF CONDUCTANCE

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

METHODOLOGY: TranSIESTA (II)

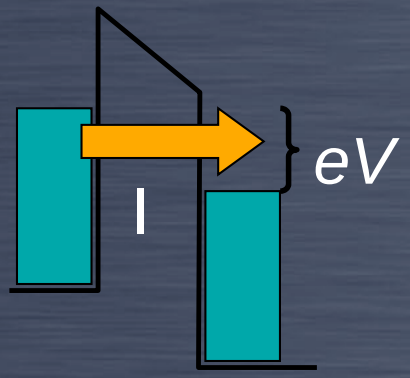
Landauer Formulation: Conductance as Transmission

- Transmission probability of an incoming electron at energy ε:

$$T(E) = Tr\left[t^{+} t\right](E)$$

transmission matrix: $\psi_{out} = t\,\psi_{in}$

- Current:

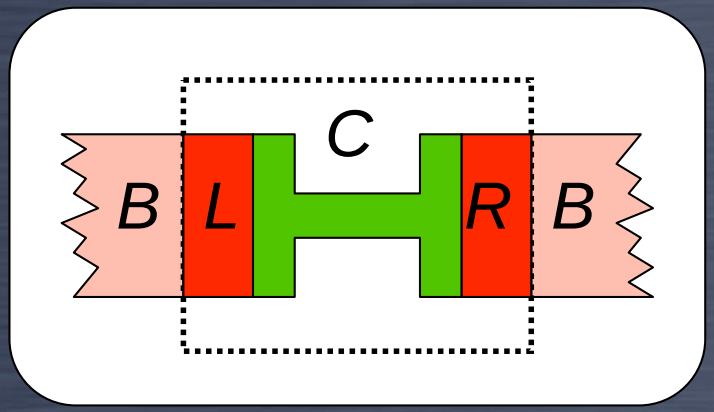


$$I = \frac{2e^2}{h}\int d\varepsilon \; \left(f_L(\varepsilon) - f_R(\varepsilon)\right) T(\varepsilon)$$

- For small V, and in terms of the number of channels and the average transmision:

$$G \approx \frac{2e^2}{h} N_{channels}\; T = G_0\; N_{channels}\; T$$

METHODOLOGY: TranSIESTA (III)



Open system:

Solution in **finite** system:

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

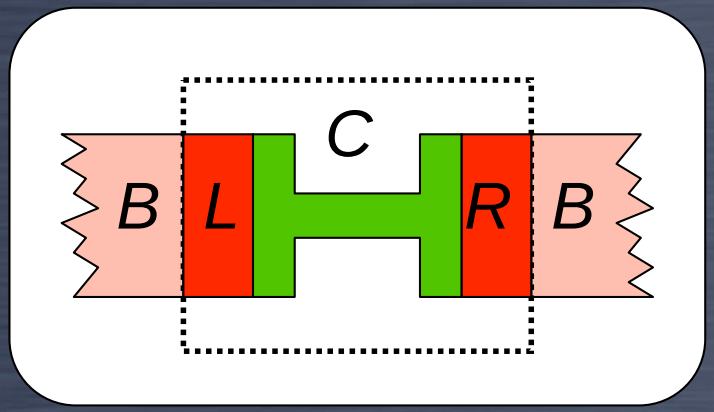
*$\Sigma(\varepsilon)$ = Selfenergies. Can be obtained from the **bulk Greens functions***

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

Landauer conductance: $T(\varepsilon) = Tr\left[t^{+} t\right](\varepsilon)$

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

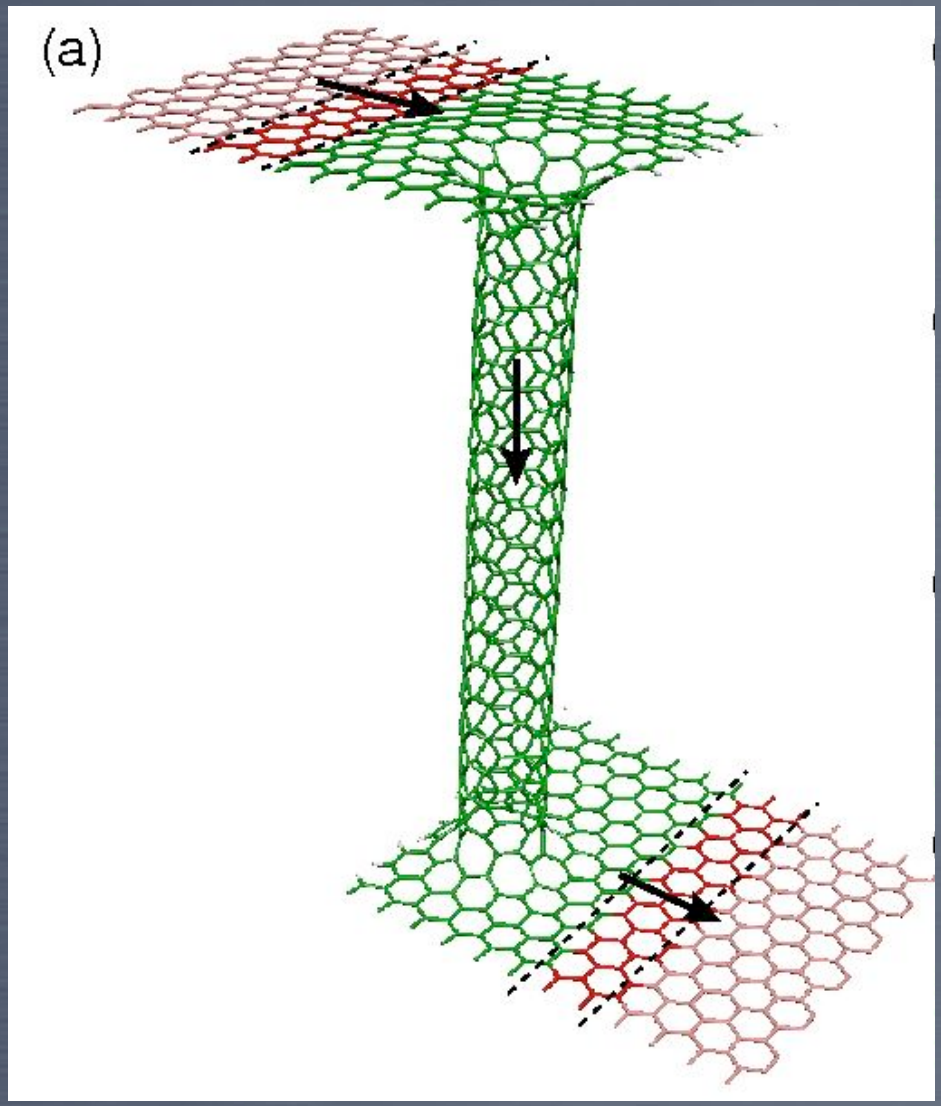
TRANSPORT SETUP



- C region: explicitly solved.

- B region: only included via the self-energies

- L and R: explicitly included in C, but H and ρ taken from bulk graphene

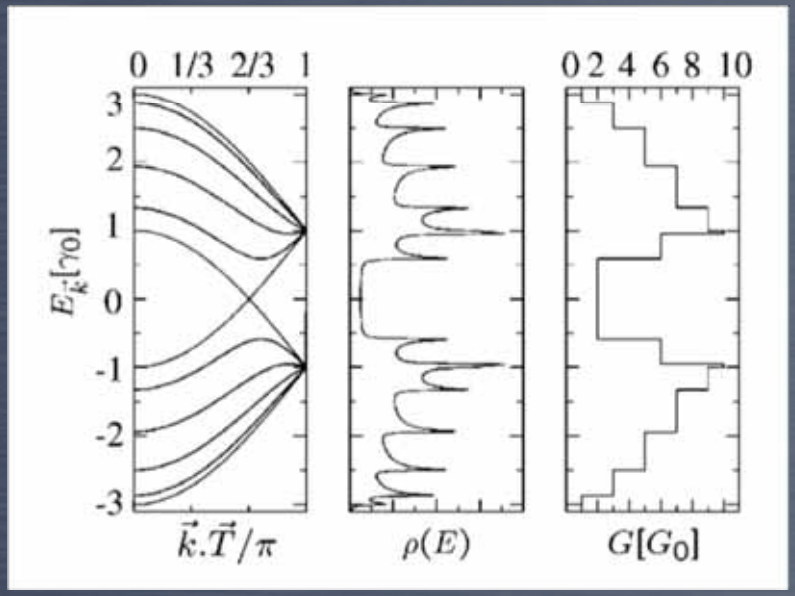


GRAPHENE AND NANOTUBES

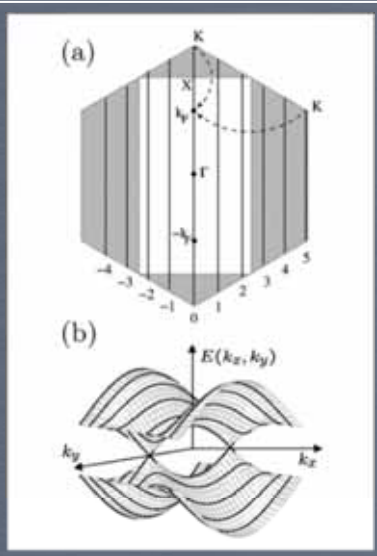
Nanotubes

(5,5) tube

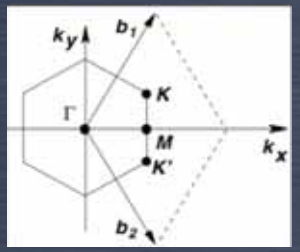
Charlier et al, RMP'07

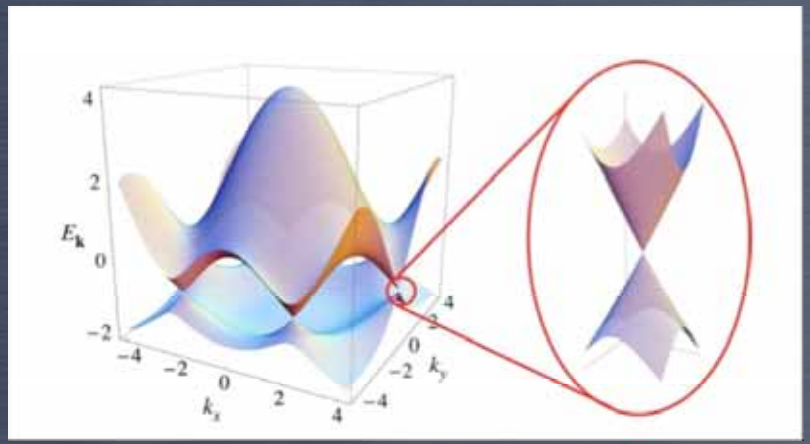


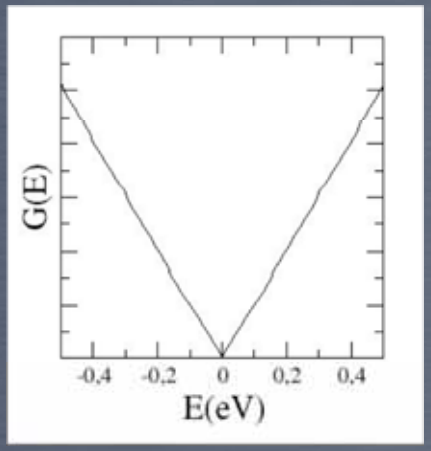
Around E=0: G = $2G_0$

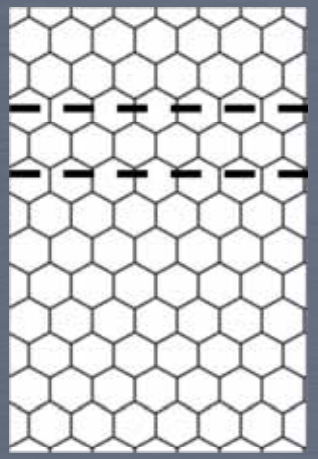


Graphene



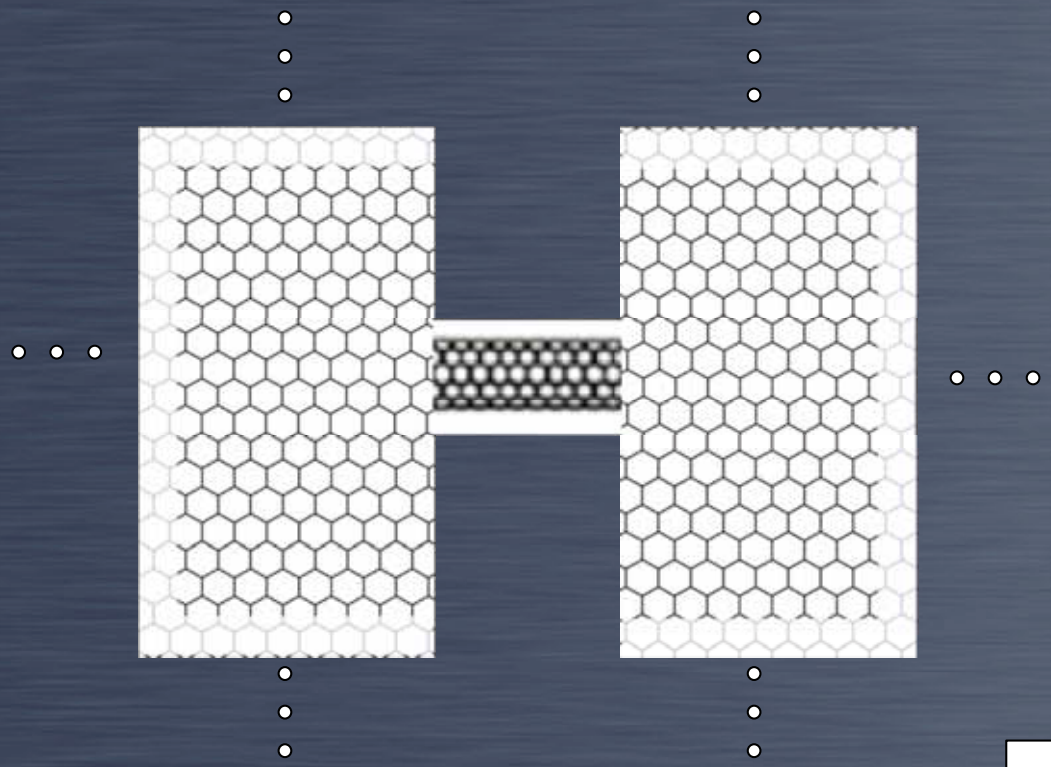






At E=0: G = $2G_0$

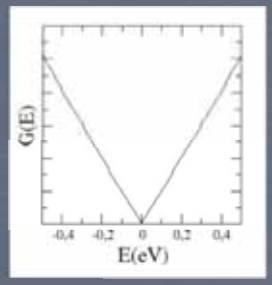
EXPECTED RESULTS



$$G \approx G_0 \; N_{channels} \; T$$

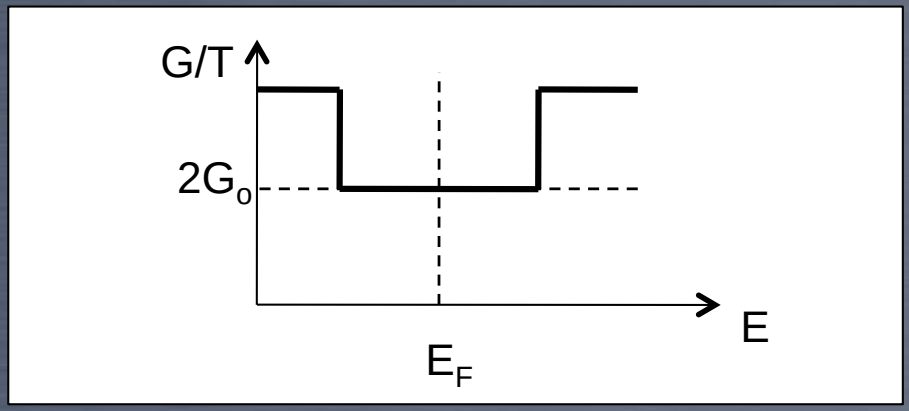
Semi-infinite graphene sheets:

N = 2 at E_F
N increases linearly with E

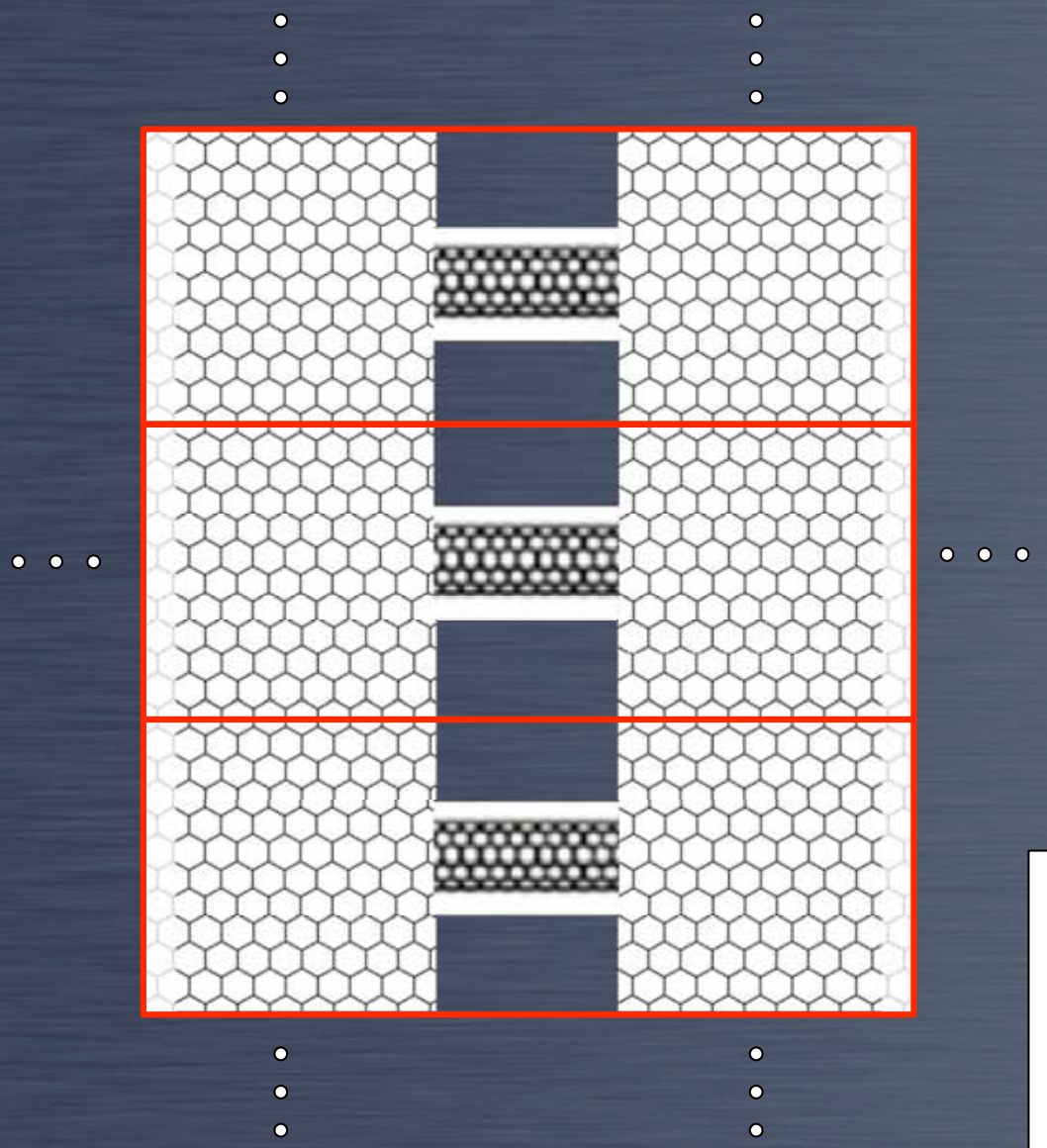


Nanotube (metallic):

N = 2 for a wide range of energies around E_F



... HOWEVER: CALCULATION IN PERIODIC SUPERCELL



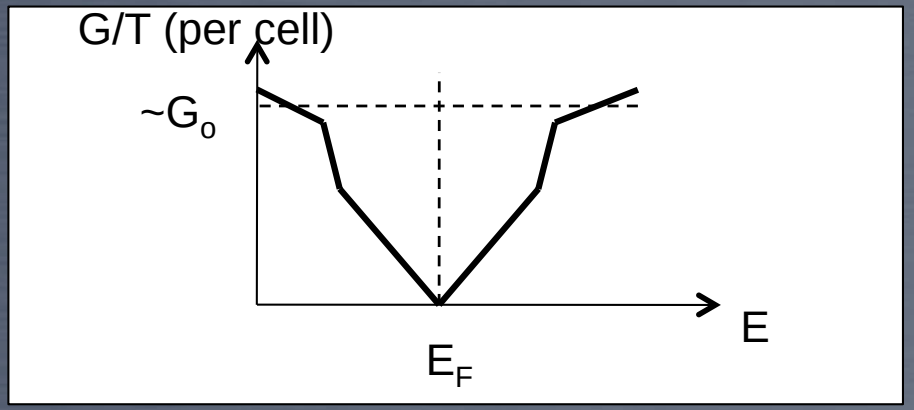
$$G(\text{per SC}) = G_0 \frac{1}{N_k} \sum_{k}^{N_k} T(k_{||}) \approx$$
$$\approx G_0 \; N/N_s \; \overline{T}$$

Semi-infinite graphene sheets:

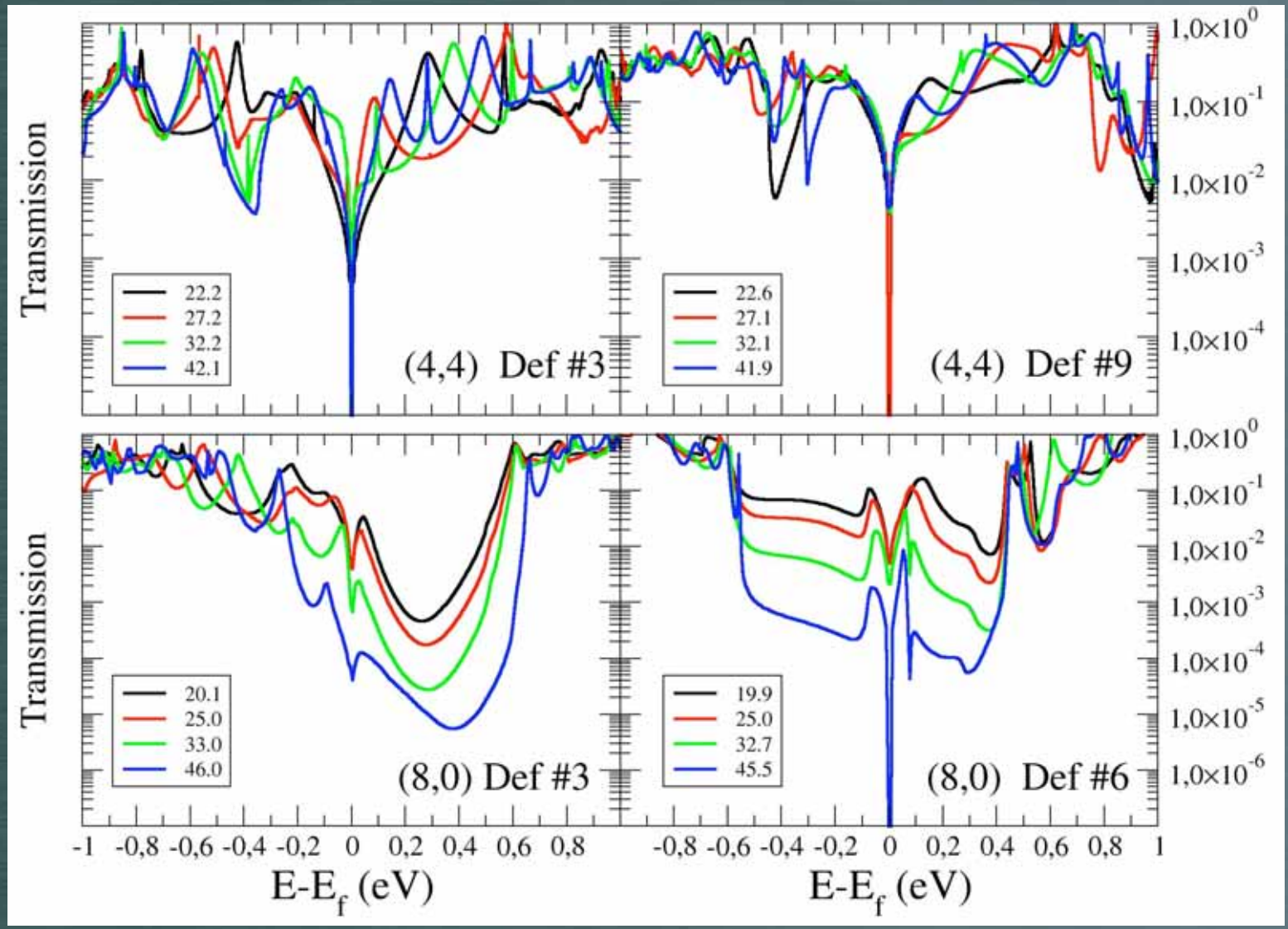
N = 2 at E_F → $N/N_s = 0$
N/N_s increases linearly with E

Nanotube (metallic):

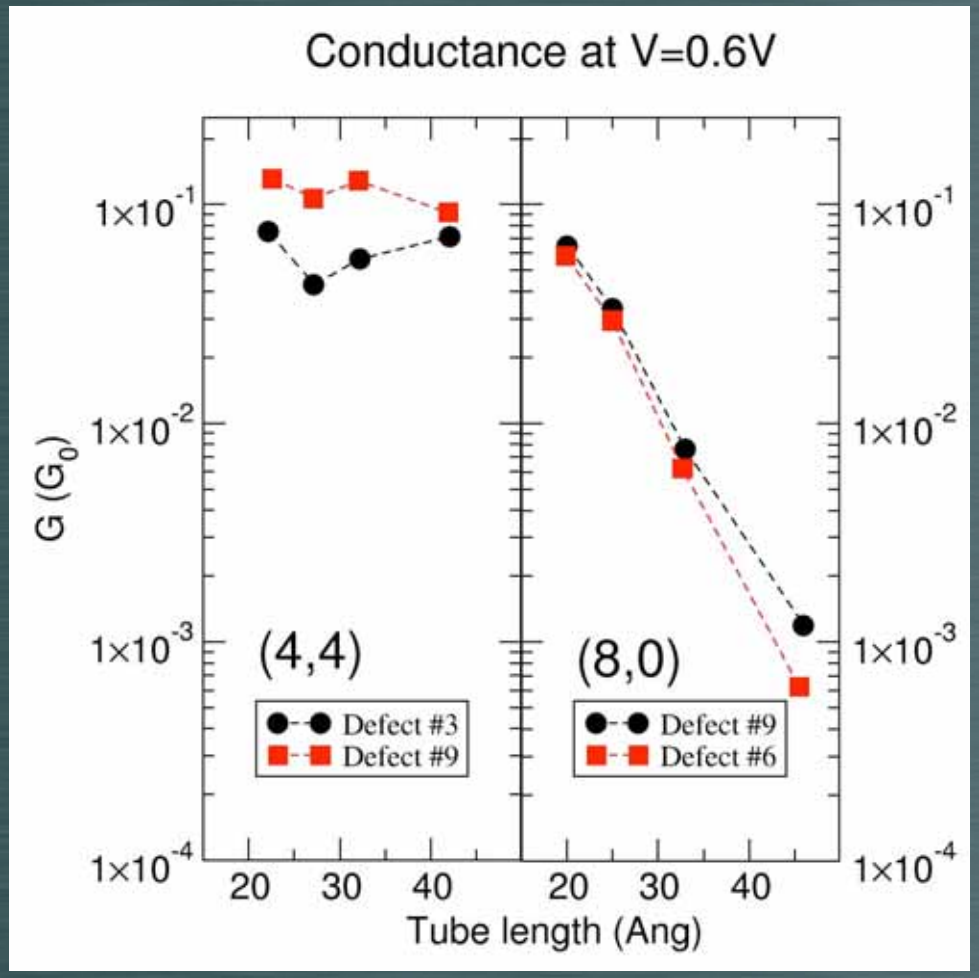
N = 2 x N_{tubes} → $N/N_s = 2$



3 ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES



CONDUCTANCE vs. CNT LENGTH



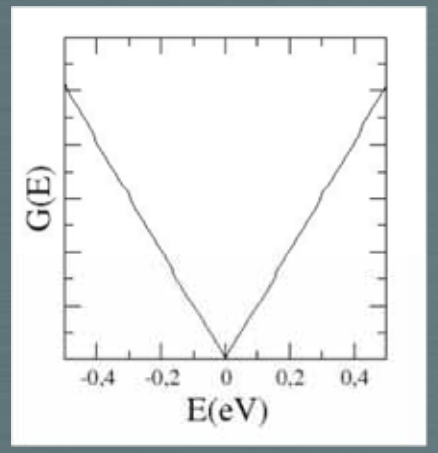
$$G = \frac{I}{V} = \frac{G_0}{V} \int_{-V/2}^{V/2} d\varepsilon \, T(\varepsilon)$$

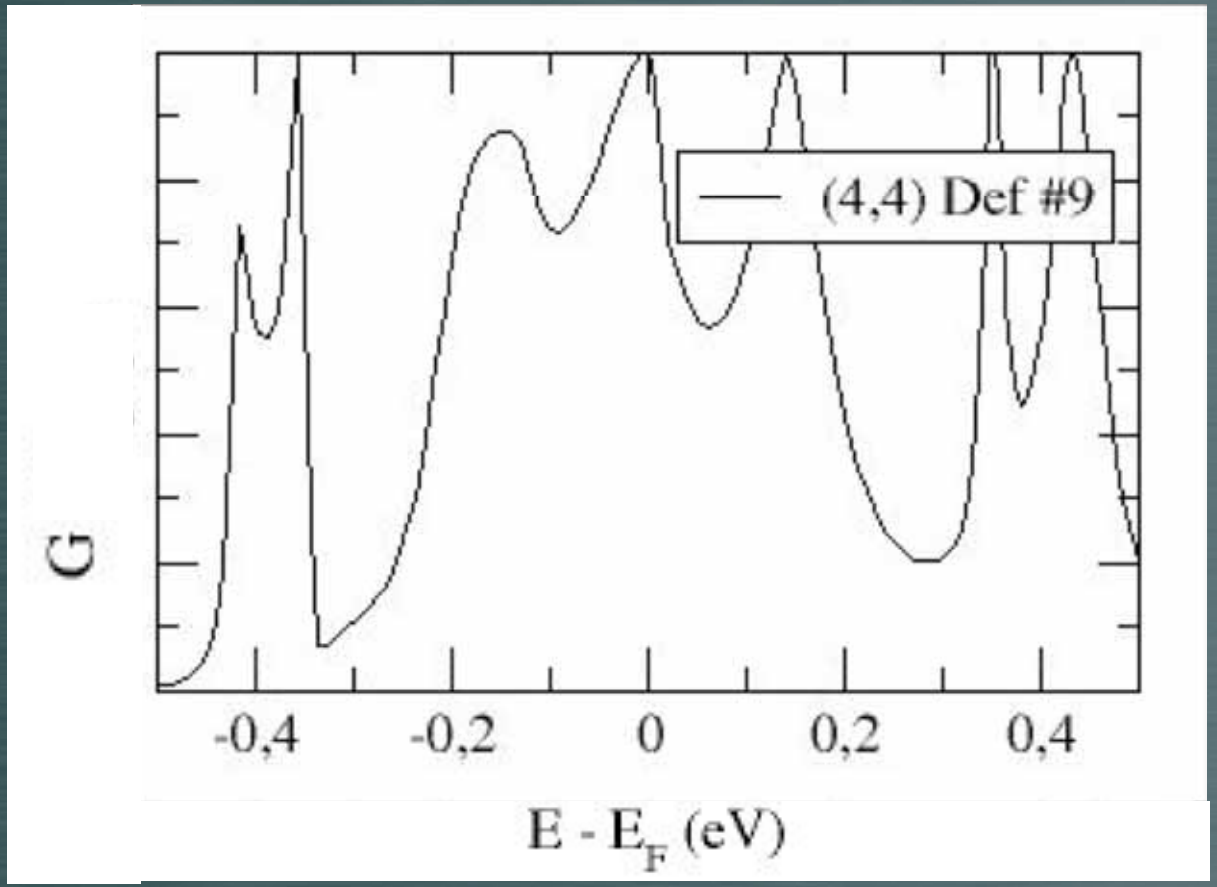
Metallic tubes: Extended states → G is nearly independent of tube length

Semiconducting tubes: No states in the gap. Conduction by tunneling → G decreases exponentially with tube length

WHICH CONDUCTANCE SHOULD DO WE PLOT?

$$G(\text{per SC}) = G_0 \frac{1}{N_k} \sum_{k}^{N_k} T(k_{||}) \approx G_0 \; N/N_s \; \overline{T}$$





$$G \approx \frac{2e^2}{h} N_{channels} \; \overline{T}$$

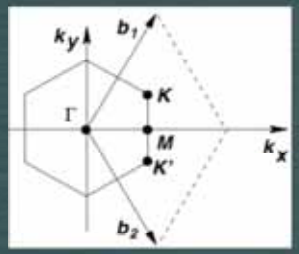
$$G \; / \; G_{graph} \approx \overline{T}$$

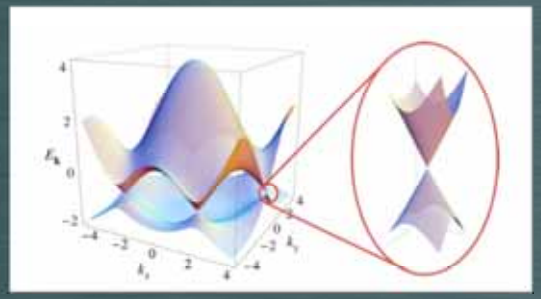
Average transmission of the nanotube per channel of graphene

WHICH CONDUCTANCE SHOULD DO WE PLOT?

k-point resolved Conductance

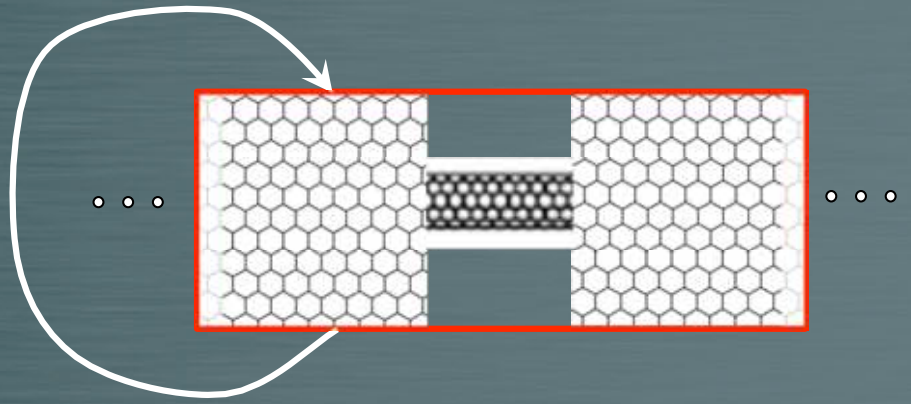
$$G(k_{||}) = G_0 T(k_{||})$$



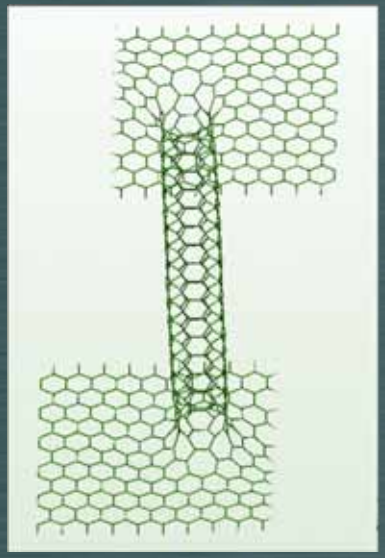


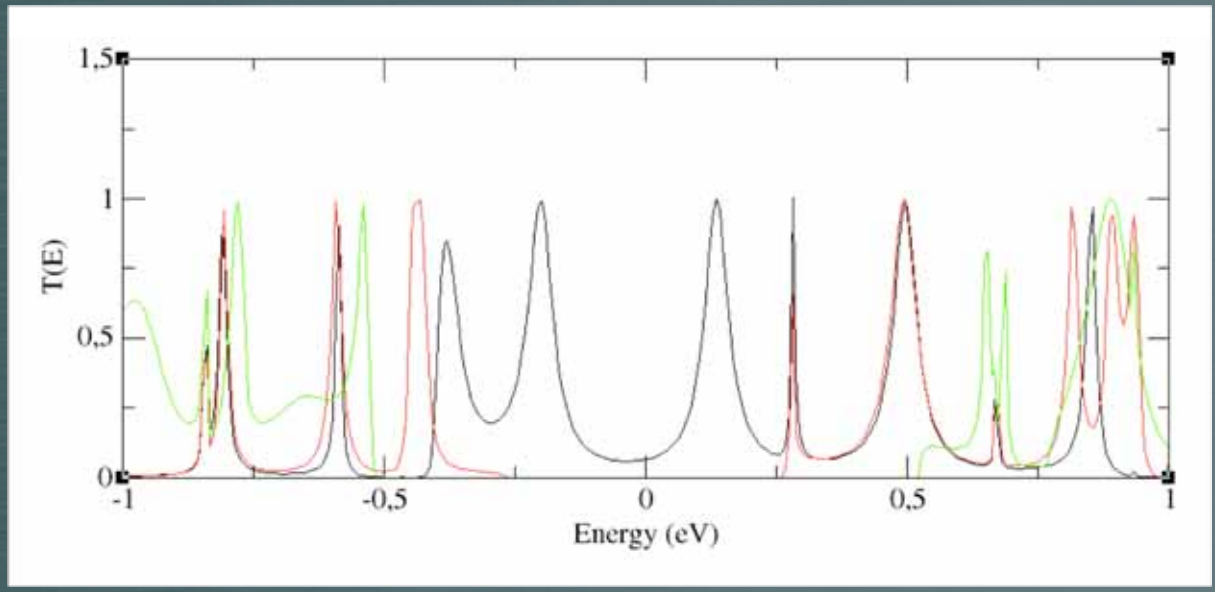
Supercell: Finite system with Twisted BC:

$$\psi(L) = e^{ikL}\psi(0)$$



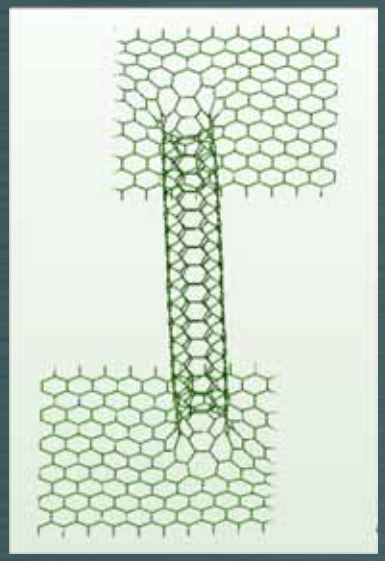
(4,4) tube, defect #3

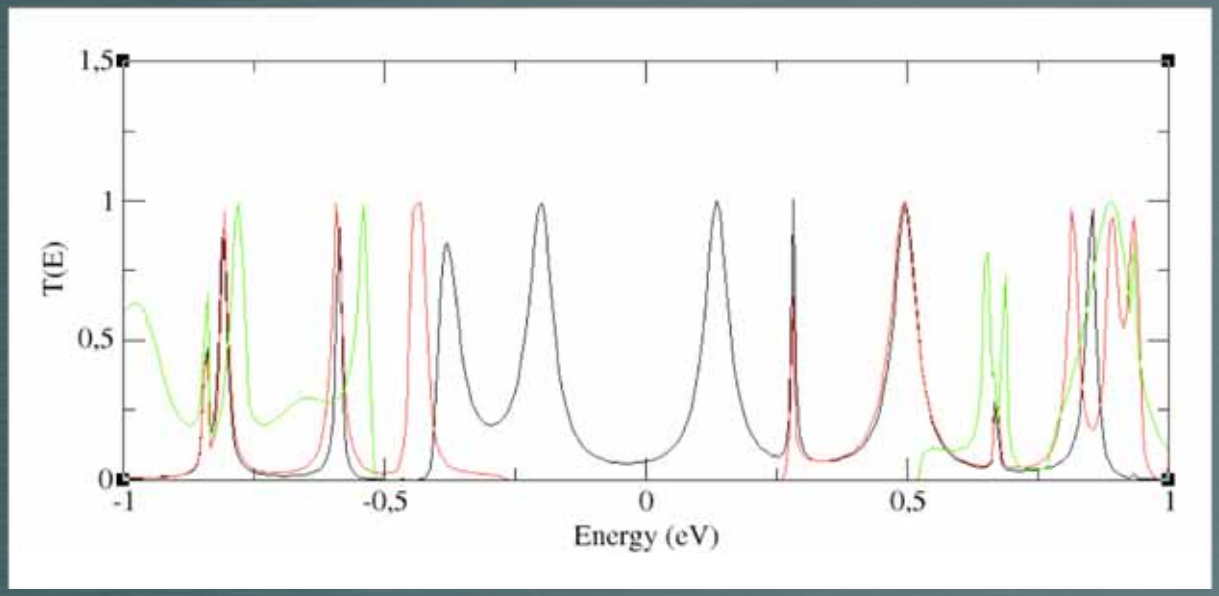


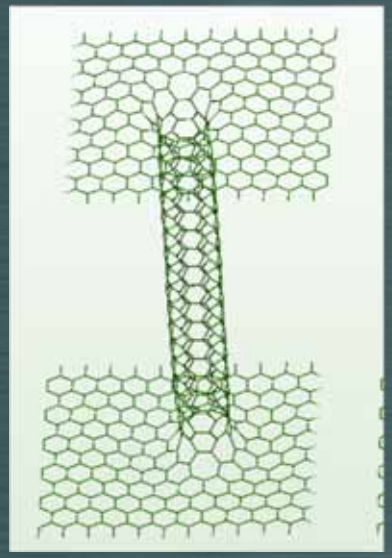


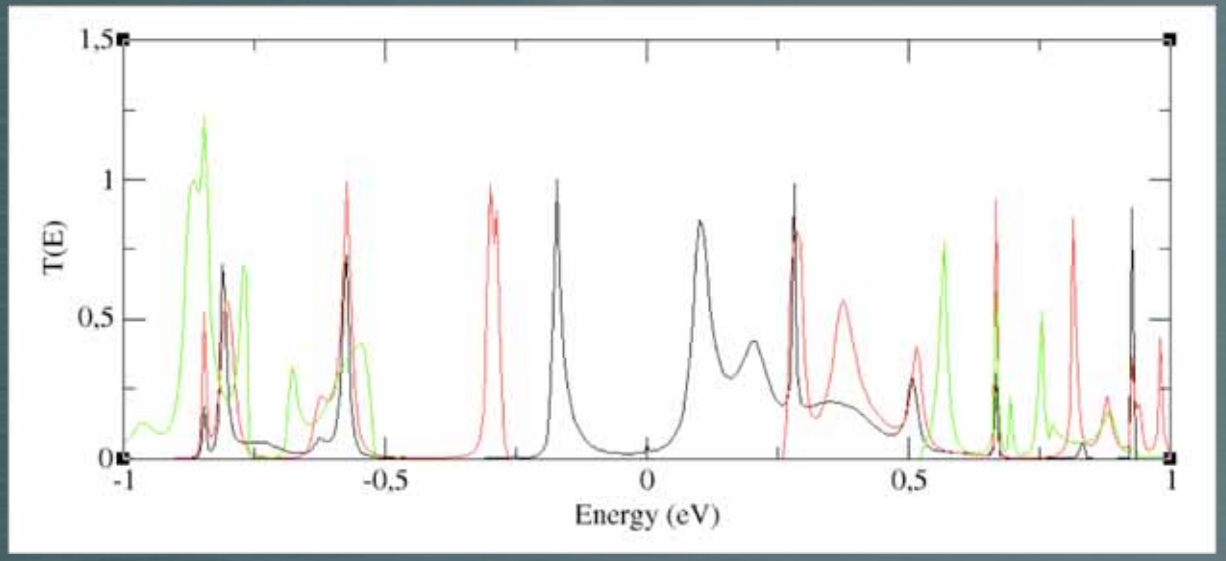
CONDUCTANCE vs. ENERGY

(4,4) tube, defect #3 - Dependence on distance to edge







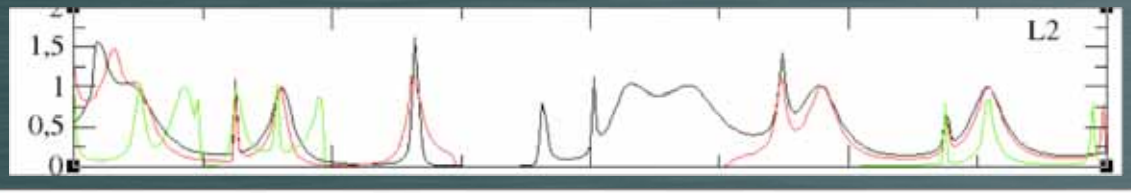


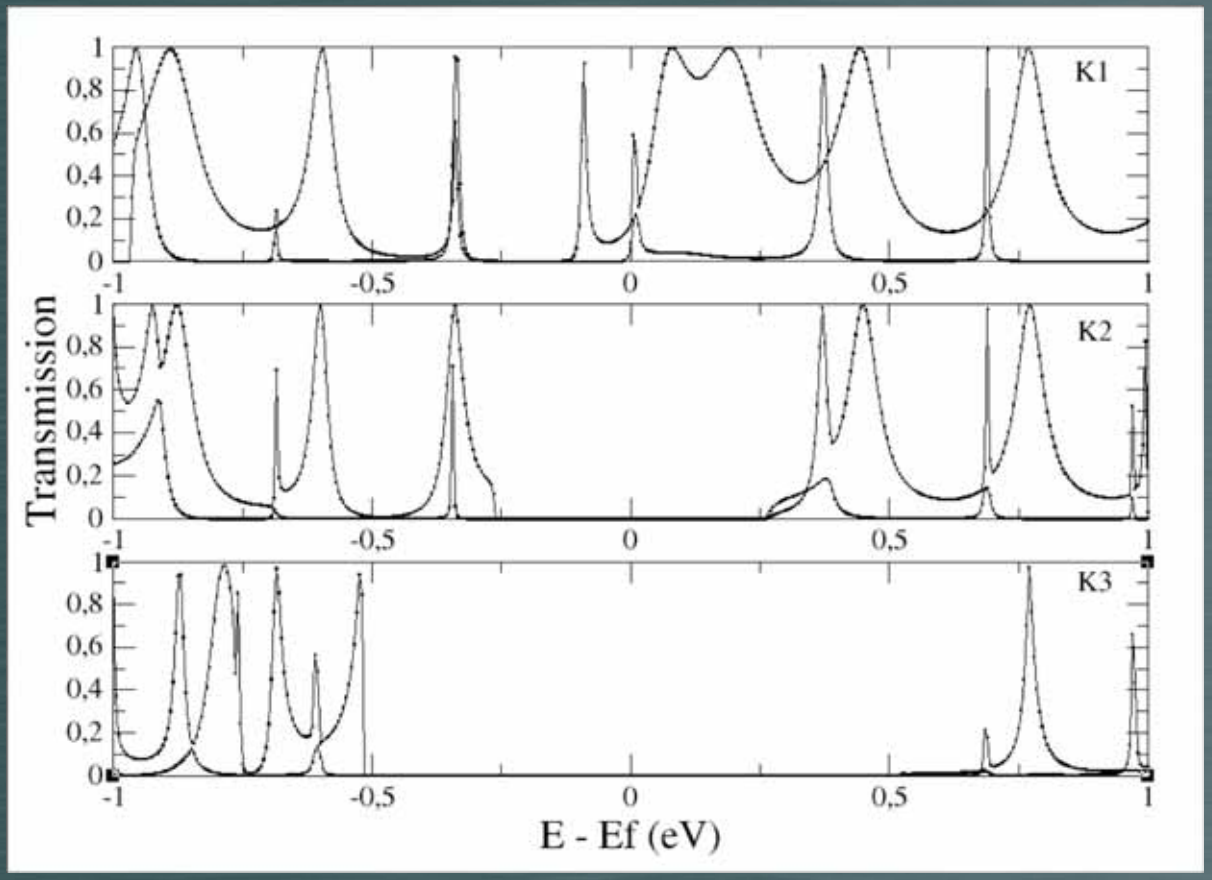
CONDUCTANCE vs. ENERGY

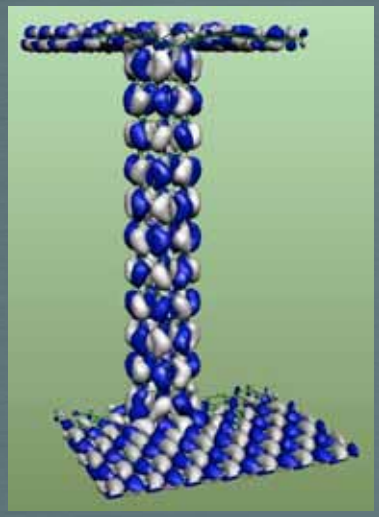
(4,4) tube, defect #9

Eigenchannel analysis: Two channels contribute to the resonances

Different positions and different coupling

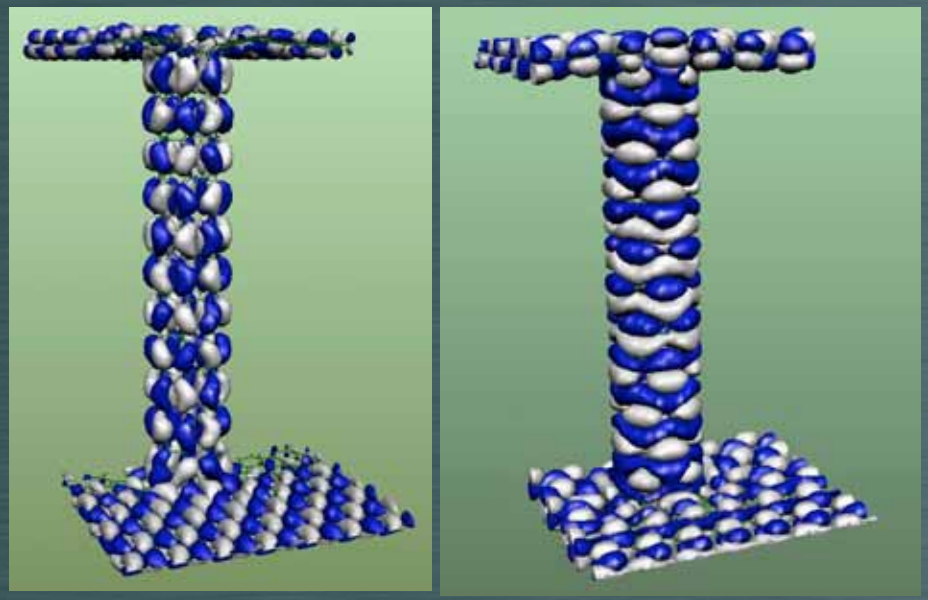


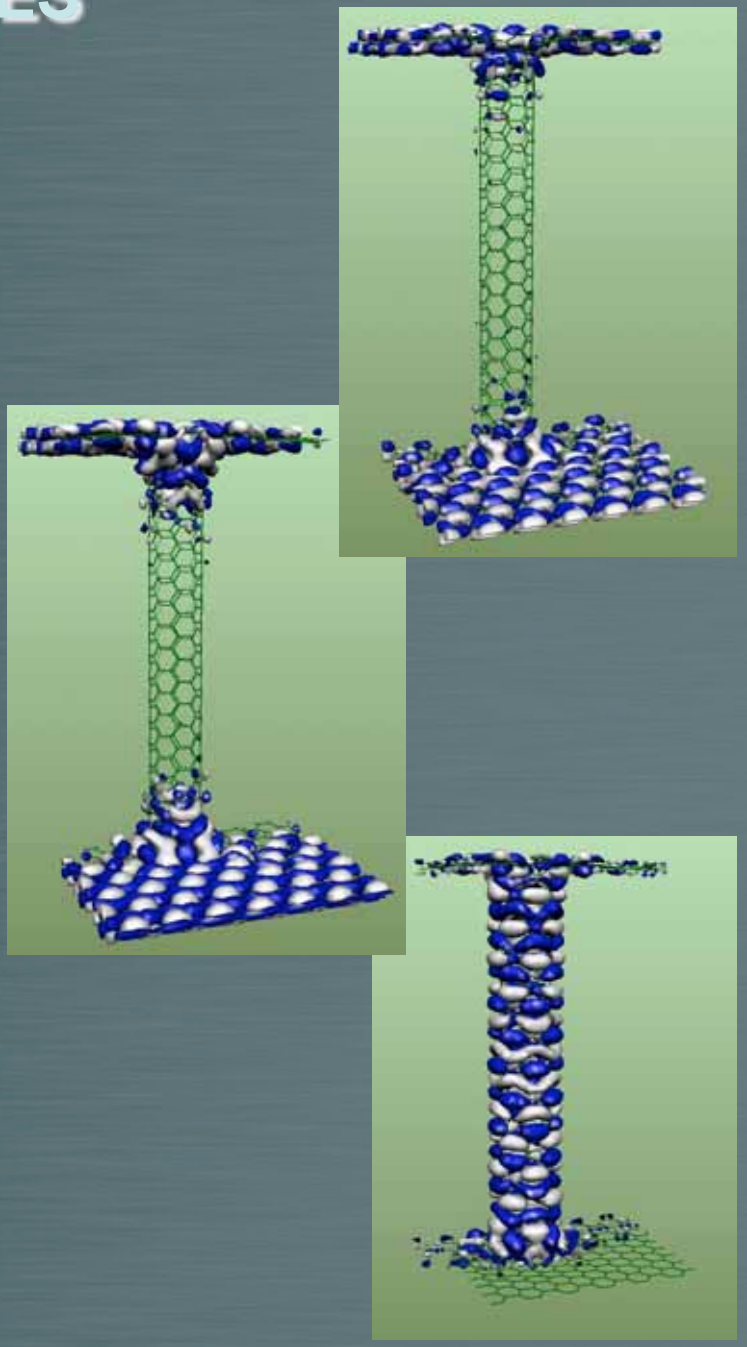




COUPLING OF ELECTRONIC STATES

(4,4) tube, defect #9

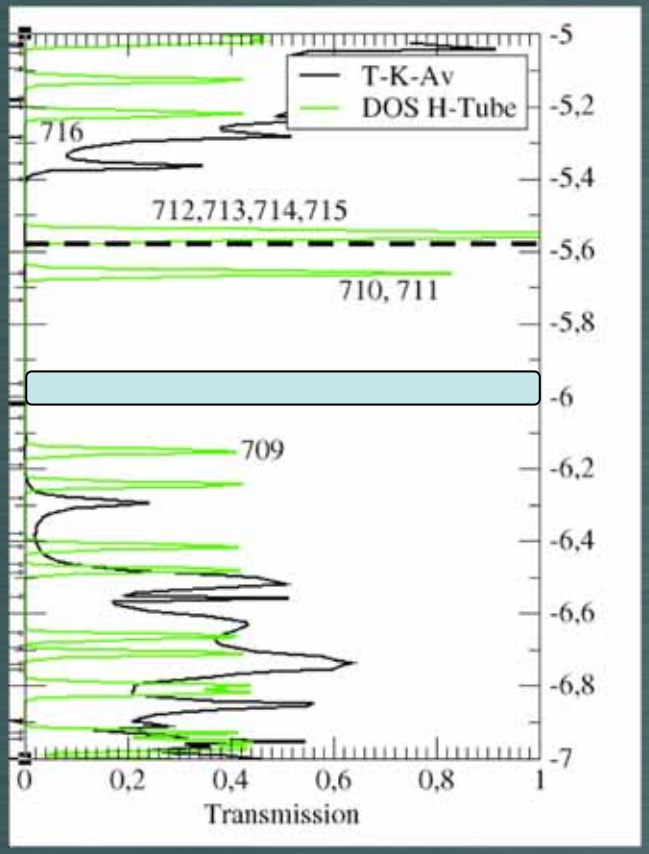




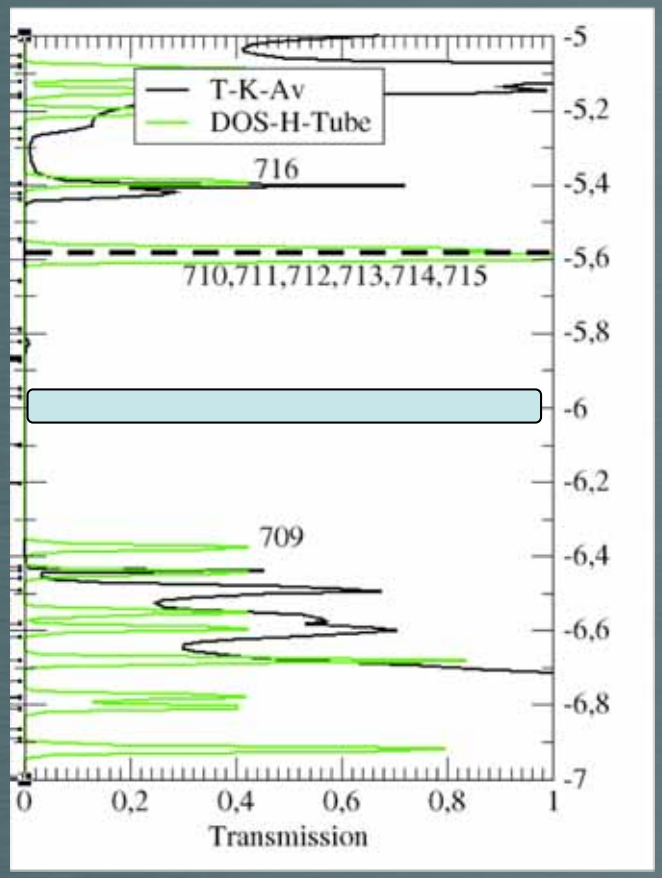
SEMICONDUCTING TUBES: BAND ALIGNEMENT

(8,0) tube

defect #3



defect #6



- Band alignment changes due to stress.
- Leads to different effective tunnel barriers, and to I vs length exponential decay with different exponent.

CONCLUDING REMARKS

- (Short) G / CNT / G bridges are conductive, even between (undoped) semiconding tubes.
- For metallic tubes:
  - For most contacts, the conductance is very good, showing a structure of resonances with T=1. These resonances originate on the discrete level structure of the *finite* nanotube.
  - For very long nanotubes, we expect a conductance of nearly $2G_0$ for a wide range of energies
  - Roughly, the conductance does not depend on the length, indicating delocalized wave functions and ballistic transport.
  - However, the detailed values of the conductance depend on the contact structure (defects), nanotube length and anchoring position at the graphene layer (distance to edge).
- For semiconducting tubes:
  - The conductance depends exponentially on the tube length, with a (nearly) common decay constant, indicating transport by tunneling. Resonances within the energy gap due to interface (defect) states.
  - The conductance depends on the contact structure, due to differences in the defect-induced interface states, and to different strains.

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