DSM

DÉPARTEMENT DE RECHERCHE FONDAMENTALE SUR LA MATIÈRE CONDENSÉE

Unconventional Mesoscopic Transport in Carbon Nanotubes

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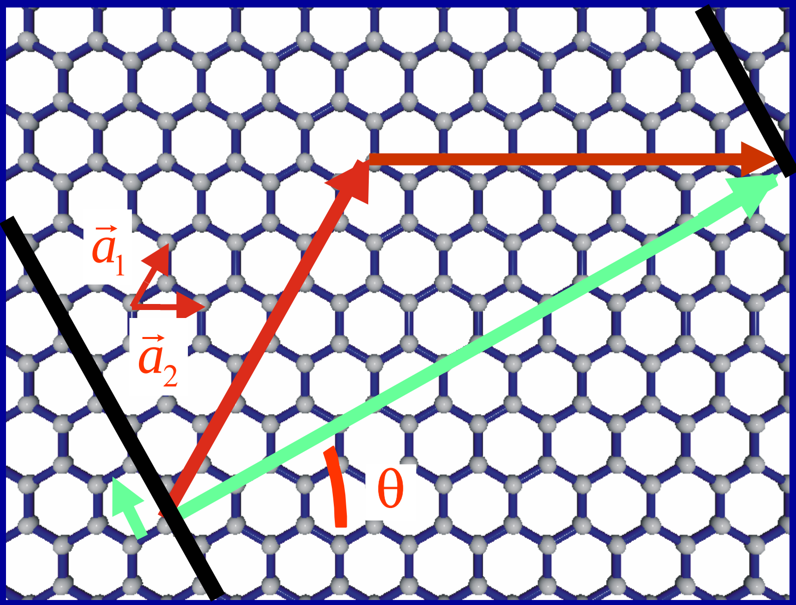
DSM/DRFMC/SPSMS

Regensburg Univ. Feb. 05

Synopsis

- Reminder - electronic properties of NTs
- Energy dependent transport length scales & quantum interferences
- Transport in Chemically doped nanotubes
- Transport features under molecular physisorption
- Anomalous conduction in defect-free MWNTs

From graphene to nanotubes



Helicity

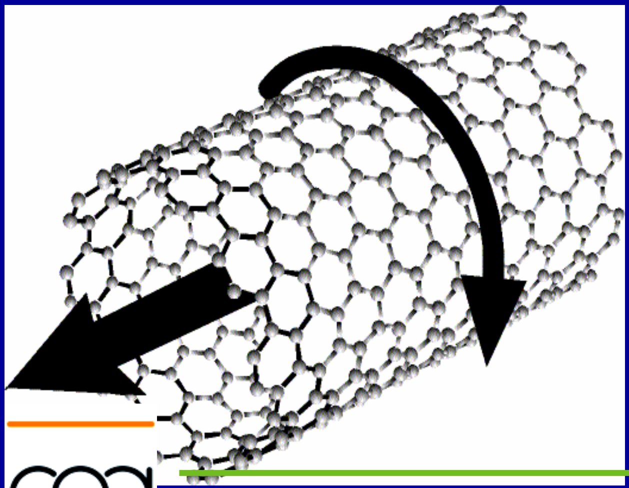
$$\vec{C}_{(l,m)} = l\,\vec{a}_1 + m\,\vec{a}_2$$

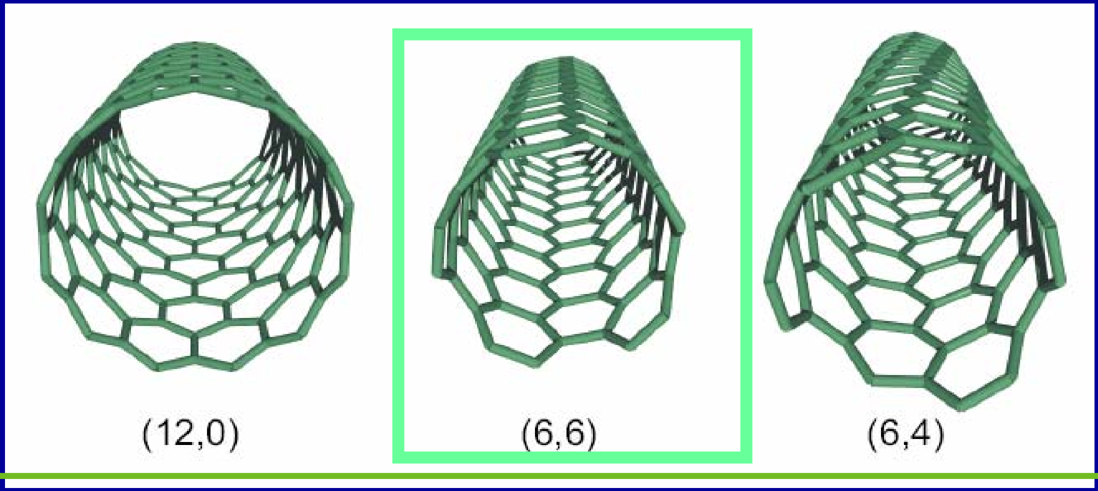
Diameter

$$d_{(l,m)} = \frac{\left|\vec{C}_{(l,m)}\right|}{\pi}$$

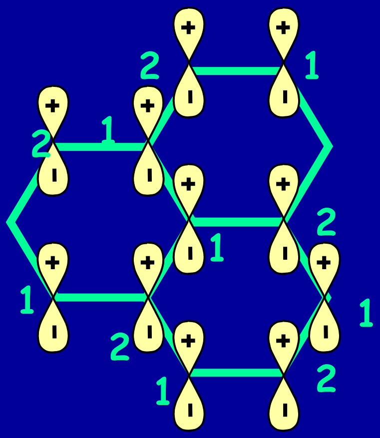
Unit cell length

$$\left|\vec{T}_{(l,m)}\right|$$





Effective π electrons-model



Hybrid molecular orbitals $sp_x p_y$, p_z

$sp_x p_y$ σ bonds (cohesion)

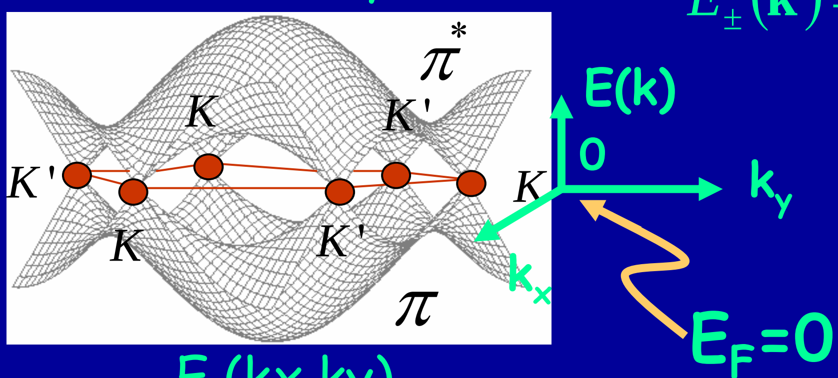
p_z π bonds (electronic properties close to E_F)

2 atoms/ unit cell - γ_0 coupling between p_z orbitals

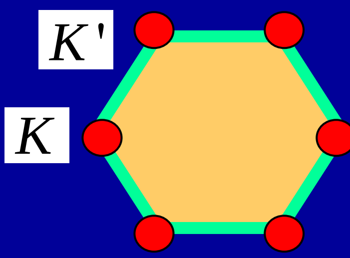
$$H(\mathbf{k}) = \begin{pmatrix} 0 & f(\mathbf{k}) \\ f^*(\mathbf{k}) & 0 \end{pmatrix} \qquad f(\mathbf{k}) = \gamma_0 \sum_{\alpha} \exp(i\mathbf{k}.\tau_\alpha)$$

$$E_{\pm}(\mathbf{k}) = \pm\gamma_0 \left[3 + 4\cos\left(\frac{\sqrt{3}}{2}k_x a\right)\cos\frac{k_y a}{2} + 2\cos k_y a \right]^{1/2}$$

$E_+(kx,ky)$

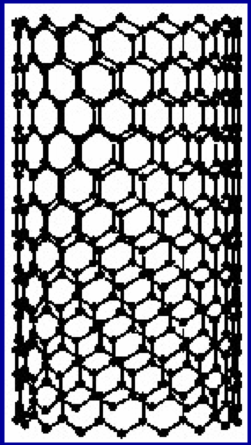


$E_-(kx,ky)$



1th Brillouin Zone

Nanotubes



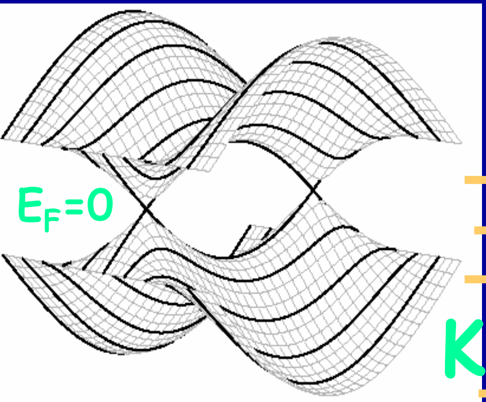
Periodic boundary conditions

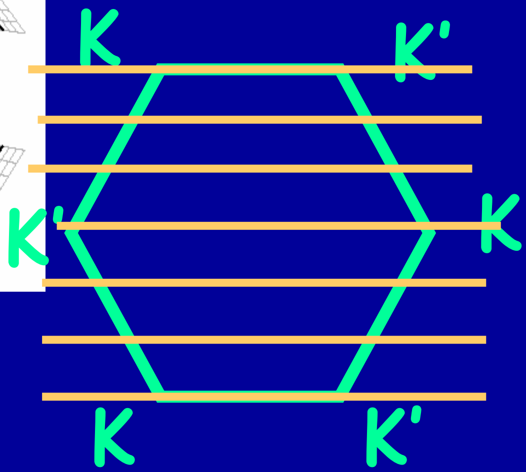
$$\frac{-\pi}{\left|\vec{T}_{(l,m)}\right|} \le k_y \le \frac{\pi}{\left|\vec{T}_{(l,m)}\right|}$$

$$k_x = \frac{2\pi q}{\left|\vec{C}_{(l,m)}\right|} \quad (q = 1, N)$$

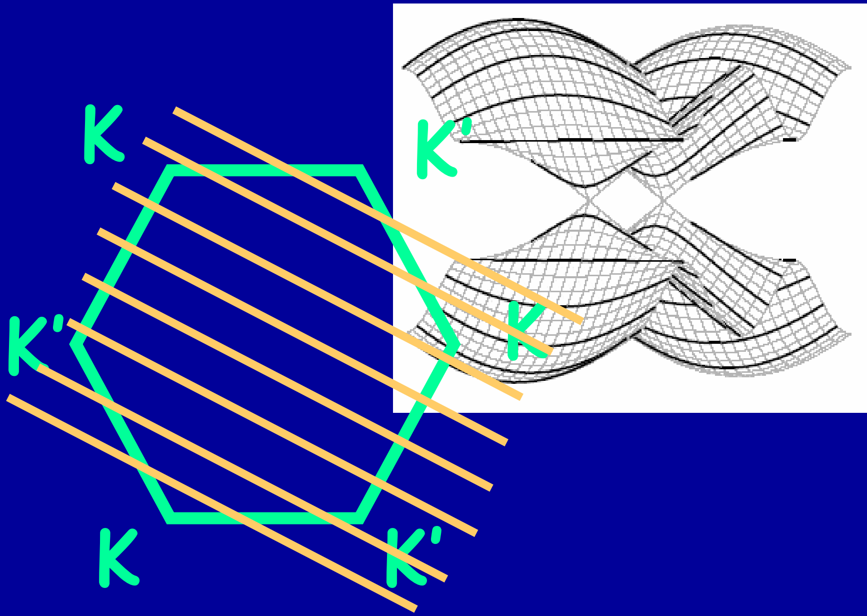
Helicity

$$\vec{C}_{(n,n)} = \mathrm{n}\left(\vec{\mathrm{a}}_1 + \vec{\mathrm{a}}_2\right) \qquad \vec{C}_{(l,m)} = (3\mathrm{p} \pm 1)\,\vec{\mathrm{a}}_1$$



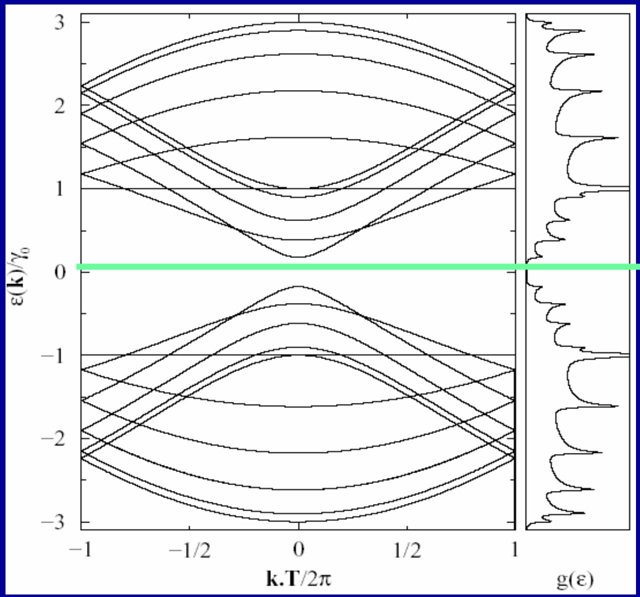


$2\pi / \left|\vec{C}_{(l,m)}\right|$

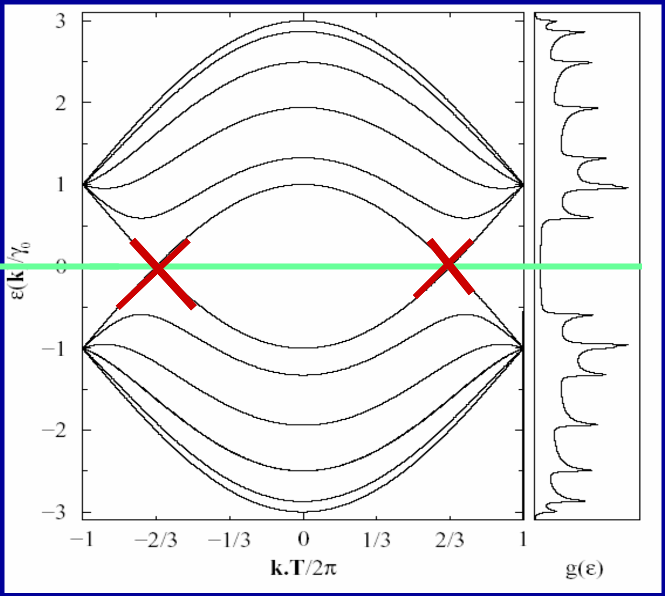


Metal & Semiconductor

Semiconducting NT (10,0)



Metallic nanotube (5,5)



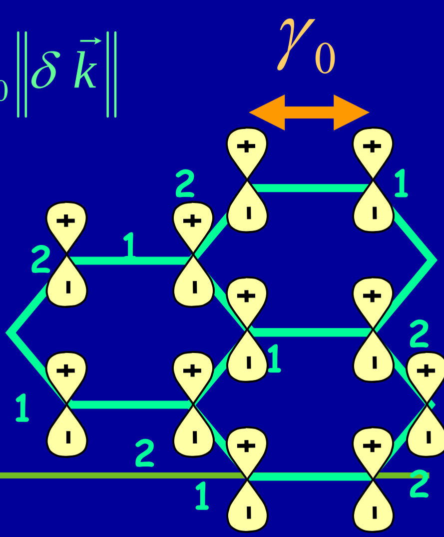
E_F

$$E_+(k=0) - E_-(k=0) \equiv \frac{2\pi a \gamma_0}{\sqrt{3}\left\|\vec{C}_h\right\|}$$

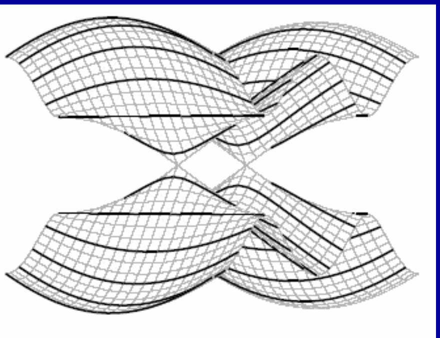
$d_t = 1.4\,\text{nm} \rightarrow \Delta_g = 0.59\,\text{eV}$

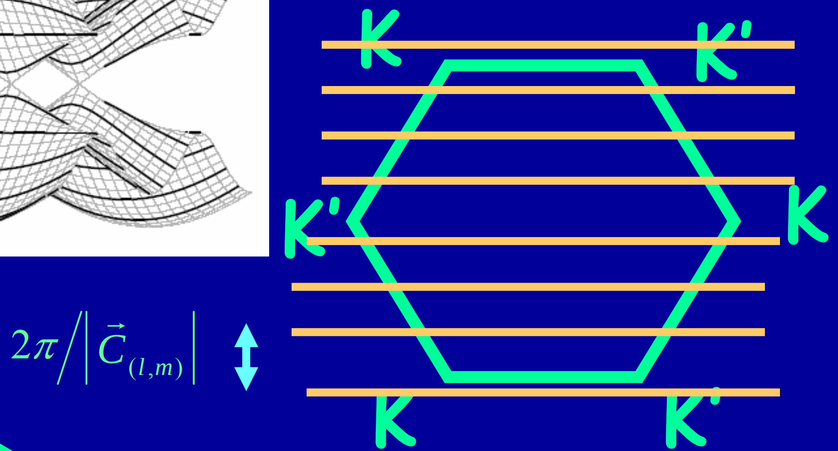
$$E_\pm(\delta k) \equiv \pm \frac{\sqrt{3}a}{2} \gamma_0 \left\|\delta \vec{k}\right\|$$

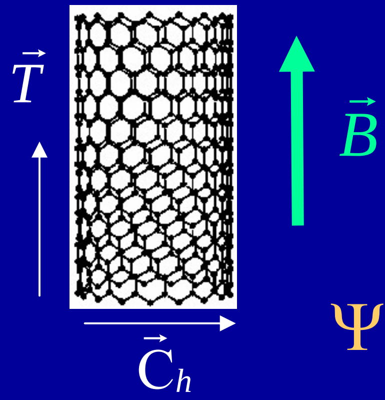
$$\hat{H} = \gamma_0 \sum_{<i,j>} \left| p_\perp^j \right\rangle \left\langle p_\perp^i \right|$$



Nanotubes & Aharonov-Bohm



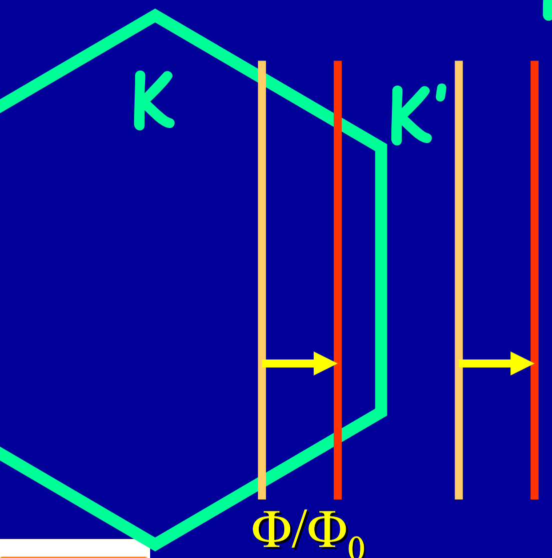




Wavefunction phase

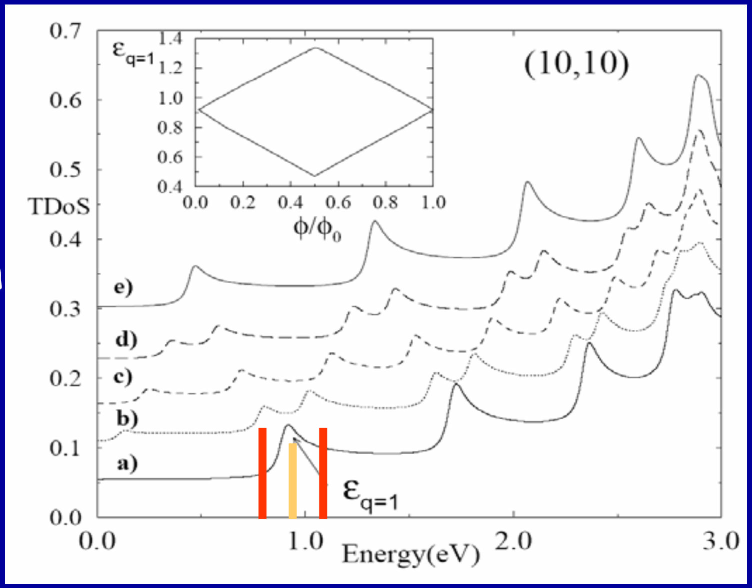
$$\Psi \approx e^{ik_y y} e^{i\left(k_x x + \frac{e}{h}\int \vec{B} dS\right)}$$

$$k_x = \frac{2\pi q}{C_h} + \frac{2\pi\Phi}{\Phi_0}$$



Gap opening at CNP
with Φ_0-periodic modulation

Splitting of VHs
proportional to B



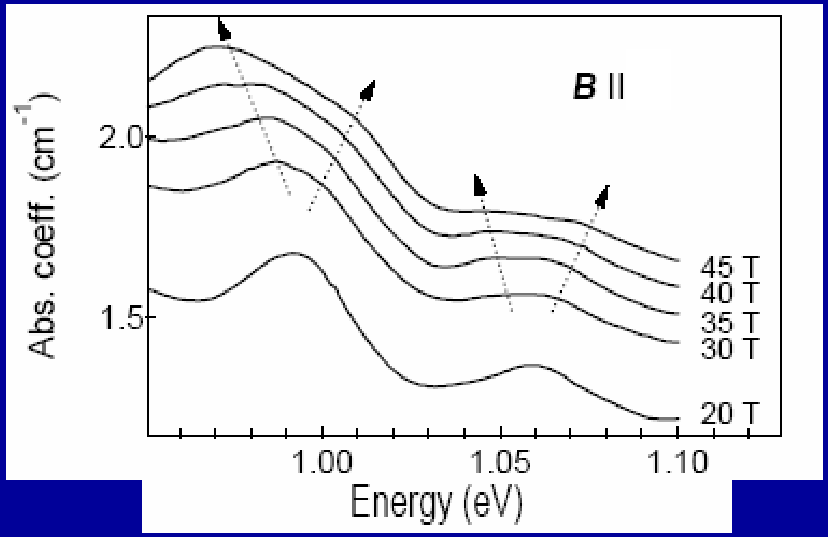
H.Ajiki and T. Ando, J. Phys. Soc. Jpn 62,1255 (1993)

S. R., G. Dresselhaus, M. Dresselhaus & R. Saito, Phys. Rev. B 62, 16092 (2000)

Optical signature

Magneto-optical spectrum for a bundle of
SWNT (diameter 1nm)
Bmax = 45 Tesla

Shifting and splitting of absorption peaks and photoluminescence
Linearly with Φ/Φ_0



30-40meV at 45T

Junichiro Kono et al.
Rice Quantum Institute (USA)

S. Zaric et al., Science 304, 1129 (2004)

Quantun Transport (compt. App)

Kubo-framework (linear resp. ohmic contact/coherent reg.)

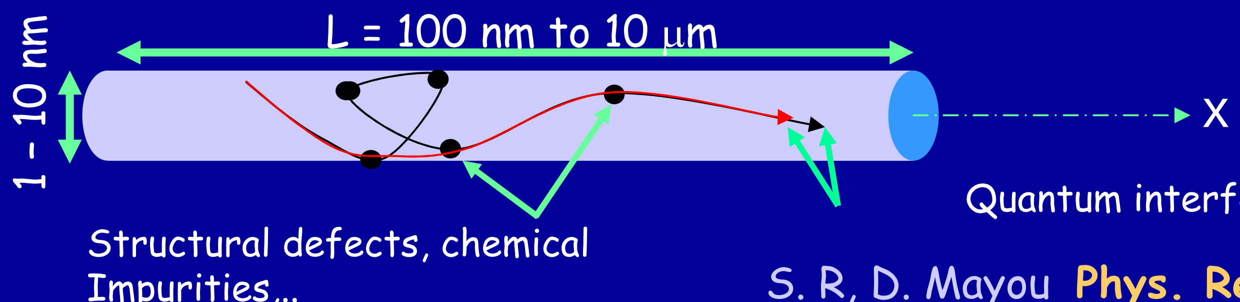
Solving **time dependent Schrödinger** equation

$$|\Psi(t)\rangle = \exp\left(-\frac{i\hat{H}t}{\hbar}\right)|\Psi_0\rangle \approx \sum_{n=0}^{N}\left(\int n(E)\, e^{\frac{-iEt}{\hbar}} Q_n(E)dE\right)Q_n(\hat{H})\,|\Psi_0\rangle$$

Transport coefficient computing (diffusion constant)

$$\frac{e^2 h}{\Omega} Tr\left[\hat{V}_x \delta(E-\hat{H})\hat{V}_x \delta(E-\hat{H})\right] \approx Tr\left[\delta(E_F-\hat{H})\frac{\left(\hat{X}(t)-\hat{X}(0)\right)^2}{t}\right]$$

Quantum dynamics of propagating wavepackets $D_E(t) = \frac{1}{t}\left\langle \{X(t)-X(0)\}^2 \right\rangle_E$



S. R, D. Mayou **Phys. Rev. Lett. 79, 2518 (1997)**
S. R, R. Saito **Phys. Rev. Lett. 87, 246803 (2001)**

Diffusion & Conductance-scaling

Transport regimes

$$D_E(t) = \frac{1}{t}\left\langle \{X(t) - X(0)\}^2 \right\rangle_E$$

Conductance scaling

$$G_E = \frac{2e^2}{L} \lim_{t \to \tau_L} Tr\left[\delta(E-H) D_E(t)\right]$$

τ_L : propagation time over L

Ballistic regime & Conductance quantization

$$D(t) \approx v_F^2 t \quad \Rightarrow \quad G_E = \frac{2e^2}{h} N_E$$

Diffusive regime & mean free path

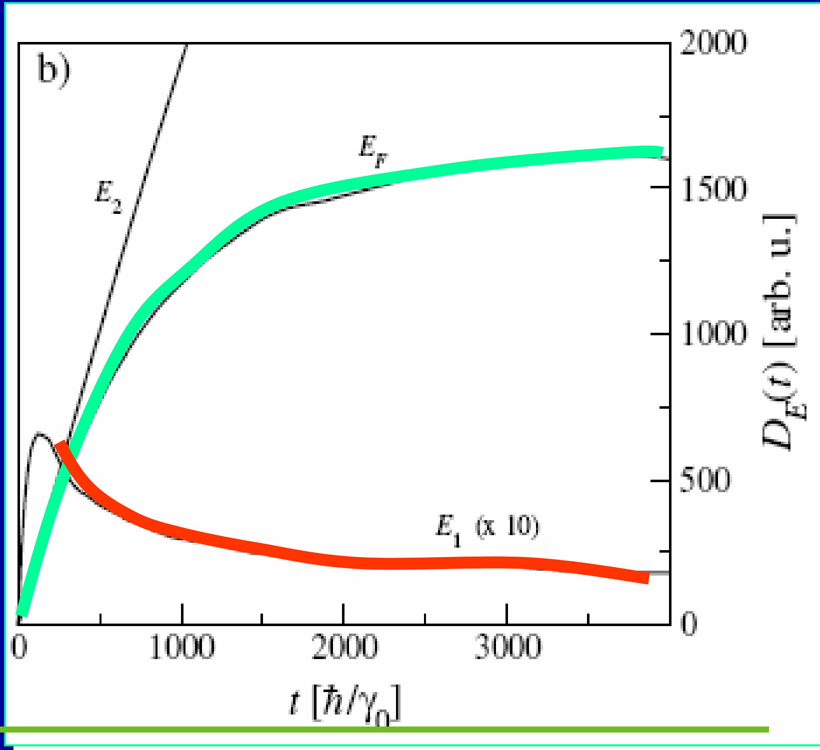
$$D(t > \tau) \approx v_F l_e \Rightarrow \quad G_E = \frac{2e^2}{h} \frac{l_e}{L_{sys}}$$

Quantum interference effects

Weak & Strong localization effects

Correction & exponential decrease of cond.

$$G_E = \frac{2e^2}{h}\left(\frac{l_e}{L_{sys}} - \delta\sigma\right) \qquad G_E = \frac{2e^2}{h} \exp\left(-\frac{l_e}{L_{sys}}\right)$$

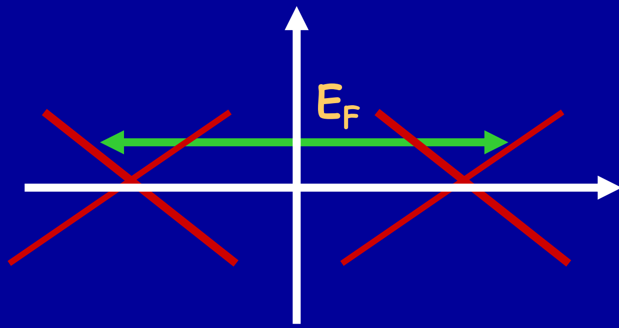


Mean free path of metallic tubes

Elastic scattering time and Fermi golden rule

$$\frac{1}{2\tau(\mathrm{E_F})} = \frac{2\pi}{\hbar}\left|\langle\Psi_{n1}(k_F)\right|\ \hat{\mathrm{U}}\left|\Psi_{n2}(-k_F)\rangle\right|^2 \rho(\mathrm{E_F})N_c N_{ring}$$

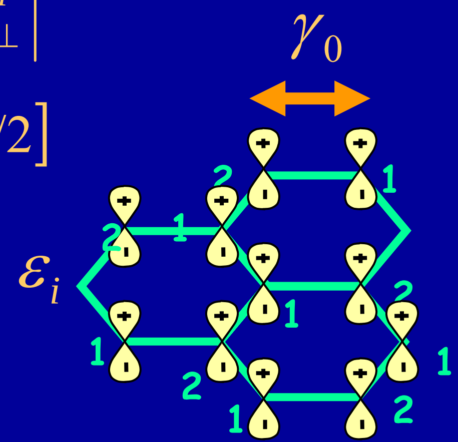
Mean free path $\ell_e = \mathrm{v_F}\tau \quad \left(\mathrm{v_F} = \sqrt{3}a\gamma_0 / 2\hbar\right)$



Anderson-type disorder $\hat{H} = \gamma_0 \sum_{<i,j>} \left| p_\perp^j \right\rangle\left\langle p_\perp^i \right| + \sum_{<i>} \varepsilon_i \left| p_\perp^i \right\rangle\left\langle p_\perp^i \right|$

Vicinity of CNP

$\varepsilon_i \in [\text{-}\ \mathrm{W}/2, \mathrm{W}/2]$



$$\ell_e = \frac{18}{\sqrt{3}}\left(\frac{\gamma_0}{W}\right)^2 \left\| \vec{C}_\mathrm{h} \right\|$$

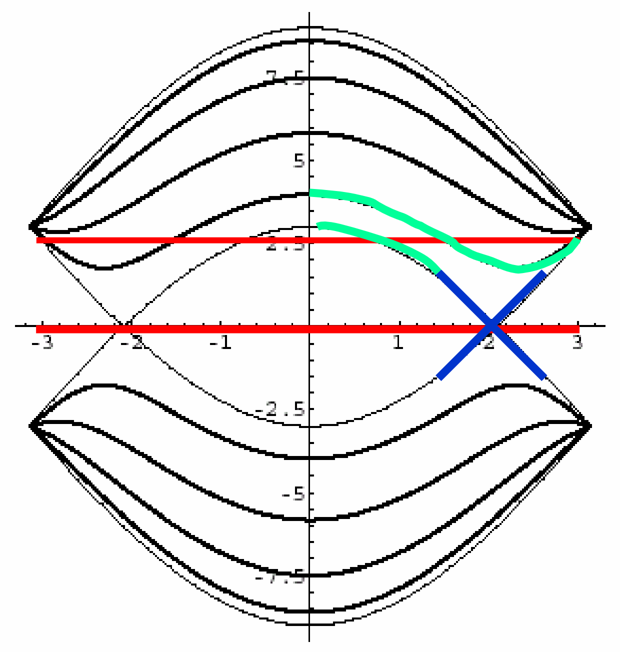
For a given disorder strength, the mean free path upscales with diameter!!!

C. White, T.N.Todorov, **Nature 393, 240 (1998)**

S. R., G. Dresselhaus, M. Dresselhaus & R. Saito, **Phys. Rev. B 62, 16092 (2000)**

Energy-dependent mean free path

(5,5) Energy

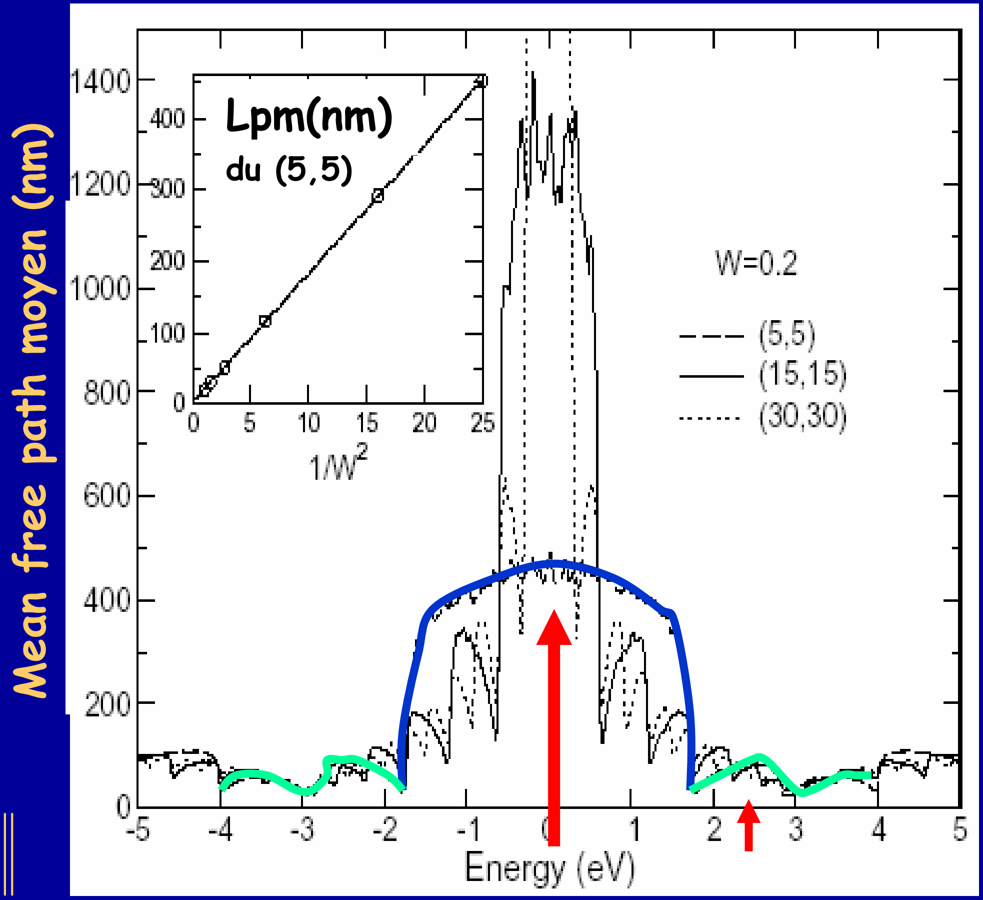


k

Charge neutrality point

$$\ell_e = \frac{18}{\sqrt{3}}\left(\frac{\gamma_0}{W}\right)^2 \| \vec{C}_h \|$$

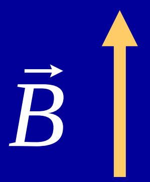
Under Fermi level shift

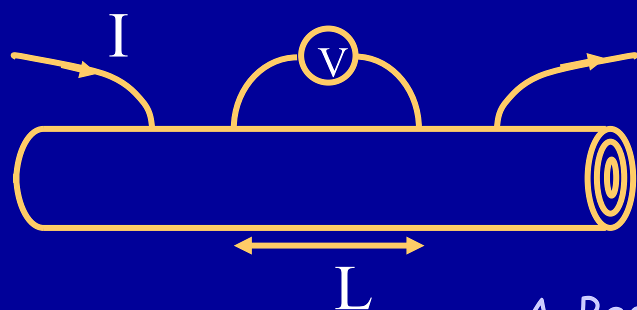


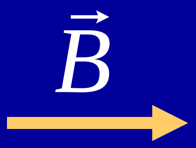
Energy (eV)

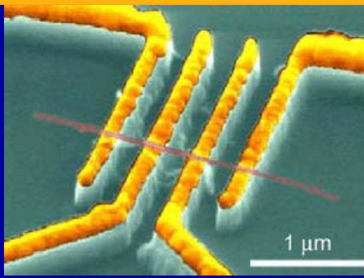
F. Triozon, S. R, A. Rubio, D. Mayou, **Phys. Rev. B 69, 121410 (2004)**

Magnetotransport (Quant. Interferences)



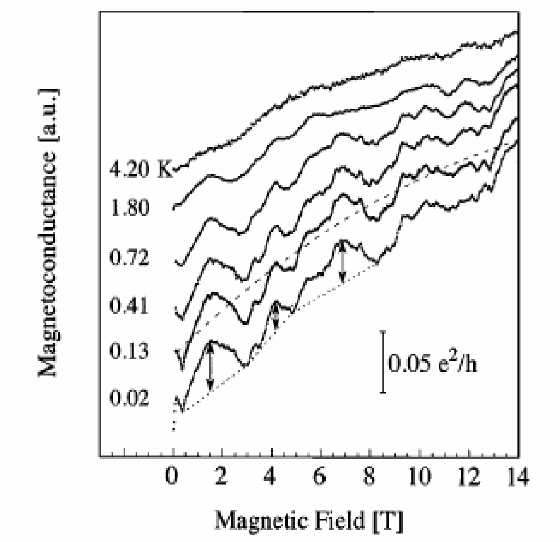


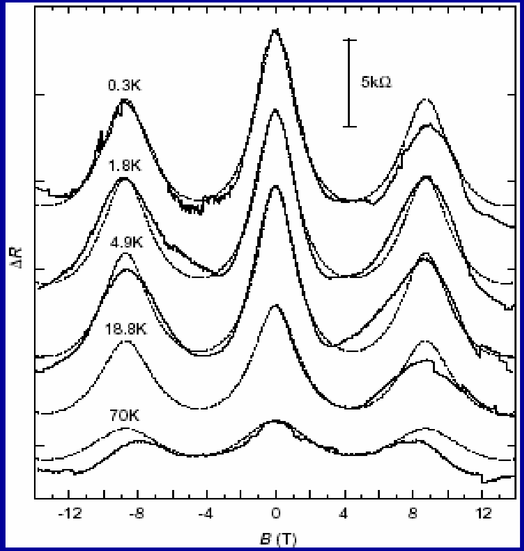




L. Langer et al,
Phys. Rev. Lett 76, 479 (1996)

A. Bachtold et al, **Nature 397, 673 (1999)**





Evidences for a weak localization regime

Negative Magnetoresistance
Universal Fluctuations of conductance

Negative MR
Φ_0 /2 -periodic AAS oscillations

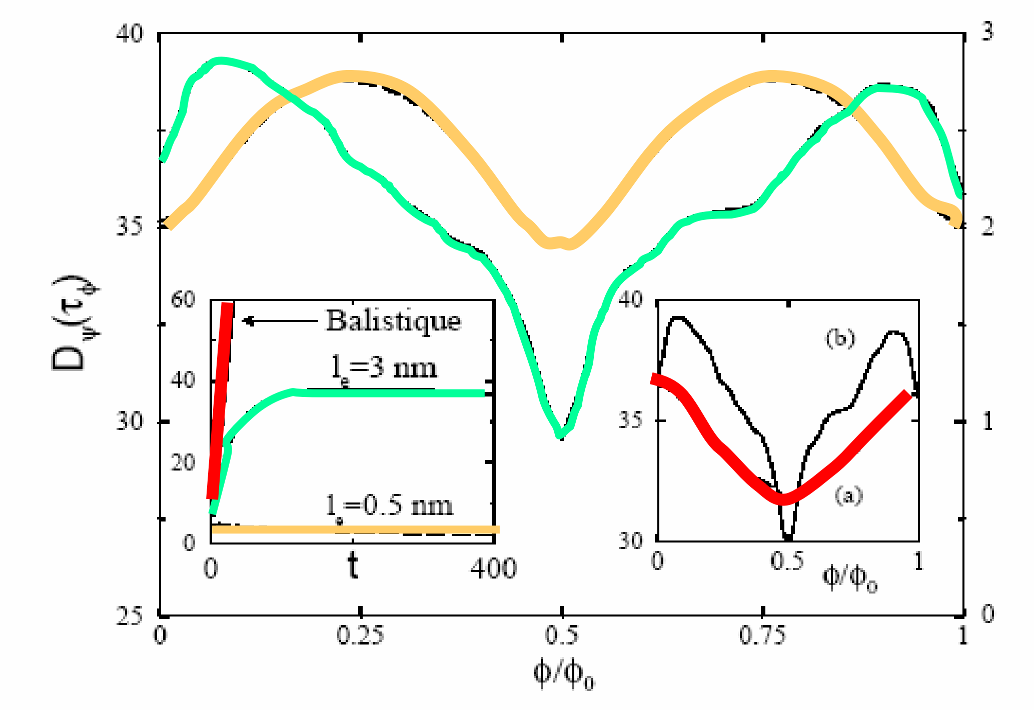
Magnetoresistance

Approximation : No effect of B on density of states

l_e < tube circonference
Negative MR
$\Phi_0/2$ - periodic AB oscillations

$L_{tube} > l_e$ > tube circonference
Negative MR
Φ_0 -periodic AB oscillations

$l_e > L_{tube}$
Positive MR
Φ_0 -periodic AB oscillations



S. R, F. Triozon, A. Rubio, D. Mayou,
Phys. Rev. B 64, 121401 (2001)

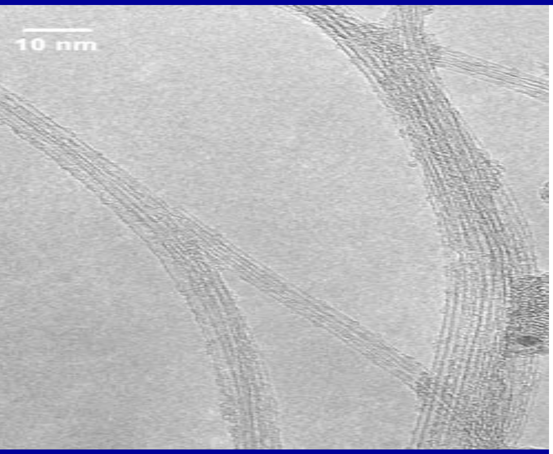
Doped nanotubes with Nitrogen (n-doped sc)

Incorporation of N_2(gas) during the synthesis

Defected multiwall nanotubes obtained (bamboo-shape)

R. Czerw *et al.* Nanoletters **1**, 457 (2001)

Bundles of Nitrogen-doped Single-wall nanotubes



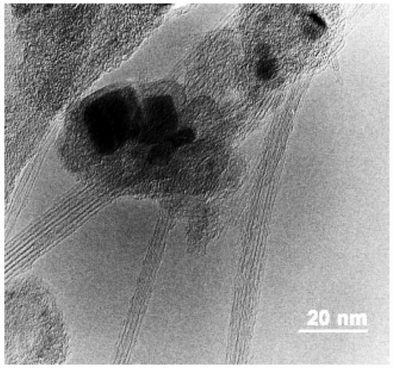


Fig. 2. HRTEM image of sample 4 (CN_x nanotubes, N = 1 at.%).

EELS spectrum

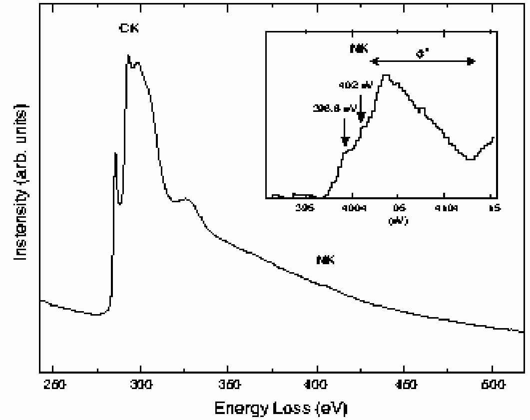


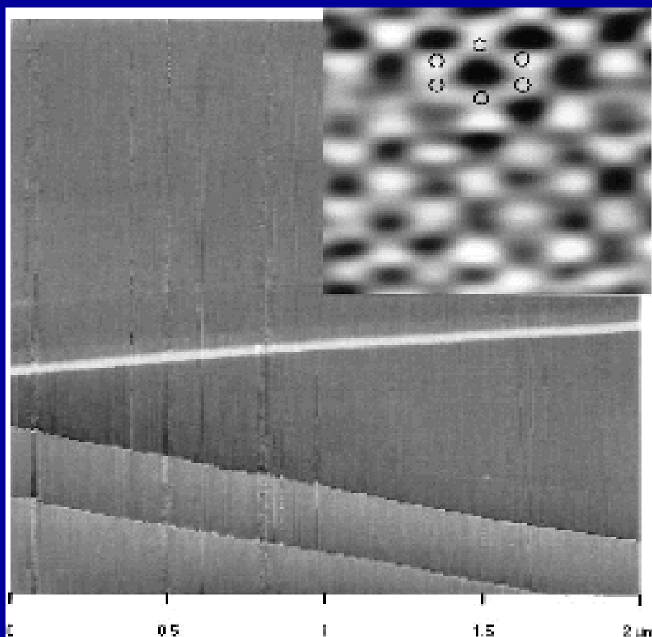
Fig. 3. EEL core electron K-shell spectra of CN_x nanotube bundles (sample 4). The nanotubes are doped with around 1 at.% nitrogen. For the C-K edge well defined π^* and σ^* fine structure features are observed which are evidences of sp^2-hybridisation in graphitic structures. The inset is a magnification of the N-K edge.

M. Glerup *et al.* Chem. Phys. Lett. **387**, 193 (2004).

Doped nanotubes with boron (p-doped sc)

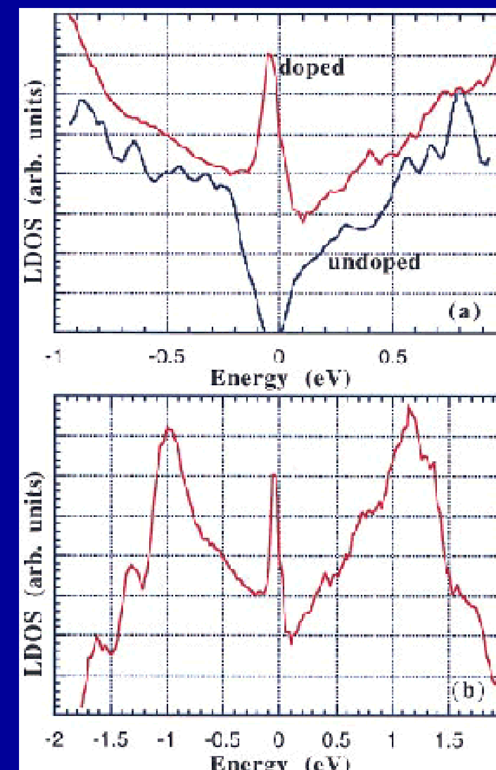
Incorporation of Boron (% 1 à 1.5) during synthesis

Long MWNTs (diameter ~ 10-20 nm)
with low disorder



D.L. Carroll *et al.* Phys. Rev. Lett. **81**, 2332 (1998),

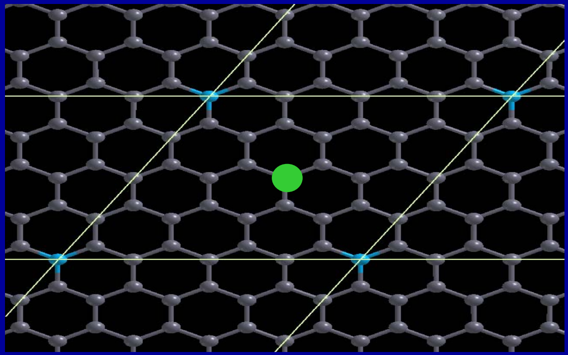
Density of states by tunneling spectroscopy (STS)



X. Blase *et al.* Phys. Rev. Lett. **83**, 5078 (1999)

Hetero-atomic compounds

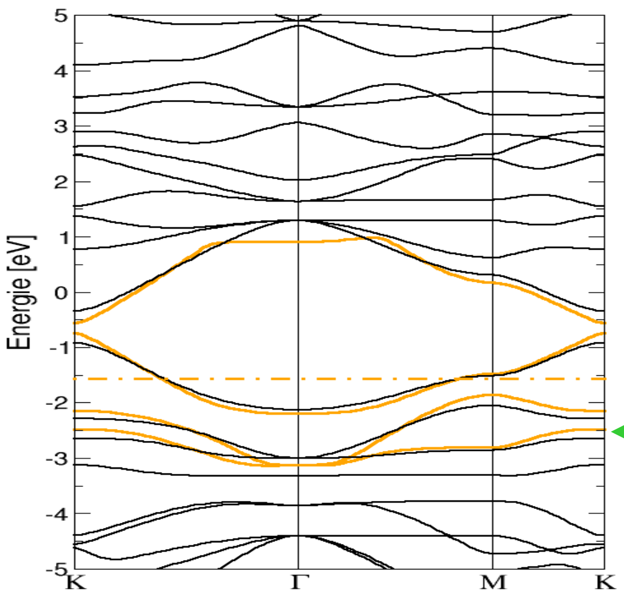
Doped nanotubes - case of Boron



Bandstructure (DFT) for a unit cell with 31 atomes C and 1 impurity (B or N)

Adjustement (fit) of tight-binding parameters up to second neighbors (for B or N)

Bandstructure



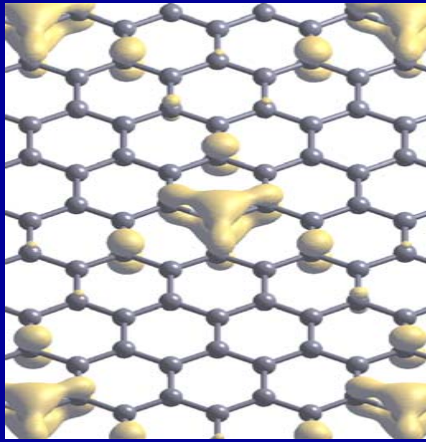
$$H = \sum_{i} \varepsilon_{i}^{q=1,P} \left| p_{\perp}^{i} \right\rangle \left\langle p_{\perp}^{i} \right| + \sum_{ij} \gamma_{0}^{k=1,M} \left| p_{\perp}^{i} \right\rangle \left\langle p_{\perp}^{j} \right|$$

Ab initio

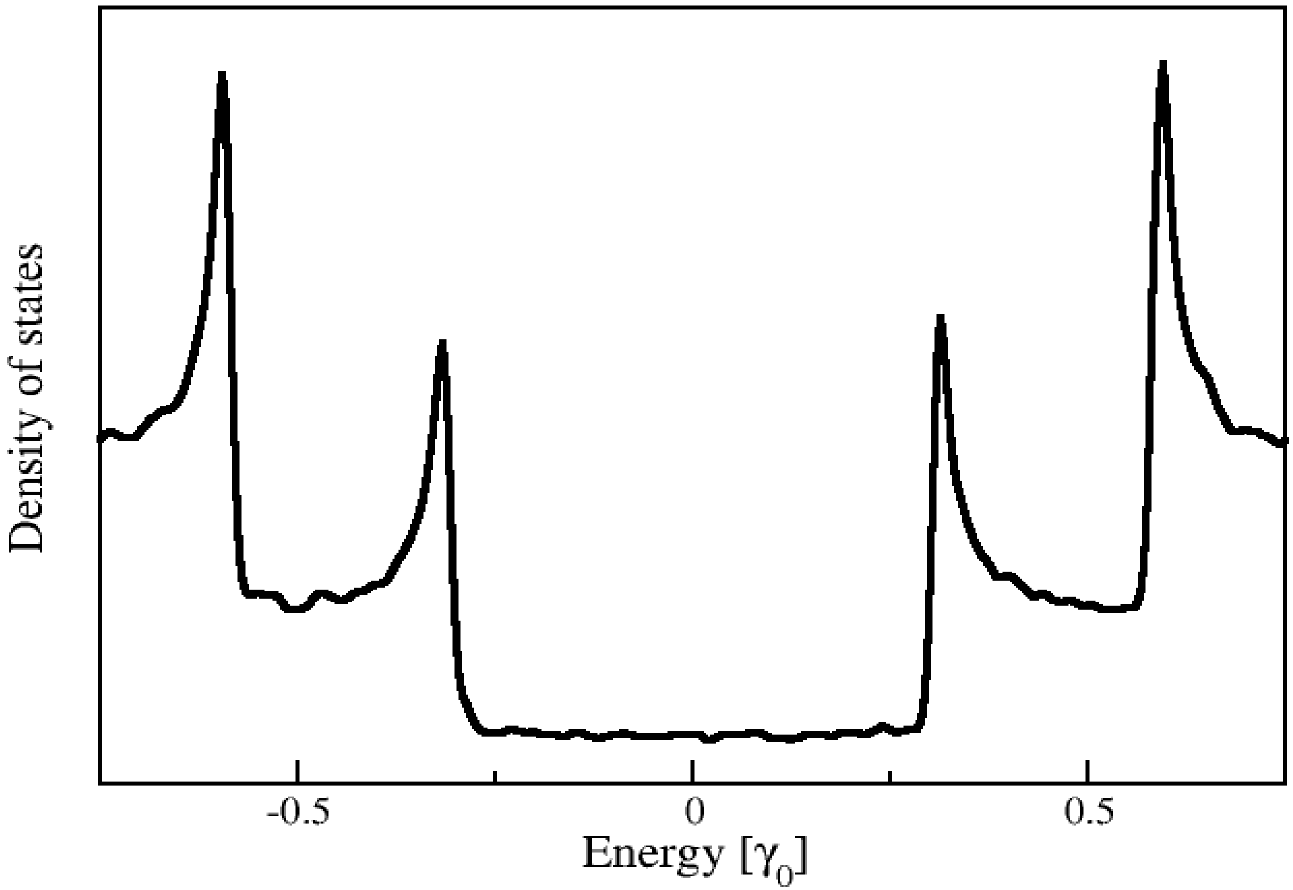
Tight-binding

Quasi-bonded states of Boron

(energy-dependent backscattering)

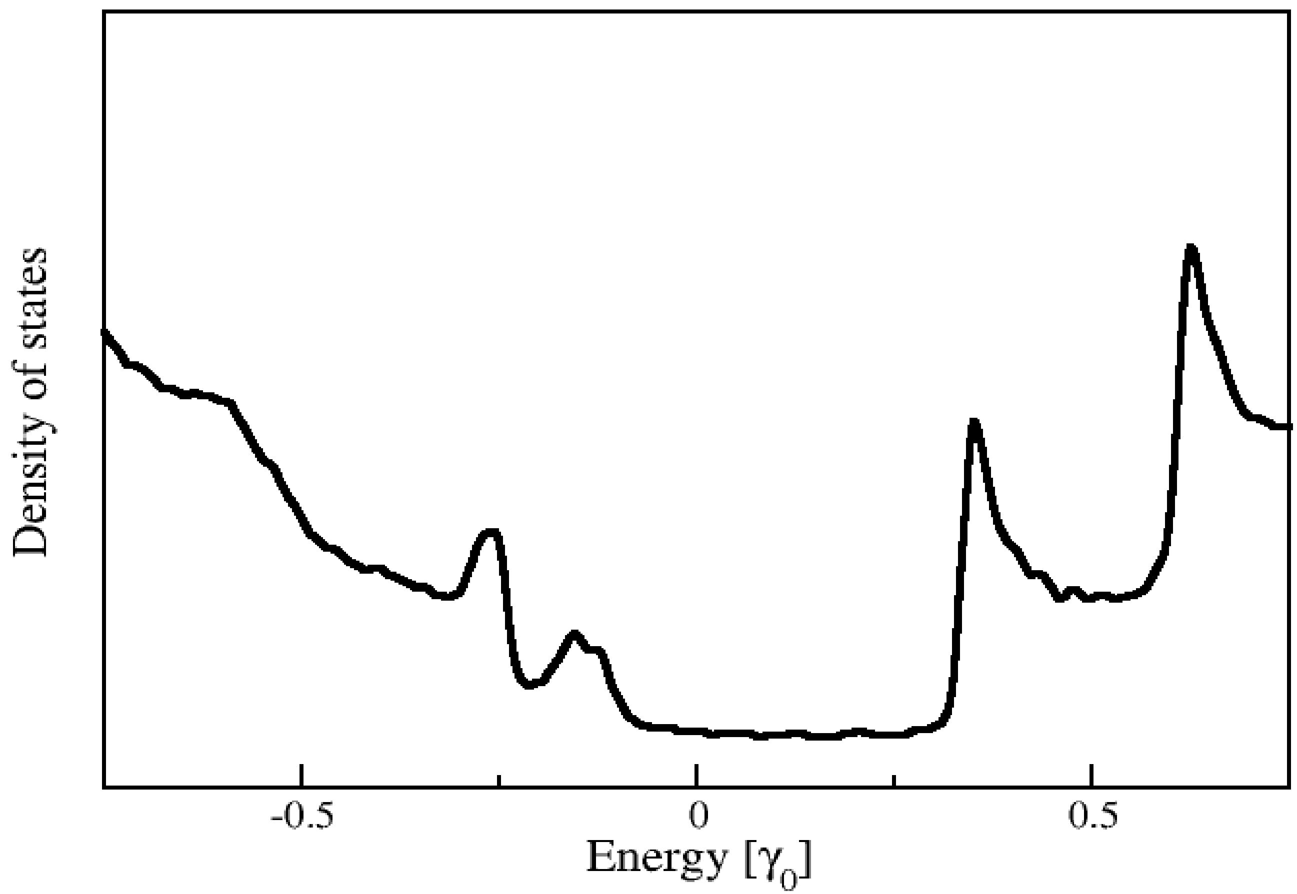


Nanotube (10,10) **BORON: 0.01 %**

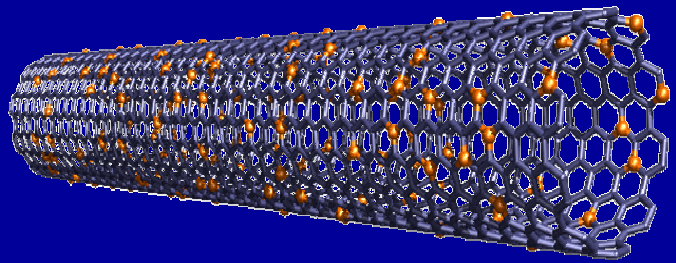


DoS effects of Boron substitution

Nanotube (10,10) **BORON: 0.5 %**

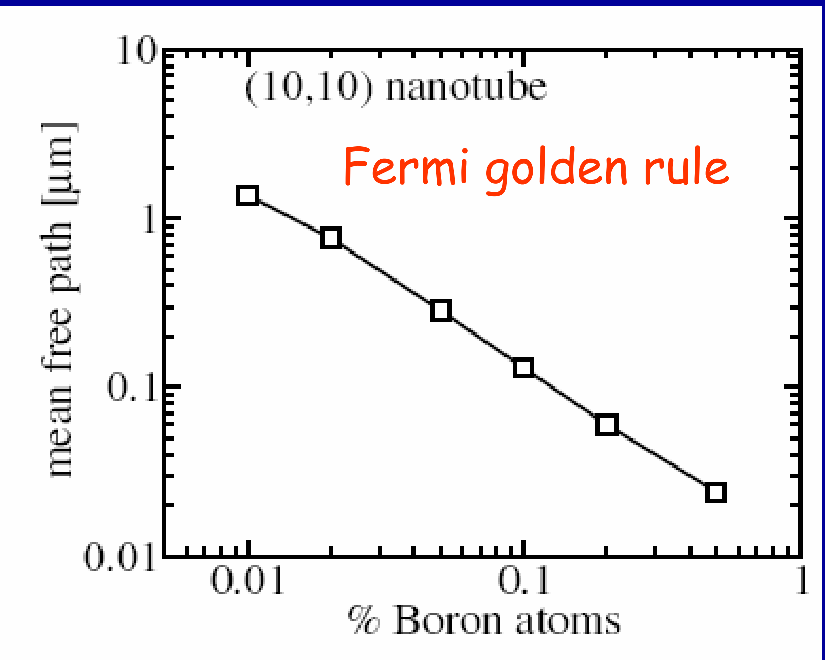


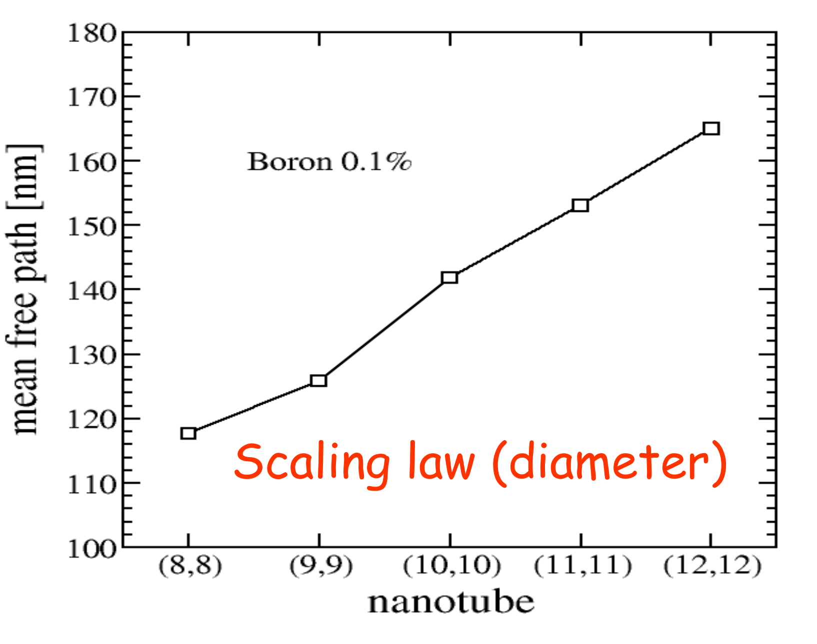
Scaling laws for mean free path



$$H = \sum_{i} \varepsilon_{i}^{q=1,P} \left| p_{\perp}^{i} \right\rangle \left\langle p_{\perp}^{i} \right| + \sum_{ij} \gamma_{0}^{k=1,M} \left| p_{\perp}^{i} \right\rangle \left\langle p_{\perp}^{j} \right|$$

Feature close to
Charge neutrality point





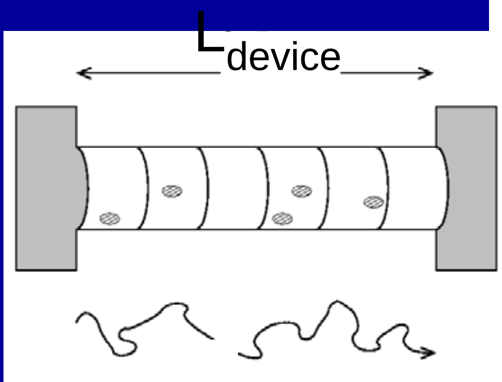
Good agreement with experimental
Estimates [0.1% Bore, 20nm diameter]
V. Krstic et al., PRB 67, 041401 (2003)

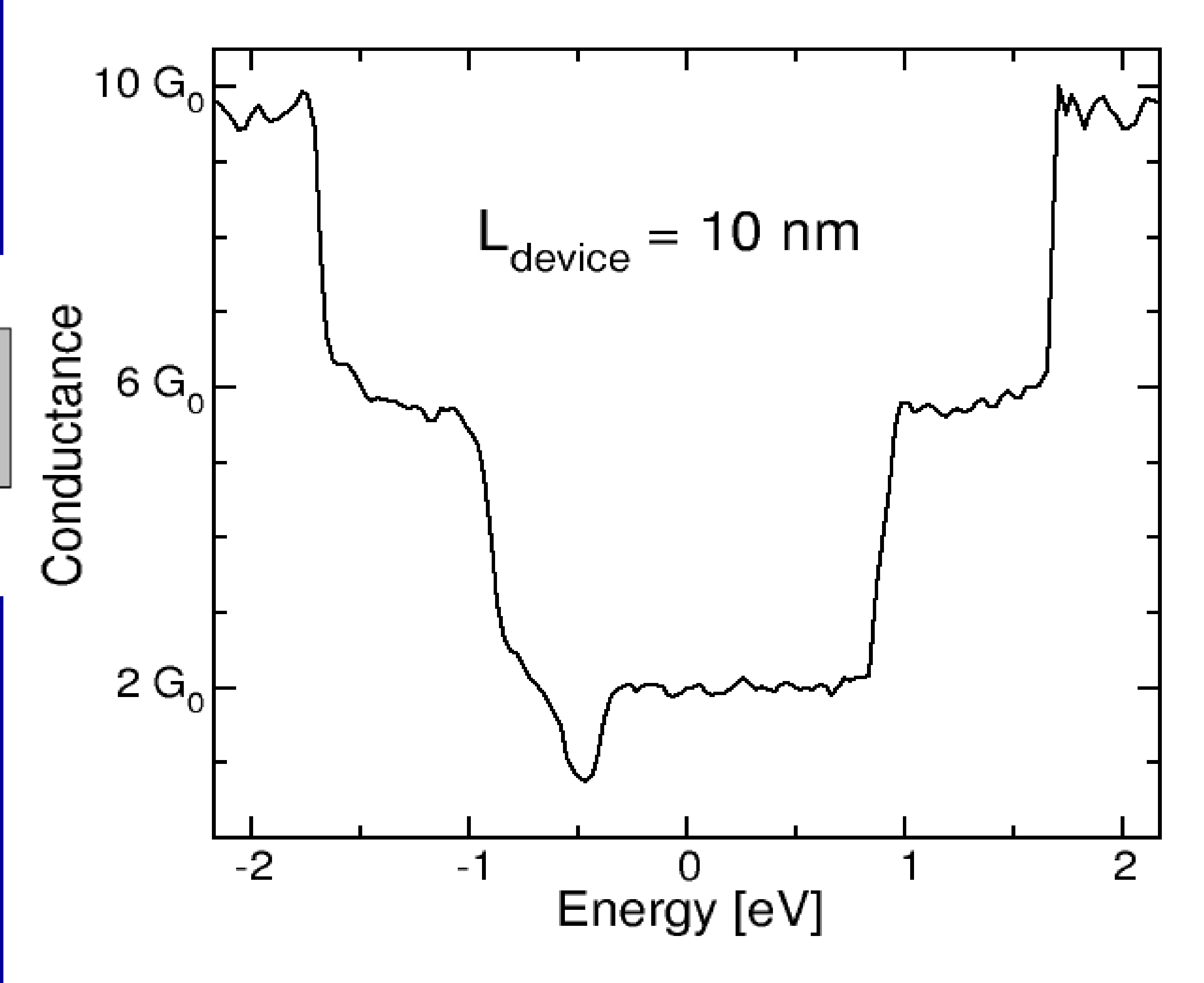
S. Latil, S. R, D. Mayou, J.C. Charlier,
Phys. Rev. Lett 92, 256805 (2004)

Metallic tubes (Boron doping)

Nanotube (10,10)

BORON: 0.1 %

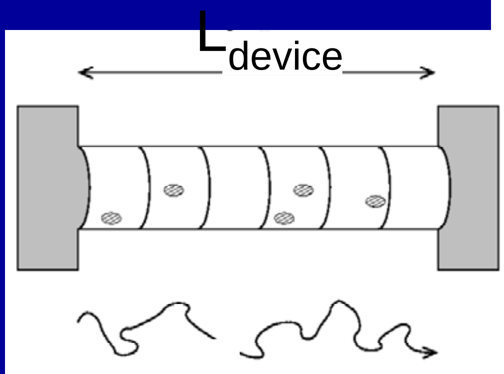


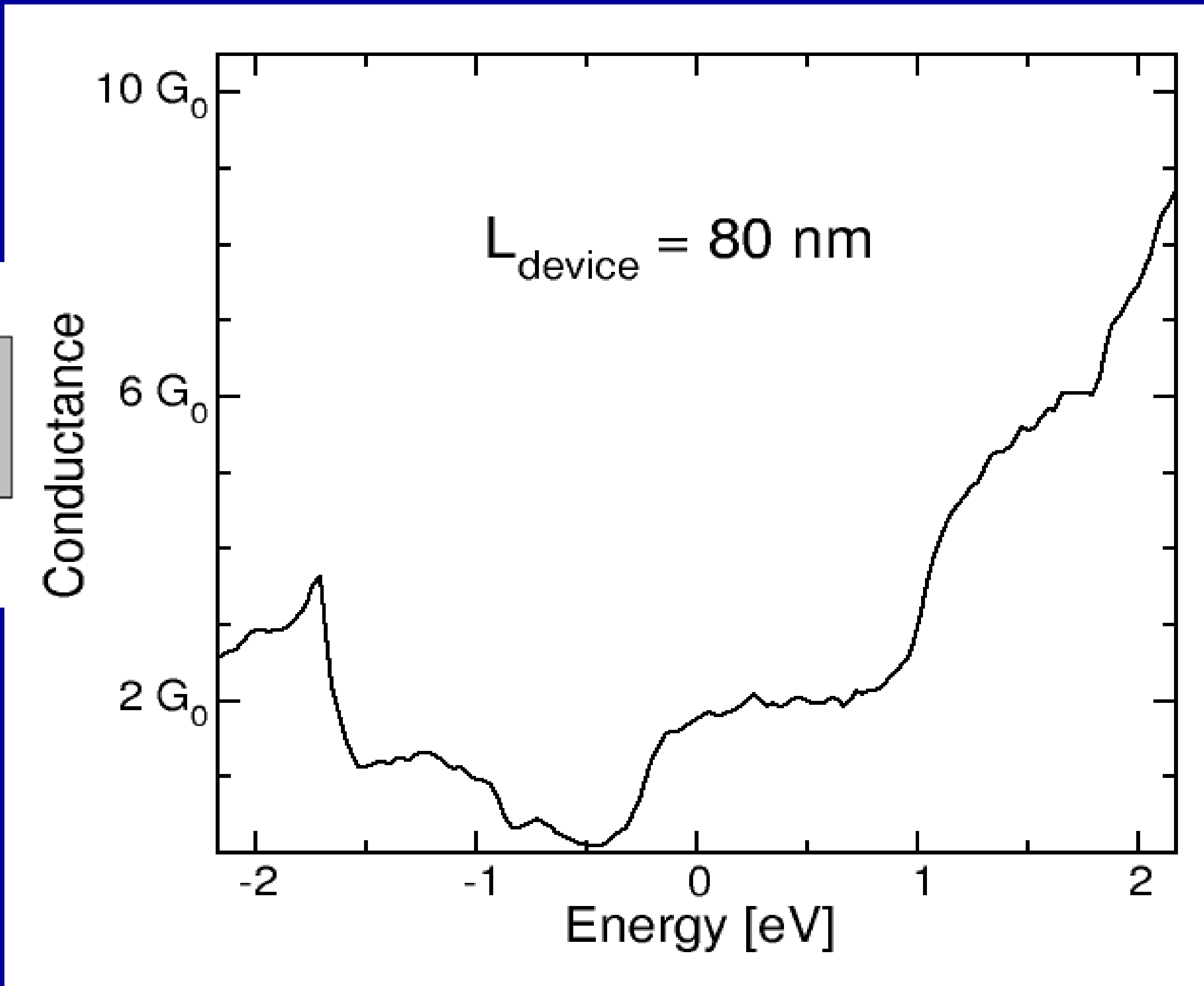


Metallic tubes (Boron doping)

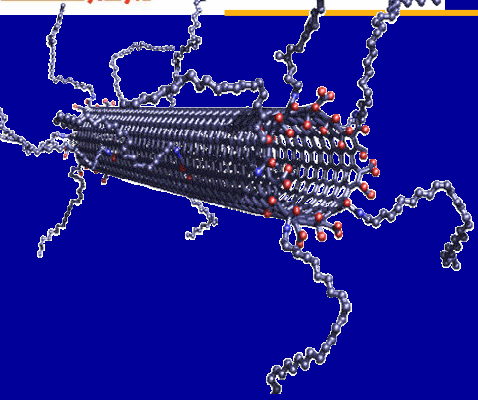
Nanotube (10,10)

Boron : 0.1 %



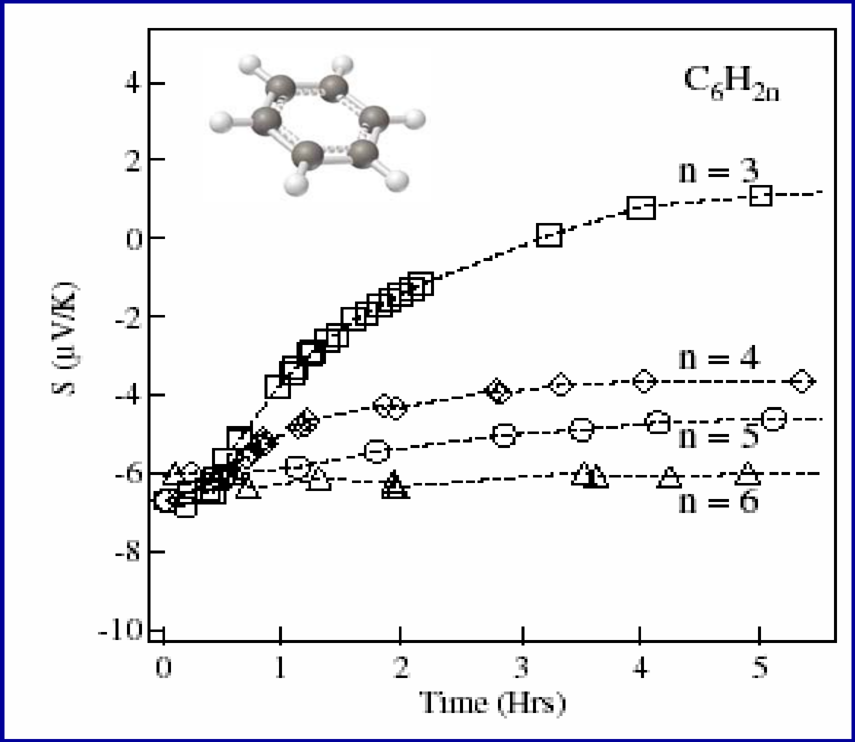


Molecular Physisorption



(Bio)-Chemical Sensitivity and Selectivity of electronic transport of Carbon nanotubes ??

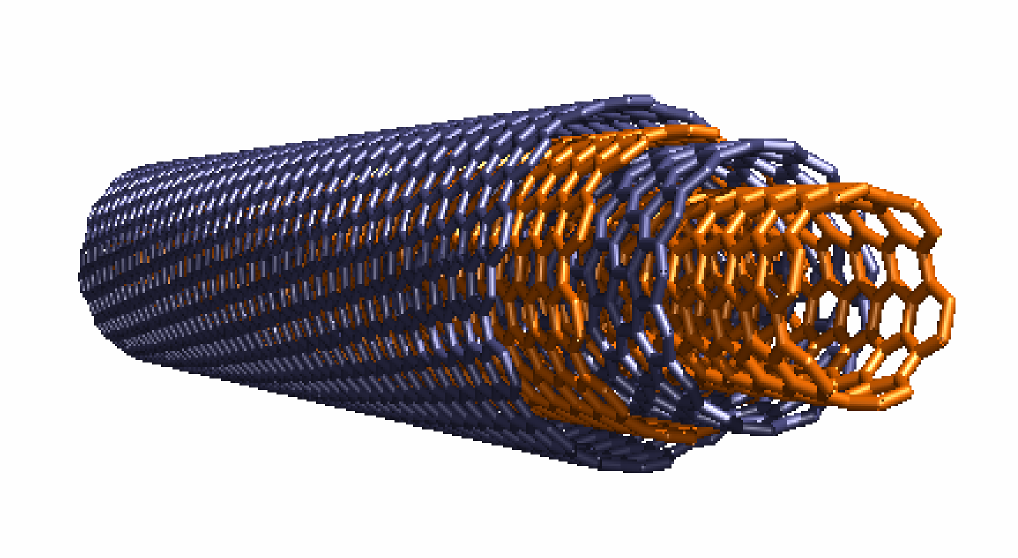
Giant variations of the Thermopower due to <u>Benzene</u> physisorption,..



G. Sumanakera et al.
Phys. Rev. Lett. 89, 166801 (2002)

$$S = -\frac{\pi^2 k_B^2 T}{3eG}\left\{\frac{d\,G(E)}{dE}\right\}_{E_F}$$

Multiwalled carbon tubes



Tight-binding model

γ_0 : intrashell coupling strength

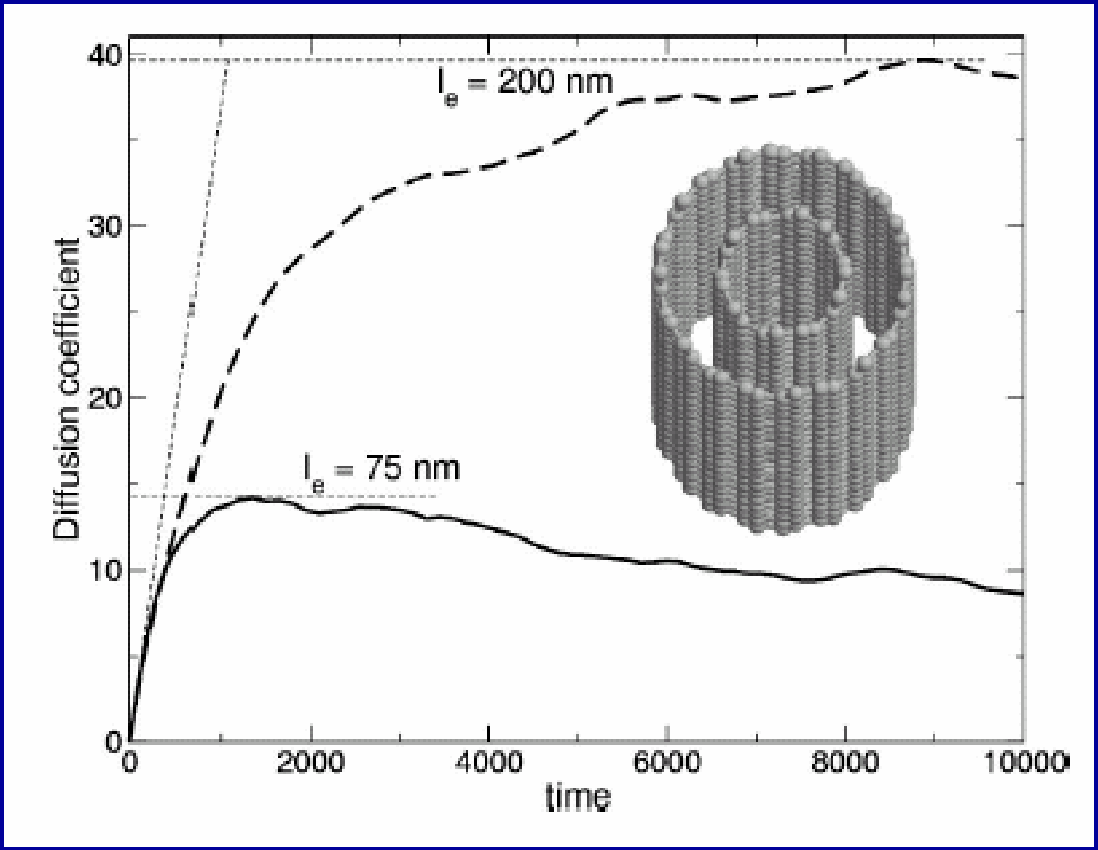
β : intershell coupling strength

J.C. Charlier & J.P. Michenaud,
Phys. Rev. Lett. 70, 1858 (1993)

$$\hat{H} = \gamma_0 \sum_{<i,j>} \left| p_\perp^j \right\rangle \left\langle p_\perp^i \right| - \beta \sum_{<<i,j>>} \cos(\theta_{ij}) \exp\left(\frac{d_{ij} - a}{\delta} \right) \left| p_\perp^j \right\rangle \left\langle p_\perp^i \right|$$

Is (and how) intershell coupling acting
on transport mechanism ????

Metallic double-wall tubes



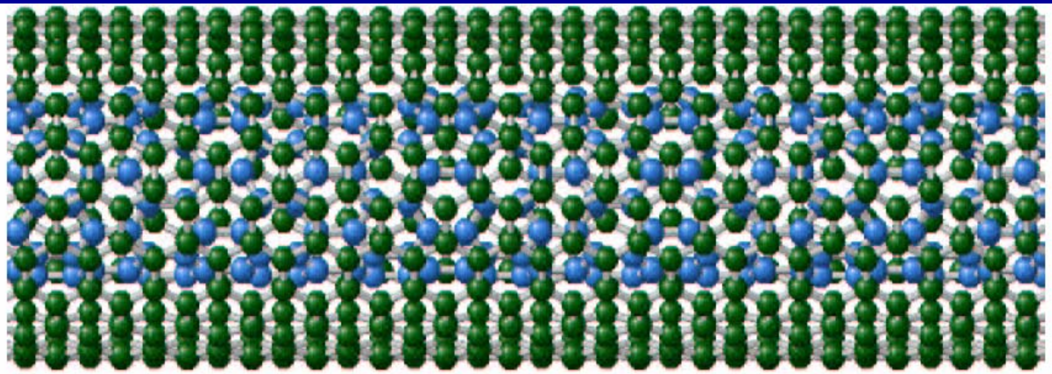
(5,5)@(10,10)

With Anderson-like Disorder (CNP: mfp ~ 75 nm)

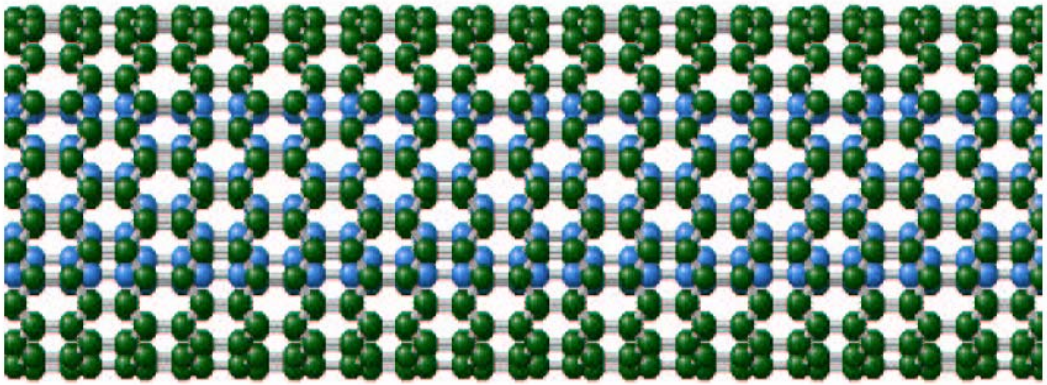
Inner shell : Disorder-free

Intershell coupling in this situation favors delocalization and results in mean free path increase !!!

Incommensurability ...



(9,0)@(10,10)



(9,0)@(18,0)

Incommensurate Syst.
Aperiodic
-No Bloch theorem-
??

$$\left|\vec{T}_{(10,10)}\right| = \sqrt{3}\left|\vec{T}_{(9,0)}\right|$$

Commensurate Syst.
Periodic
-Bloch theorem-
Bandstructures/mfp,...

$$\left|\vec{T}_{(18,0)}\right| = \left|\vec{T}_{(9,0)}\right|$$

Energy-dependent conductance Scaling

Non-ballistic propagation modes

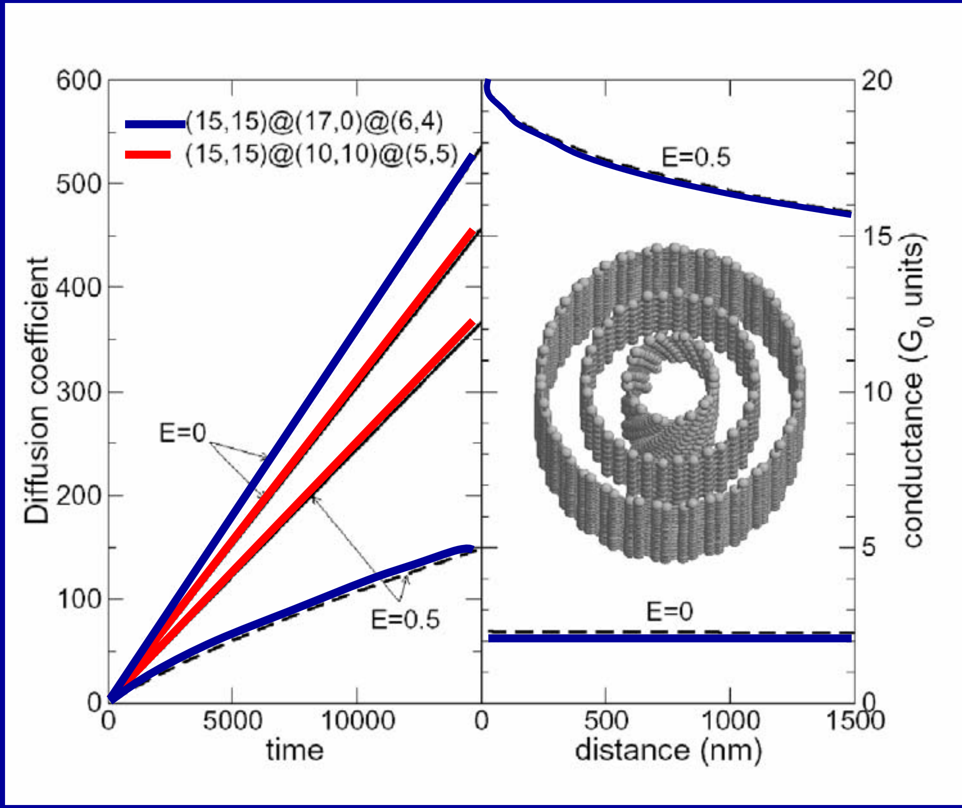
Scaling law for conductance (power-law exponents)

commensurate

$$D_\Psi(t) \approx t \qquad G(L) \approx \frac{e^2}{h} N_\perp$$

incommensurate

$$D_\Psi(t) \approx t^{2\eta - 1} \qquad G(L) \approx \frac{e^2}{h}\left(\frac{L}{L_0}\right)^{\frac{\eta-1}{\eta}}$$



Experiment

V. Krstic et al.,

Phys. Rev. B 67, 041401 (2003)

S. R, F. Triozon, A. Rubio, D. Mayou, Phys. Rev. B (RC) 64, 121401 (2001)

F. Triozon, S. R, A. Rubio, D. Mayou, Phys. Rev. B (RC) 69, 121410 (2004)