1st M4nano Symposium (madrid, 4 december 04)

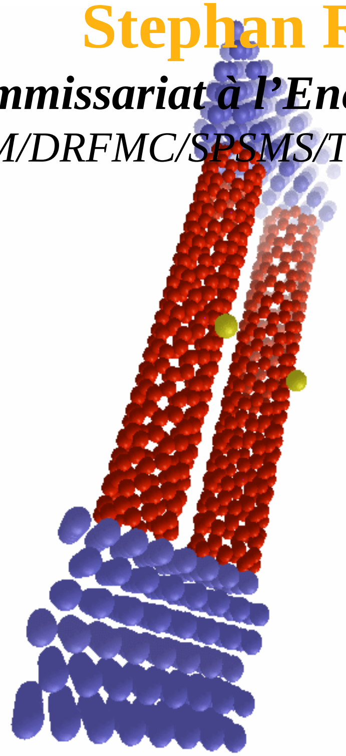
Quantum Transport in Post-CMOS Molecular Material and Devices:

Carbon Nanotubes & Semiconducting Nanowires

Stephan Roche

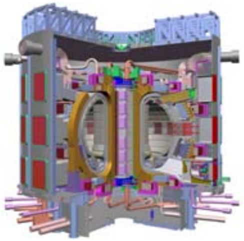
Commissariat à l'Energie Atomique

DSM/DRFMC/SPSMS/Theoretical Group



M4nano
Symposium
Madrid (Spain)

Commissariat à l'Energie Atomique in Y2006



ITER: *Mastering nuclear fusion*

The main goal of ITER is the study of burning plasmas, i.e. plasmas where heating is mainly provided by the alpha particles created from fusion reactions.

TERA10: *Supercomputing leading facility*

Europe's largest supercomputer

Rank 5th Top500 (august 2006)

Performance *60 Teraflops of computing power, 27 Terabytes of memory*

1 Petabytes of disc space with a throughput of 100GB/s

NEUROSPIN: *From Physics to the Human Brain*

pushing as far as possible the current limits of Magnetic Resonance Imaging (MRI) and spectroscopy to study the central nervous system, from mice to humans.

MINATEC:

European leading Centre for innovation in micro & nanotechnology

Minatec
Centre for Innovation in micro & nanotechnology

TNT2006 !

POST-CMOS molecular materials & devices

Carbon Nanotubes -- Semiconducting Nanowires -- Graphene

Nanodevices performances

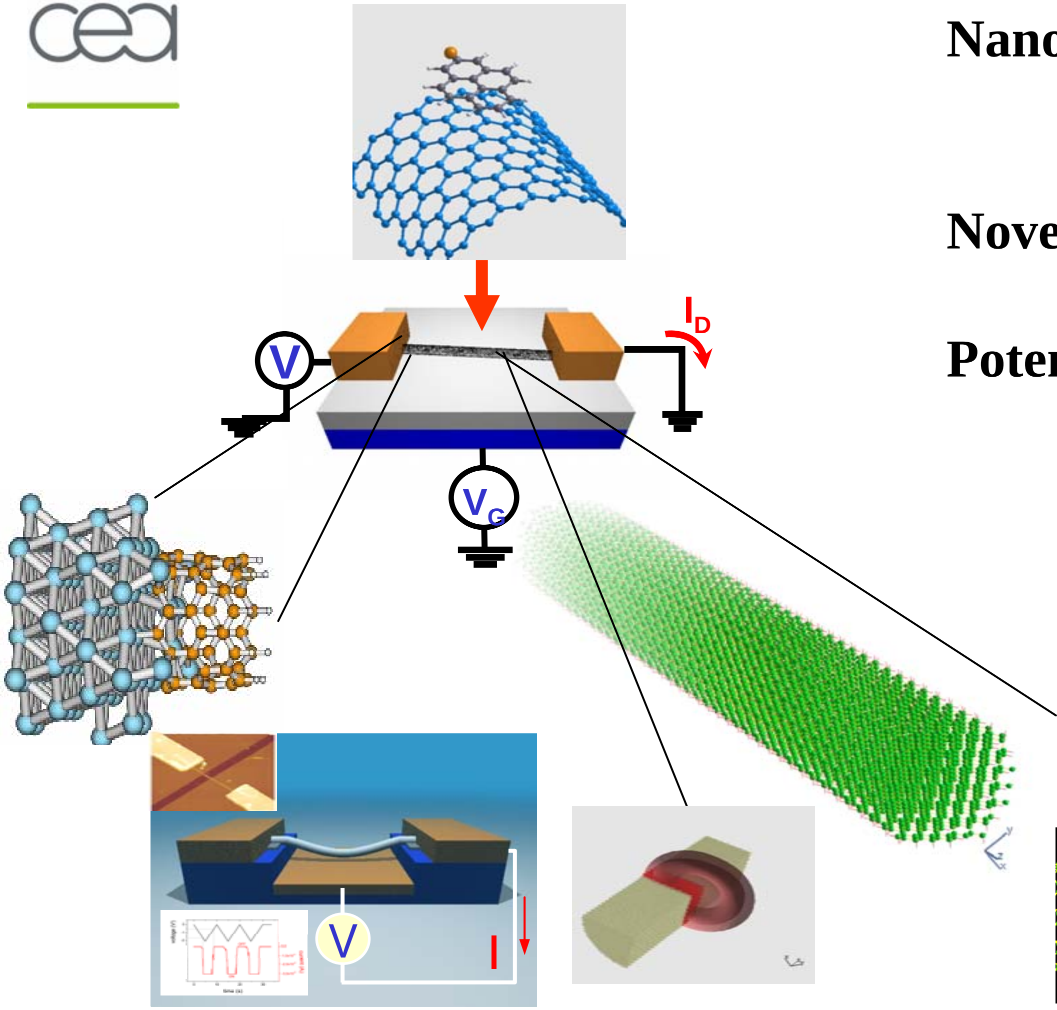
- *nanoelectronics*
- *optoelectronics*

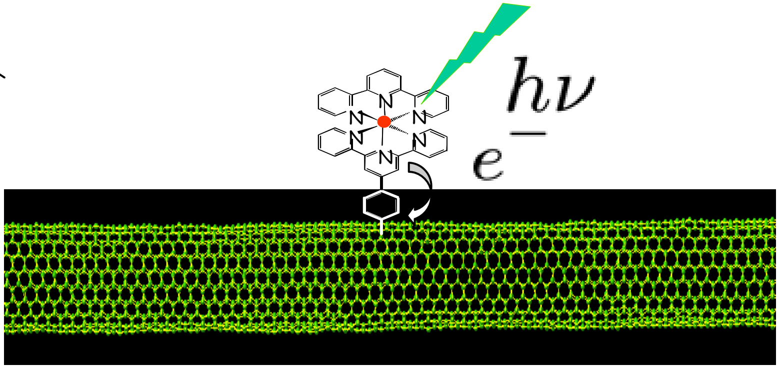
Novel Physical behaviors

- *spintronique,…*

Potential for novel functionalities

- *(bio)-chemical Sensing*
- *molecular memories,*
- *photo-switches,…*
- *NEMS*





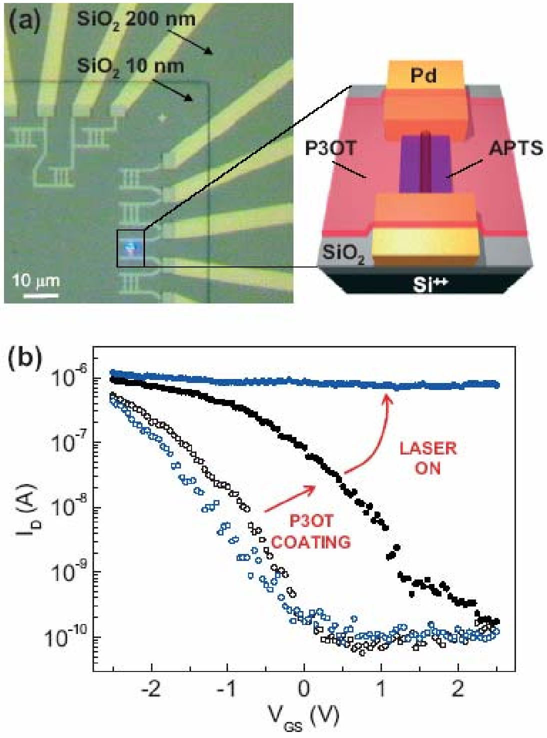
ADVANCED MATERIALS

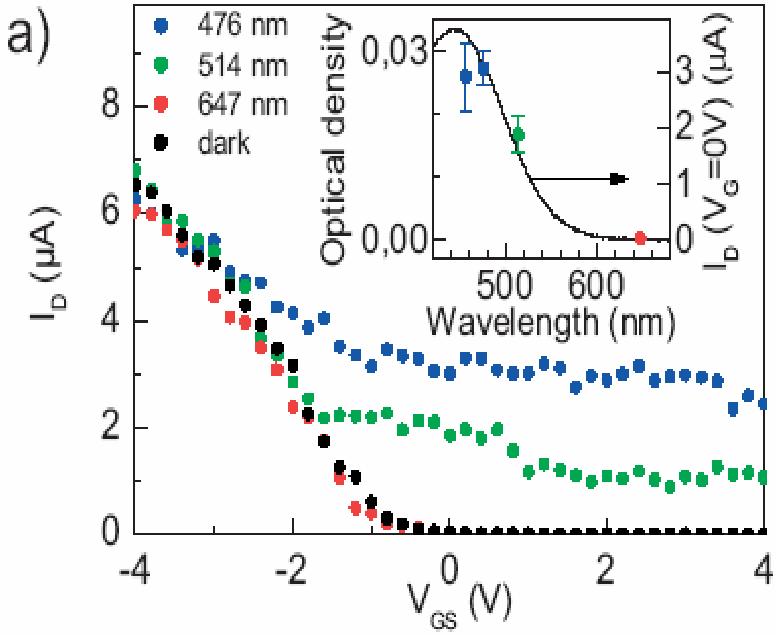
COMMUNICATIONS

DOI: 10.1002/adma.200601138

Optoelectronic Switch and Memory Devices Based on Polymer-Functionalized Carbon Nanotube Transistors**

By *Julien Borghetti*, *Vincent Derycke*,* *Stéphane Lenfant*, *Pascale Chenevier*, *Arianna Filoramo*, *Marcelo Goffman*, *Dominique Vuillaume*, and *Jean-Philippe Bourgoin*





Quantum Transport Modelling & Simulation

Our strategy : *Development of quantum transport approaches*
to tackle fundamental physics ***in realistic models***
(predictability efficiency)

This implies : *Order N methods*
Ab-initio & sophisticated tight-binding models
Pushing the limits beyond mean field and DFT…

This TALK

Coherent Transport

Intrinsic transport / linear response regime (Kubo formula)

- *Elastic mean free path in disordered systems (charge mobilities, etc..)*
- *Weak localization regimes (magnetoresistance patterns)*
- *Conductance scaling*

Quantum Transport for open systems (Landauer-Büttiker formula)

- *Ballistic transport and contact dependent transmission phenomena*

Out-of –equilibrium regimes & Inelastic Transport

Poisson-Schrödinger solver *(Field-effect Transistor physics)*

QM treatment of el-ph coupling *(beyond mean field),..*

Quantun Transport by Kubo approach

Solving time dependent Schrödinger equation

Efficient order N real space methods

$$|\Psi(t)\rangle = exp(-i\frac{Ht}{\hbar})|\Psi(0)\rangle$$

$$\boxed{\frac{e^2h}{\Omega}\mathrm{Tr}[\hat{V}_x\delta(E-H)\hat{V}_x\delta(E-H)] = \lim_{t\to\infty}\mathrm{Tr}[\delta(E-H)\frac{(\hat{X}(t)-\hat{X}(0))^2}{t}]}$$

Quantum dynamics

(conduction regimes)

$$D(E,t) = \frac{1}{t}\langle(\hat{X}(t)-\hat{X}(0))^2\rangle_E$$

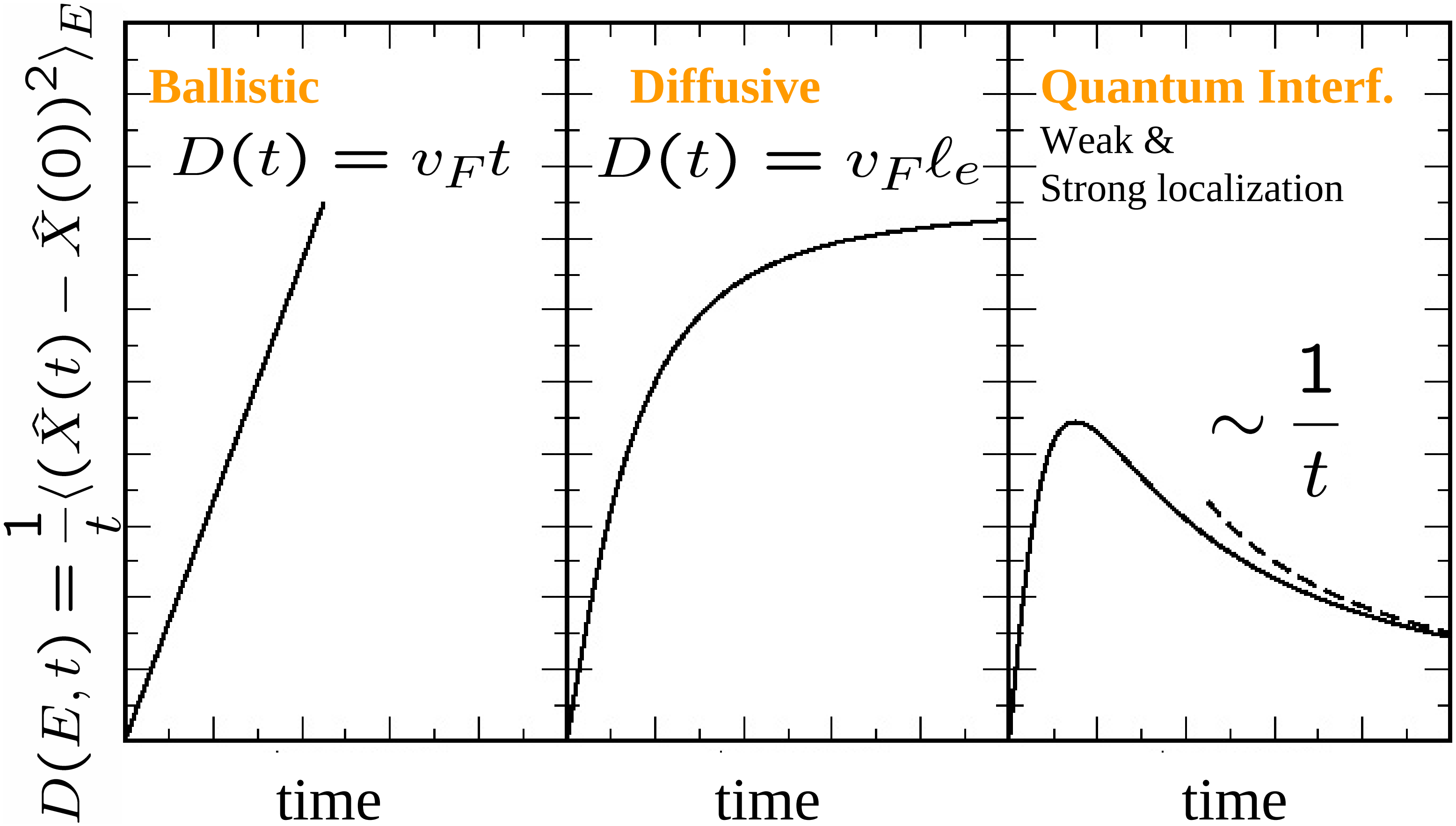
Kubo Conductance

(conductance scaling)

$$G(E) = \frac{2e^2}{L_{syst}}\lim_{t\to\tau_L}\mathrm{Tr}[\delta(E-H)D(E,t)]$$

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

Quantum Transport Regimes & Conductance scaling



$$G(E)=\frac{2e^2}{h}N(E)$$

$$G(E)=\frac{2e^2}{h}\frac{\ell_e}{L_{syst}}$$

$$G(E)=\frac{2e^2}{h}(\frac{\ell_e}{L_{syst}}-\delta\sigma)$$

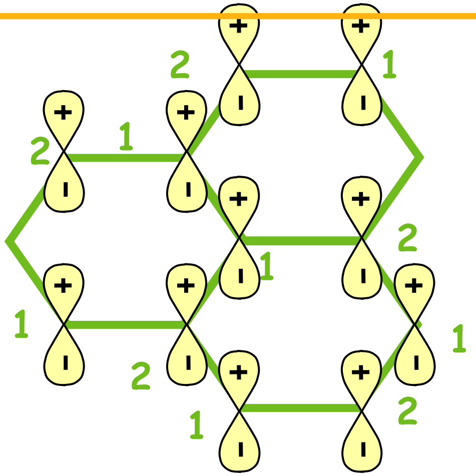
$$G(E)=\frac{2e^2}{h}exp(-\frac{\ell_e}{L_{syst}})$$

Effective π electrons-model

Hybrid molecular orbitals

Cohesion $s, p_x, p_y \equiv \sigma$

Electronic properties close to E_F $p_z \equiv \pi$

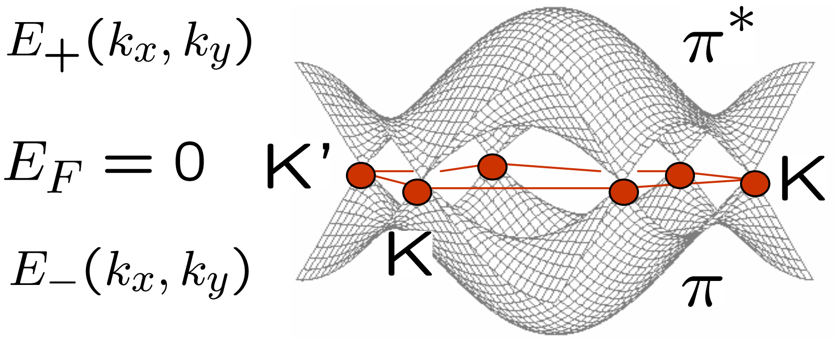


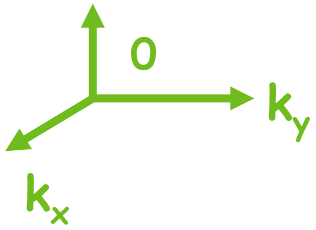
2 atoms/ unit cell

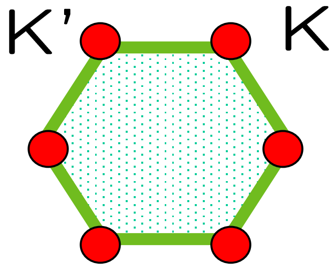
$\gamma_0$upling between orbitals p_z

$$H(\vec{k}) = \begin{bmatrix} 0 & f(\vec{k}) \\ f^*(\vec{k}) & 0 \end{bmatrix} \qquad f(\vec{k}) = \gamma_0 \sum_\alpha e^{i\vec{k}.\vec{\tau}_\alpha}$$

$$E_\pm(k_x,k_y) = \pm\gamma_0\left(3+4\cos(\frac{\sqrt{3}k_xa}{2})\cos(\frac{k_ya}{2})+2\cos(k_ya)\right)^{1/2}$$

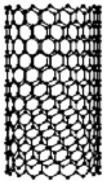






1th Brillouin Zone

Nanotubes: Electronic Properties

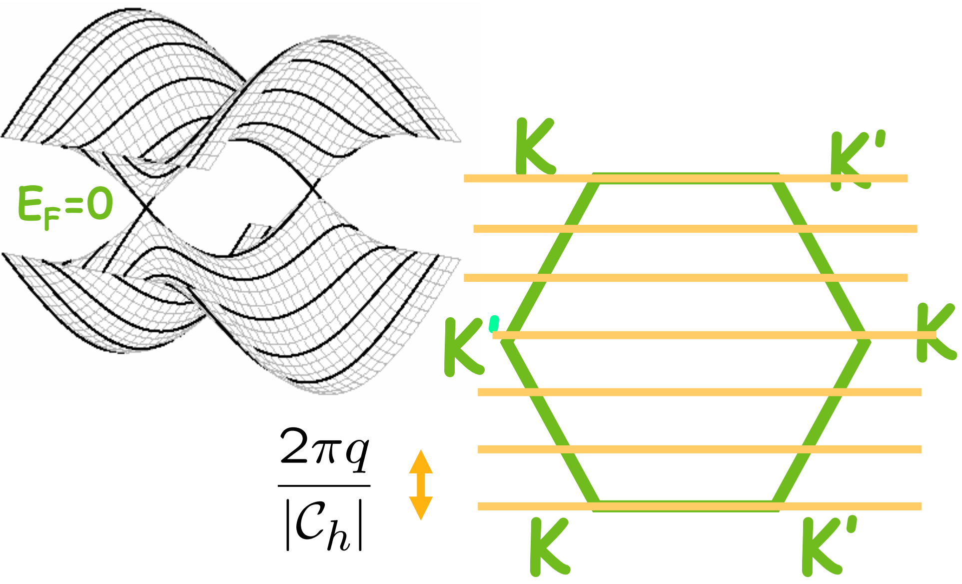


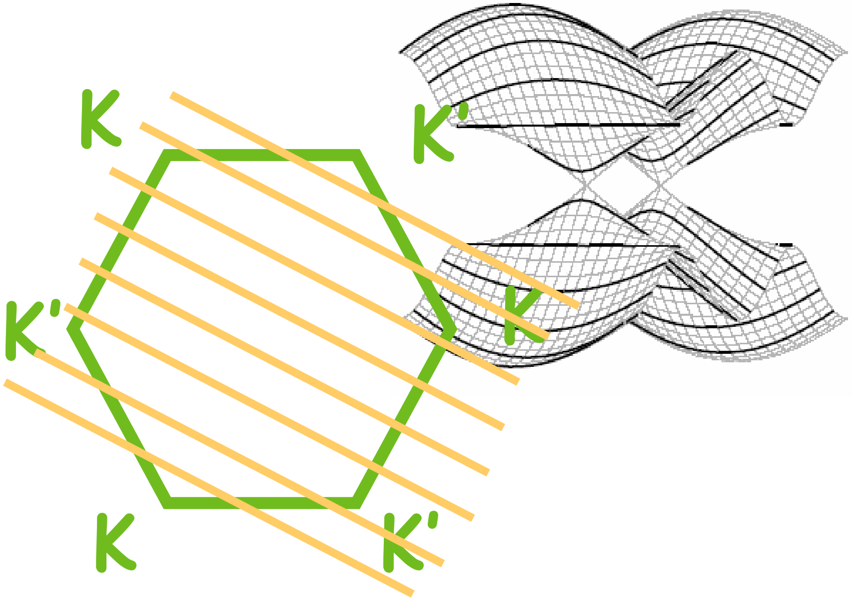
Periodic boundary conditions

$$-\frac{\pi}{|\vec{T}_{(n,m)}|} \leq k_y (= k) \leq +\frac{\pi}{|\vec{T}_{(n,m)}|} \qquad k_x = \frac{2\pi q}{|\vec{C}_{(n,m)}|} (q = 1, N)$$

Helicity

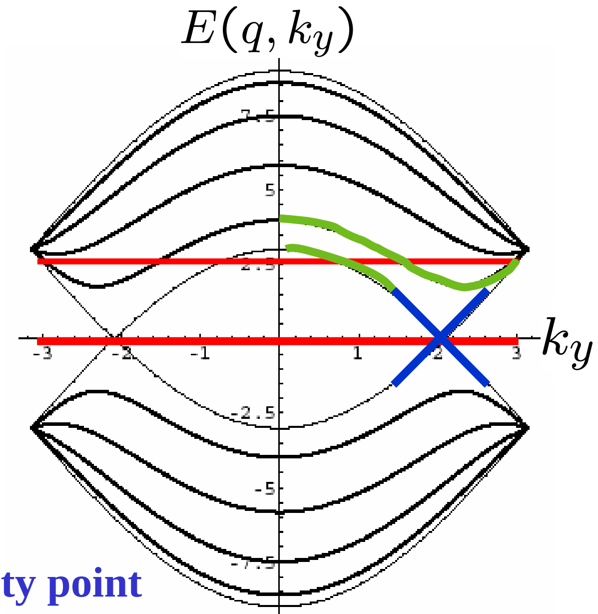
$$\vec{C}_{n,n} = n(\vec{a}_1 + \vec{a}_2) \qquad \vec{C}_{n,m} = (3p \pm 1)\vec{a}_1$$

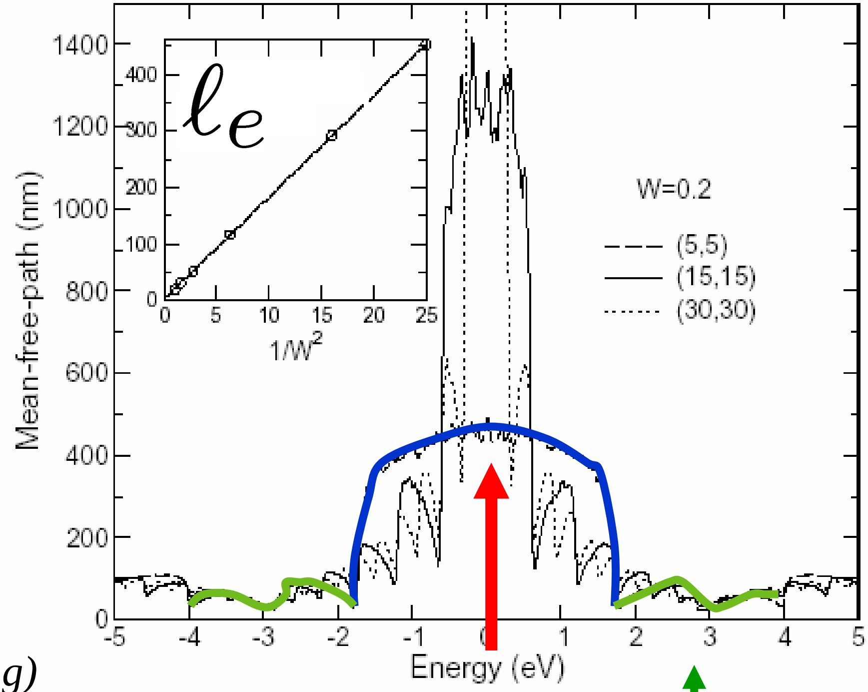




Energy-dependent mean free path

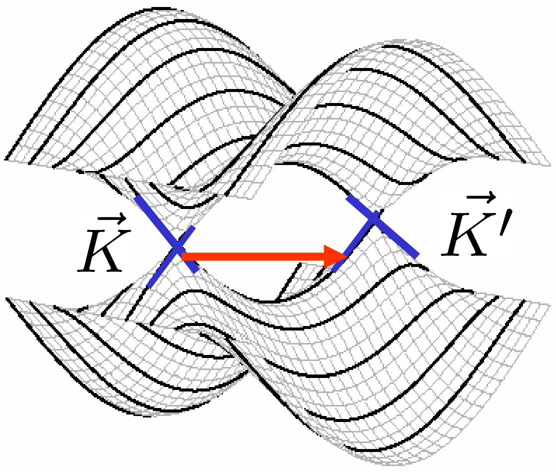
(5,5)
Nanotube





Close to the
charge neutrality point
Fermi Golden Rule (disorder-induced backscattering)

Under Fermi level shift



$$\frac{1}{\tau(E_F)} = \frac{2\pi}{\hbar}\left|\langle\Psi_{n_1}(k_F)|\hat{\mathcal{U}}|\Psi_{n_2}(-k_F)\rangle\right|^2\rho(E_F)$$

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

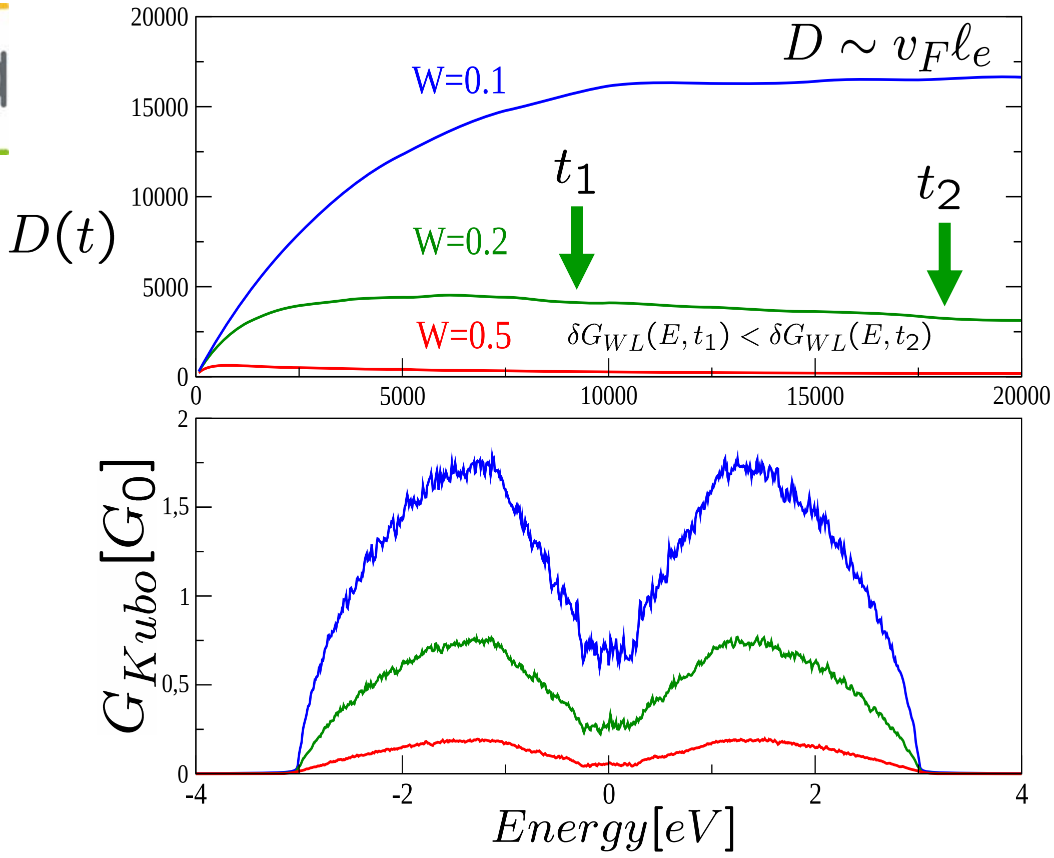
Anderson-type elastic disorder (W)

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

Weak localization & coherence length scaling

Nanotube: (10,10)

Anderson type static disorder strength = W



→ Saturation regime

Mean free path

$$\boxed{\ell_e}$$

↓

$$_{class}(E) = \frac{2e^2}{h} N_\perp \frac{\ell_e(E)}{L(E,t)}$$

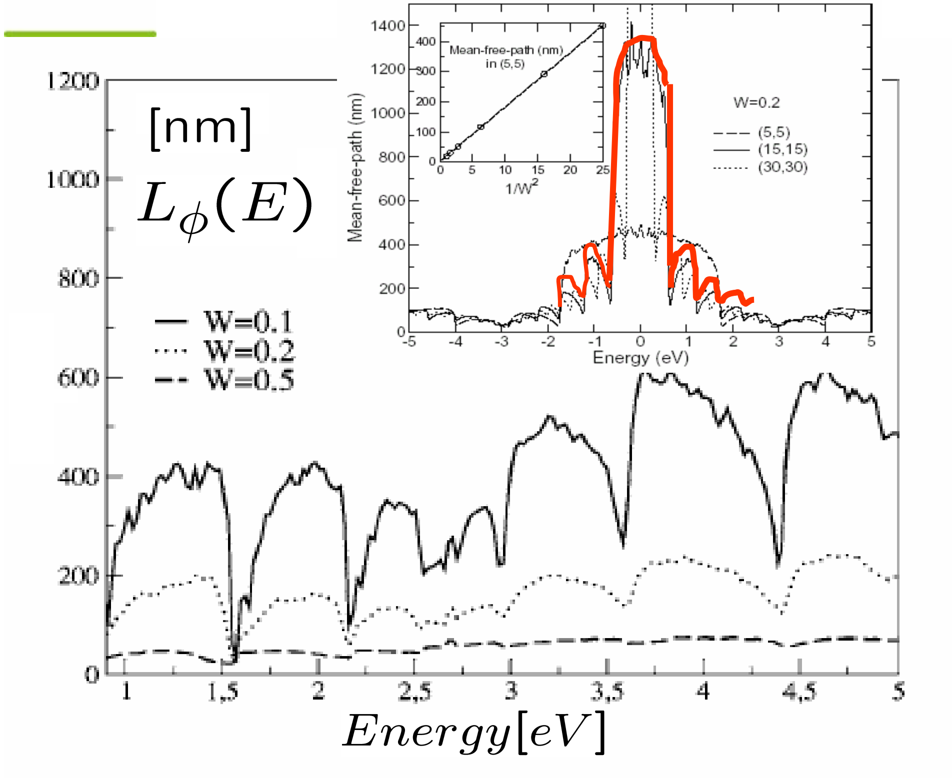
Scaling properties

Coherence length

$$\delta G_{WL}(E) = \frac{2e^2}{h} N_\perp \frac{\ell_e(E)}{L(E,t)} - G_{Kubo}(E) \rightarrow \boxed{L_\phi(E)}$$

Coherence lengths/time in the diffusive regime

$$\delta G_{WL}(E) = \frac{2e^2}{h}\frac{L_\phi(E)}{L(E,t)}$$

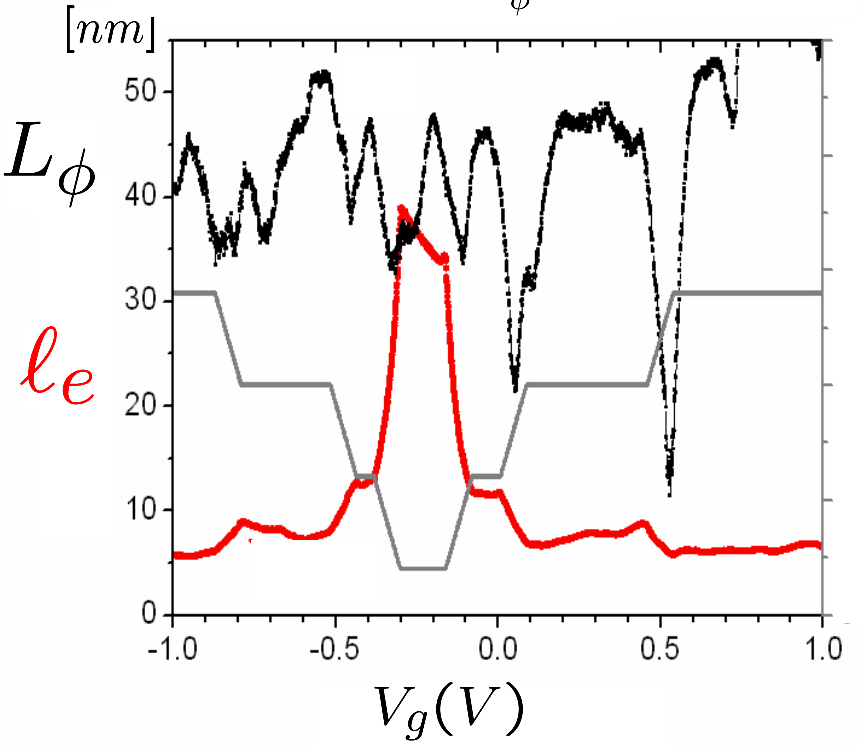


S.R, J. Jiang, F. Triozon, R. Saito,
Phys. Rev. B 72, 113410 (2005)

Exprimental results

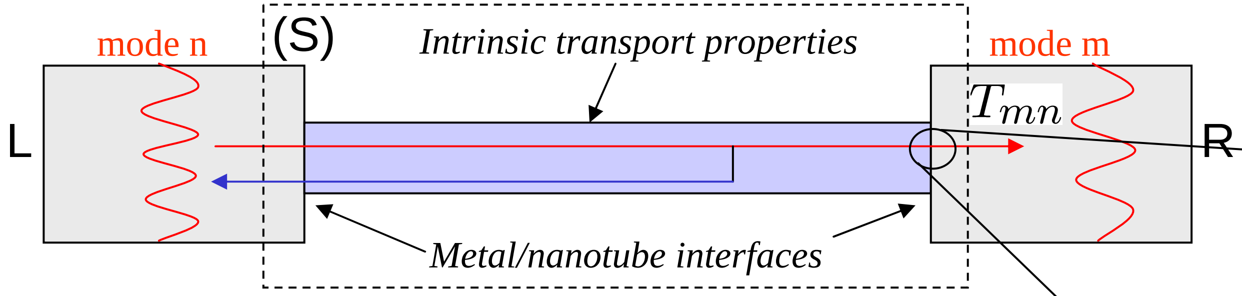
Exploring Weak localization under gate voltage

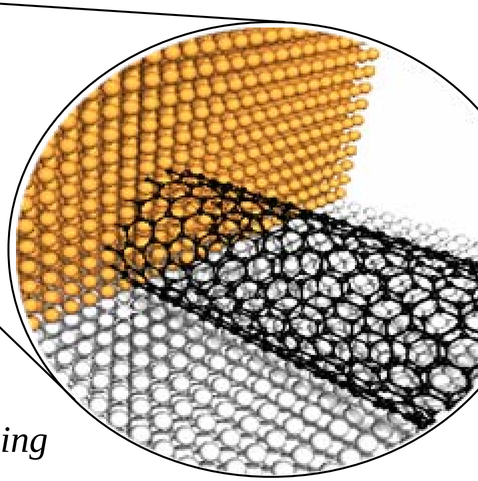
$$\delta G_{WL} = -A\frac{e^2}{\pi\hbar L}\left(\frac{1}{L_\phi^2} + \frac{W^2e^2B^2}{3\hbar^2}\right)^{-1/2}$$



B. Stojetz et al., **PRL 94, 186802 (2005)**

Quantum Transport by the Landauer-Büttiker Approach





$$\frac{dI}{dV} = \frac{2e^2}{h}\sum_{m,n} T_{mn} = \mathcal{G}(E) = \frac{2e^2}{h}\mathrm{Tr}[\Gamma_L G^r \Gamma_R G^a]$$

$$G^{r,a}(E) = \frac{1}{E - \boxed{\mathcal{H}_{Sys}} - \boxed{\left(\Sigma_L^{r,a}(E) + \Sigma_R^{r,a}(E)\right)}}$$

Self-energy due to metal/nanotube coupling

Finite size system

$$\Sigma_{L,R}^{r,a}(E) = V_{L,R-Sys}^{\dagger} g_{L,R}^{r,a}(E) V_{L,R-Sys}$$

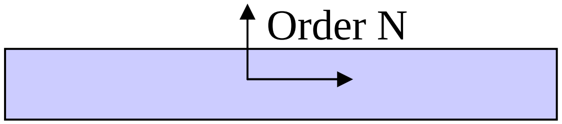
$$\Gamma_{L,R}(E) = i[\Sigma_{L,R}^{r}(E) - \Sigma_{L,R}^{a}(E)]$$

**) Decimation recursive techniques*

****) Order N (bi-orthogonalization process) and continuous fraction expansion***

$$\mathcal{H} = \mathcal{H}_{Sys} + \Sigma_L^r + \Sigma_R^r$$ Effective non-symmetric H

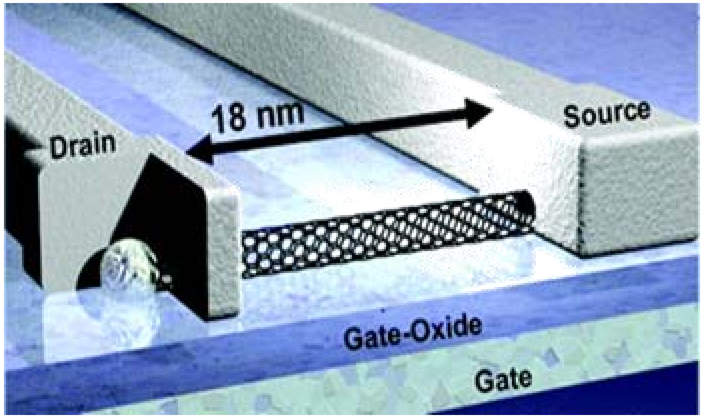
$$\mathcal{G} = \frac{2e^2}{h}\sum_{\alpha,\beta,\alpha',\beta'}\langle\beta|\Gamma_R|\alpha\rangle\langle\alpha|G^r|\alpha'\rangle\langle\alpha'|\Gamma_L|\beta'\rangle\langle\beta'|G^a|\beta\rangle$$



F. Triozon and SR, **Eur. J. Phys. B. 46, 427 (2005)**

Ballistic regimes & field effect transistors

Semiconducting CNTs

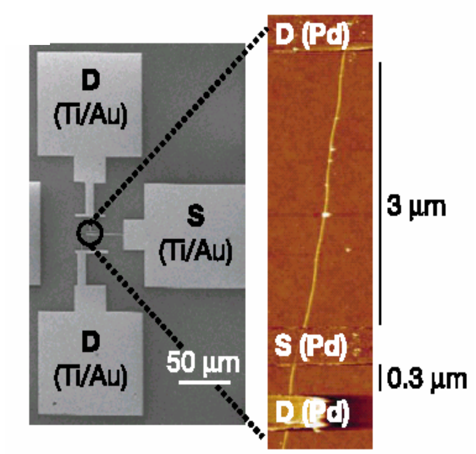


Ballistic transport $\ell_e \geq L_{\text{canal}}$

$$G(E) = \frac{2e^2}{h} N_\perp(E)$$

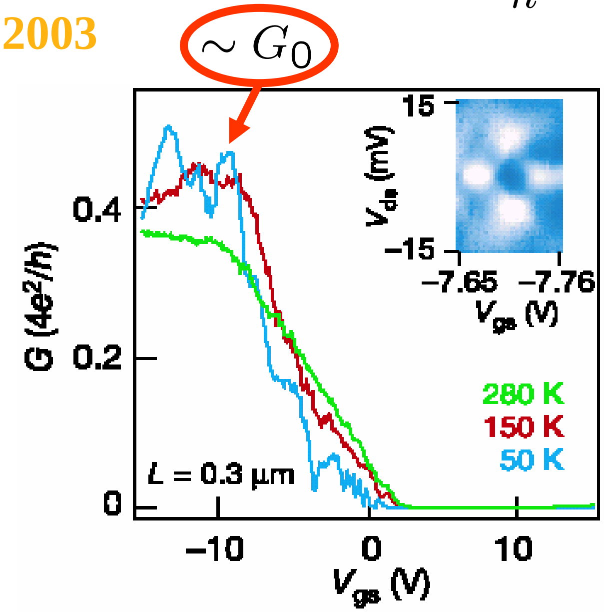
$$\frac{2e^2}{h} = G_0 = (13\text{k}\Omega)^{-1}$$

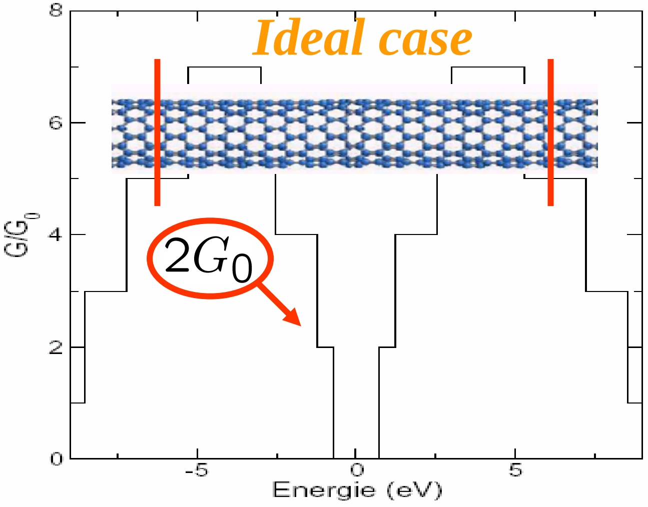
A. Javey et al., **Nature 2003**



Ohmic contact

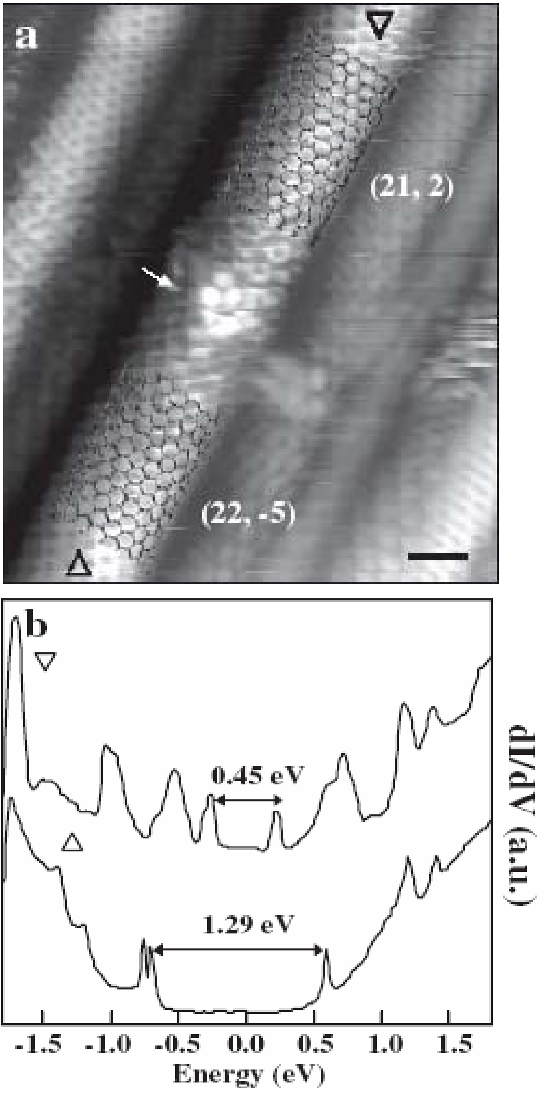
(Palladium, p-type)


$\sim G_0$

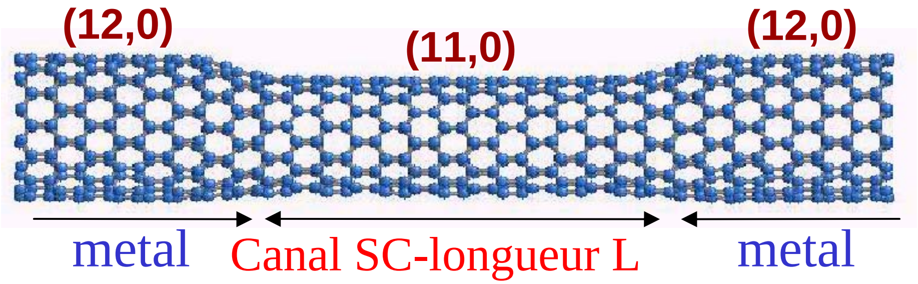

Ideal case

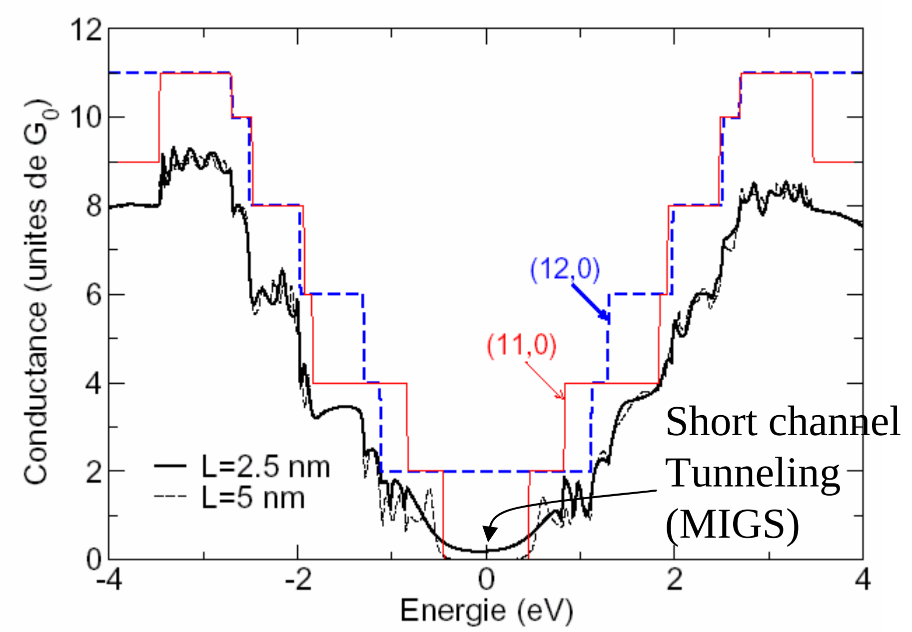
$2G_0$

Metal/SC/Metal intramolecular junctions



T. Odom, J. Huang, C.M. Lieber,
J. Phys. C. 14 R145 (2002)





T< 1 quantum reflections at interfaces

F.Triozon, Ph. Lambin, SR, **Nanotechnology (2005)**

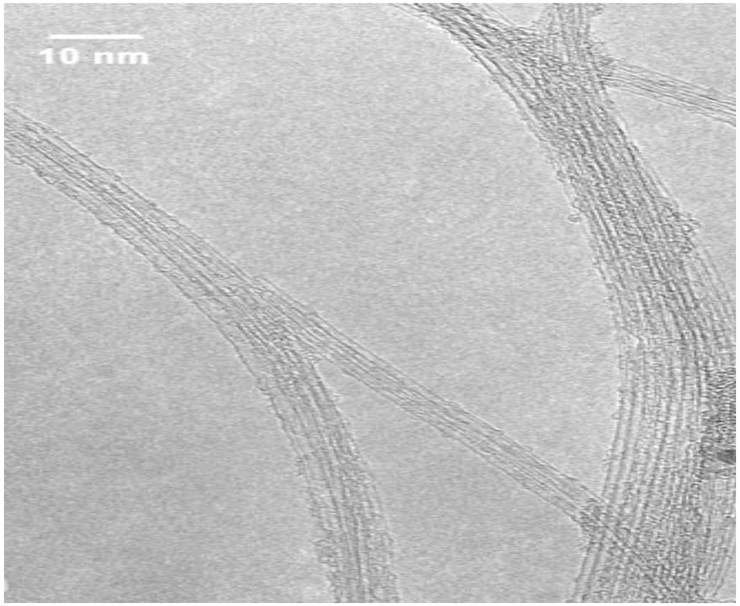
Properties of chemically modified Carbon nanotubes

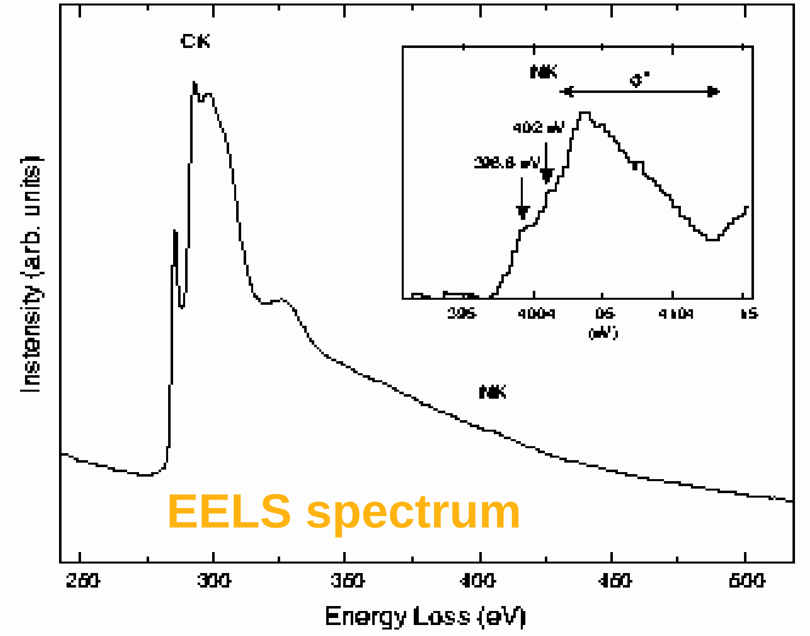
-Substitutions Nitrogen (n) or Boron (p)-
-Physisorption potassium-
-Physiorption benzene, azulene,..

Doped nanotubes with Nitrogen or Boron

Incorporation of N_2(gas) during the synthesis

Bundles of Nitrogen-doped Single-wall nanotubes





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.*

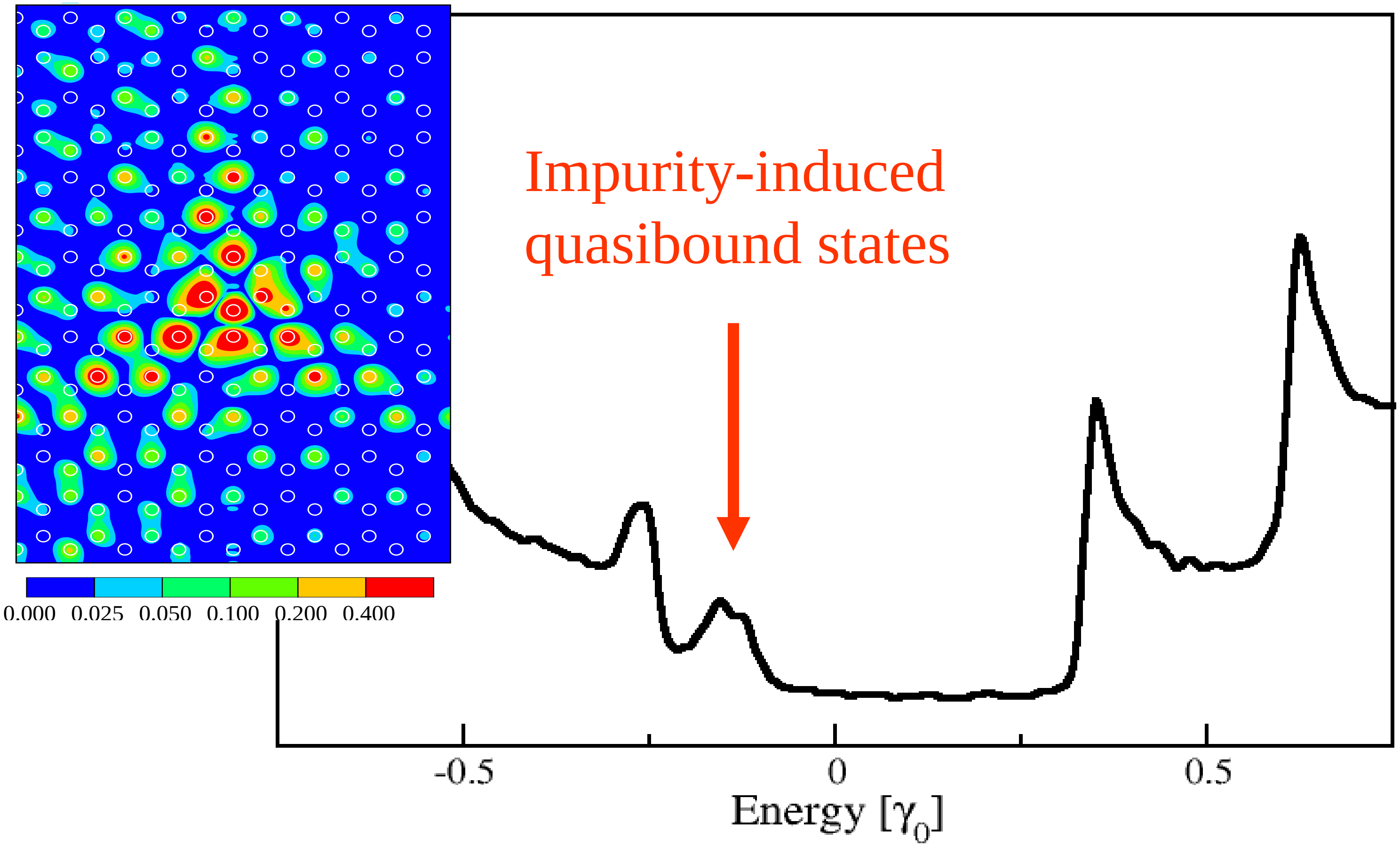
Chem. Phys. Lett. 387, 193 (2004)

Substitution de bore dans un nanotube

modèle *Zone Folding* (ZF)

Nanotube (10,10)

BORON: 0.5 %



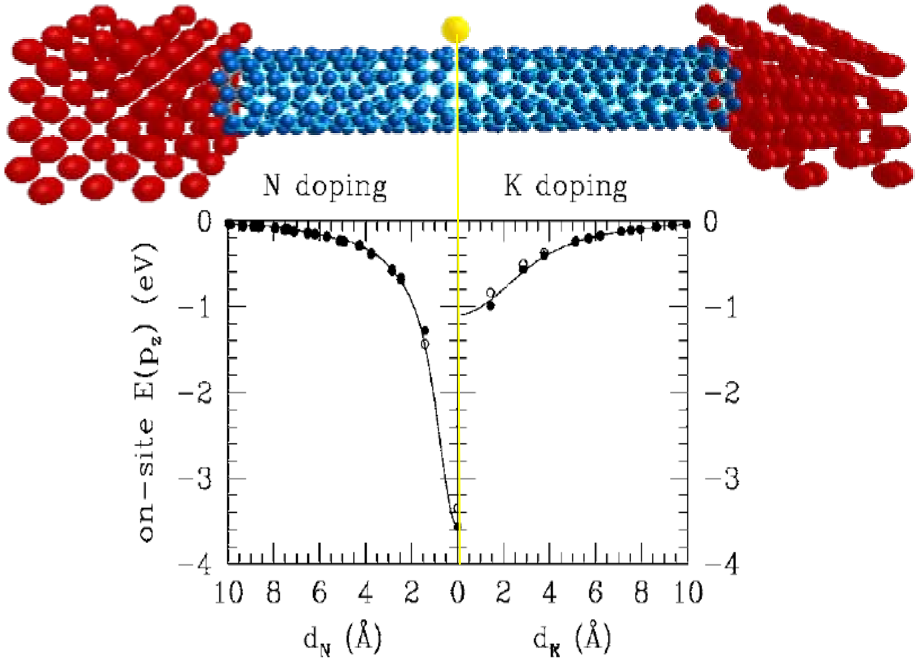
Impurity-induced quasibound states

Chemically Doped Carbon Nanotubes

Combining

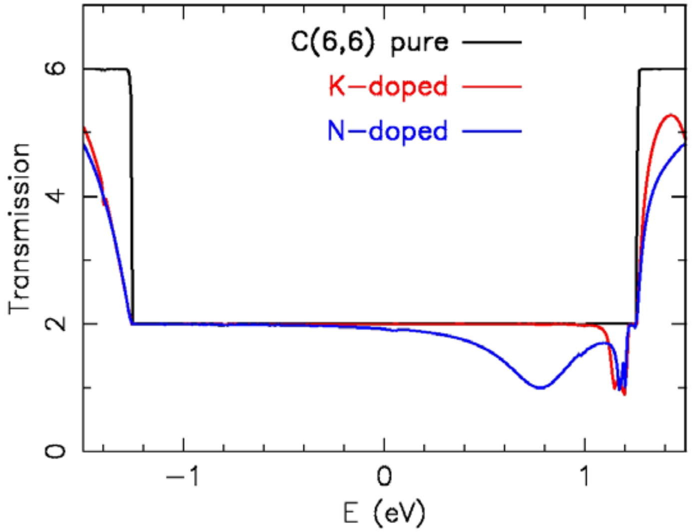
-ab-initio calculations (accuracy of energetics at atomistic level)

-effective tight-binding (performing large scale studies)



Single-impurity case (X. Blase)

Transport calculation (SIESTA)



Gaussian potential
Effective model

$$\tilde{\mathcal{H}}_{\mathrm{NT}}(\alpha) = -\tilde{\gamma}_0 \sum_{\langle i,j\rangle} \hat{c}_i^\dagger \hat{c}_j + \mathrm{hc} + \sum_i \tilde{V}_{\alpha i}\hat{c}_i^\dagger \hat{c}_i$$

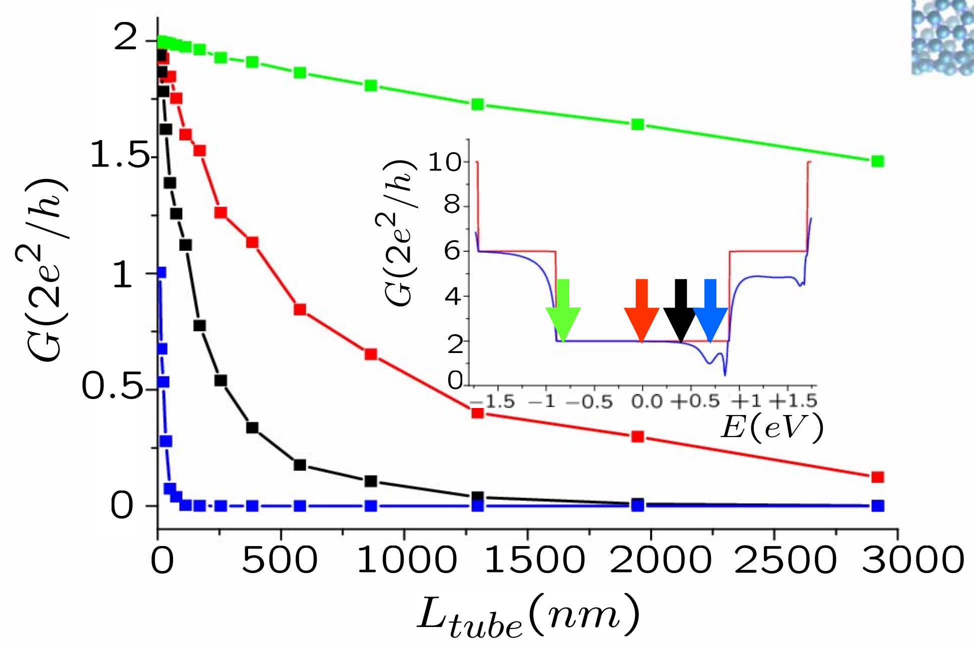
R. Avriller, S. Latil, F. Triozon, X. Blase and S.R., **Phys. Rev. B (RC) 74, 121406 (2006).**

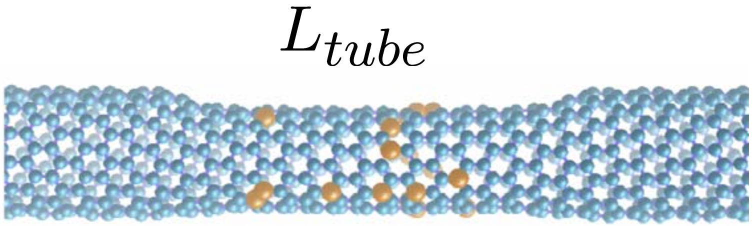
Scaling study of quantum conductance

Chemically disordered nanotubes with length up to several microns

$$\mathcal{G}(\epsilon) = \mathcal{G}_0 T(\epsilon) \qquad T(\epsilon) = \mathrm{Tr}\{\hat{t}_{LR}(\epsilon)\hat{t}^{\dagger}_{LR}(\epsilon)\}$$

Metallic nanotube (10,10)
Doping N =0.1%





Quasi-ballistic

Diffusive

elastic mean free path+QIE

Strong localization

Statistical Analysis of T(E) & Transport Regimes

Quasi-ballistic

$L \ll l_e \ll l_\phi$

$$\langle T \rangle = N_\perp(\epsilon)$$

Diffusive

$l_e \ll L \ll l_\phi$

$$\langle T \rangle = N_\perp(\epsilon) \frac{l_e(\epsilon)}{L}$$

Localized

$\xi \ll L \ll l_\phi$

$$\langle \ln T \rangle = -\frac{L}{\xi}$$

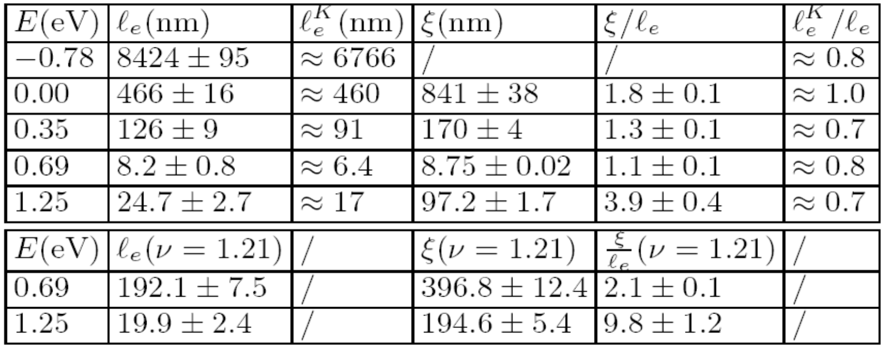
$$\langle T \rangle = \frac{N_\perp(\epsilon)}{1 + \frac{L}{l_e(\epsilon)}}$$

$$\downarrow$$

elastic mean free path

$$\ell_e$$

Thouless relationship (agreement with RMT)



E(eV)	ℓ_e(nm)	ℓ_e^K (nm)	ξ(nm)	ξ/ℓ_e	ℓ_e^K/ℓ_e
-0.78	8424 ± 95	≈ 6766	/	/	≈ 0.8
0.00	466 ± 16	≈ 460	841 ± 38	1.8 ± 0.1	≈ 1.0
0.35	126 ± 9	≈ 91	170 ± 4	1.3 ± 0.1	≈ 0.7
0.69	8.2 ± 0.8	≈ 6.4	8.75 ± 0.02	1.1 ± 0.1	≈ 0.8
1.25	24.7 ± 2.7	≈ 17	97.2 ± 1.7	3.9 ± 0.4	≈ 0.7

E(eV)	$\ell_e(\nu = 1.21)$	/	$\xi(\nu = 1.21)$	$\frac{\xi}{\ell_e}(\nu = 1.21)$	/
0.69	192.1 ± 7.5	/	396.8 ± 12.4	2.1 ± 0.1	/
1.25	19.9 ± 2.4	/	194.6 ± 5.4	9.8 ± 1.2	/

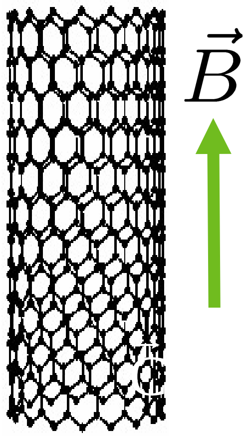
$\beta = 1$

$$\boxed{\xi = \frac{1}{2}\{\beta(N_\perp - 1) + 2\}\ell_e}$$

$\beta = 2$ breaking TRS (perp B-field)

R. Avriller, S. Latil, F. Triozon, X. Blase and S. R., **Phys. Rev. B (RC) 74, 121406 (2006).**

Aharonov-Bohm Effects on Bandstructure



$\{\vec{C}_h/|\vec{C}_h|, \vec{T}/|\vec{T}|\}$

Landau gauge

$$\vec{A} = (\phi/|\mathcal{C}_h|, 0)$$

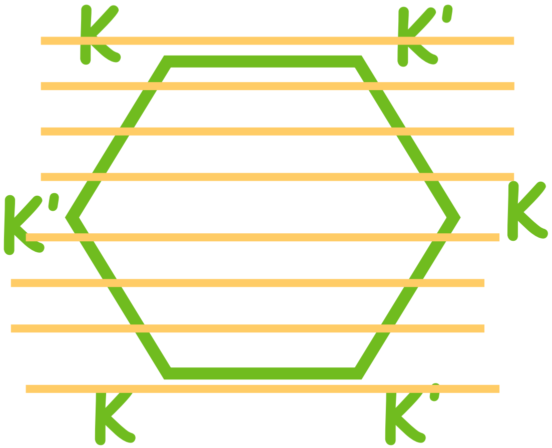
Wavefunctio

$$\Psi \sim e^{ik_y y} e^{i(k_x x + \frac{e}{h}\int \vec{A}.d\vec{r})}$$

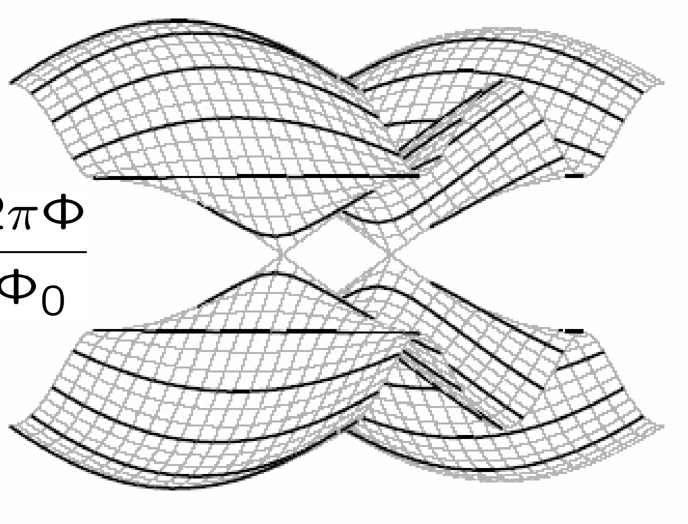
$$\Delta\varphi_{\vec{r},\vec{r'}} = \int_0^1 (\vec{r'} - \vec{r}) \cdot (\vec{A}(\vec{r} + \lambda[\vec{r'} - \vec{r}]))d\lambda$$

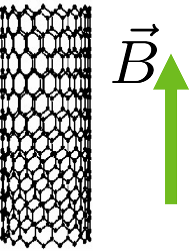
$$= i(x - x')\phi/|\vec{C}_h|$$

$$\boxed{\delta\vec{k}(\phi) \cdot \vec{\kappa}_x = \delta\vec{k}(0) \cdot \vec{\kappa}_x + 2\pi\phi/(\phi_0|\vec{C}_h|)}$$



$$k_x = \frac{2\pi q}{|\mathcal{C}_h|} + \frac{2\pi\Phi}{\Phi_0}$$



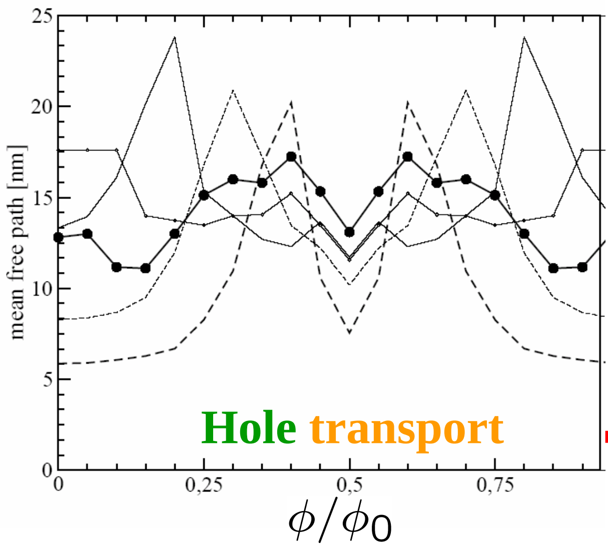


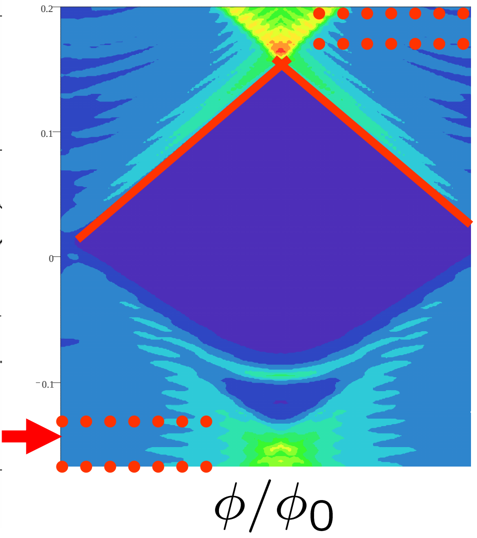
Transport under B and Aharonov-Bohm effects

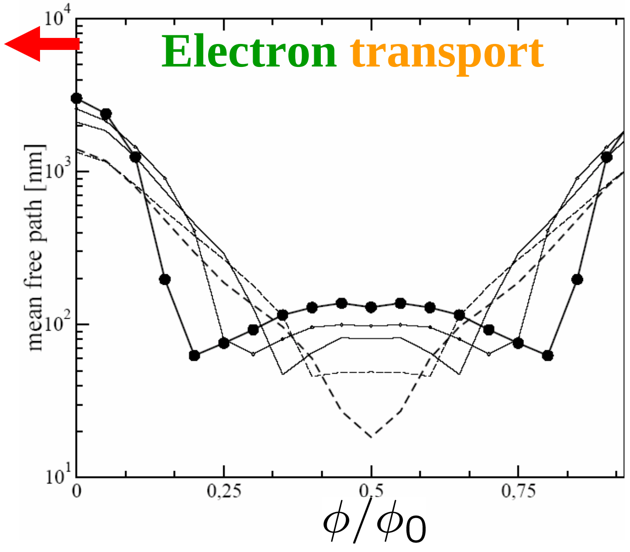
Chemical impurities

-Breaking of electron-hole symmetry

$$D(t) = v(E)\ell_e \sim v^2(E)\tau$$







Holes: $\ell_e \in [5nm, 25nm]$

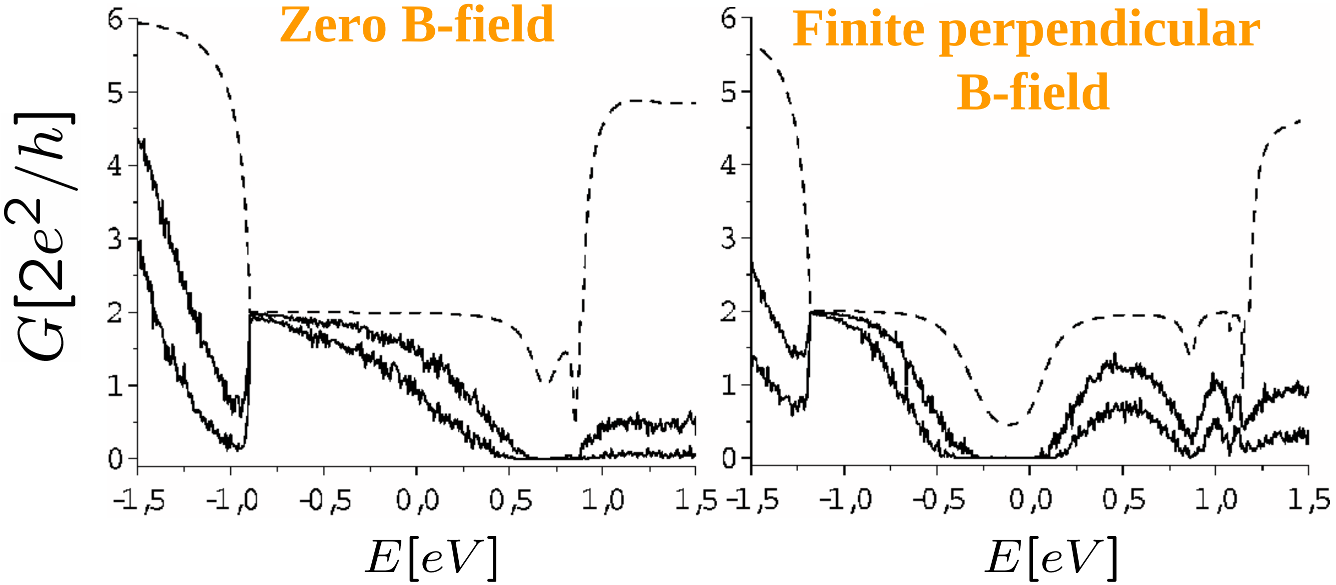
Electrons: $\ell_e \in [200nm, 4\mu m]$

P-doped but hole current *is vanishingly small* compared to electron current

Colossal Magnetoresistance fluctuations (Nitrogen doped)

$$\tilde{\mathcal{H}}_{\mathrm{NT}}(\Omega,\vec{A}) = -\tilde{\gamma}_0 \sum_{\langle i,j\rangle} e^{-i\theta_{ij}(\vec{A})}\hat{c}_i^\dagger \hat{c}_j + \mathrm{hc} + \sum_{\alpha\in\Omega}\sum_i \tilde{V}_{\alpha i}\hat{c}_i^\dagger\hat{c}_i$$

$$\theta_{ij}(\vec{A}) = \frac{1}{B\ell_B^2}\int_i^j \vec{A}.d\vec{l} \qquad \ell_B = \sqrt{\frac{\hbar}{eB}}$$



- - - - - - - - Single impurity

—— Many impurities

Doping : 0.1 %

L_{tube}

250 nm

570nm

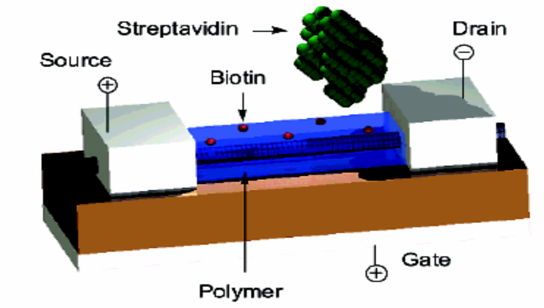
R. Avriller, S. Latil, F. Triozon, X. Blase and S.R., **Phys. Rev. B (RC) 74, 121406 (2006).**

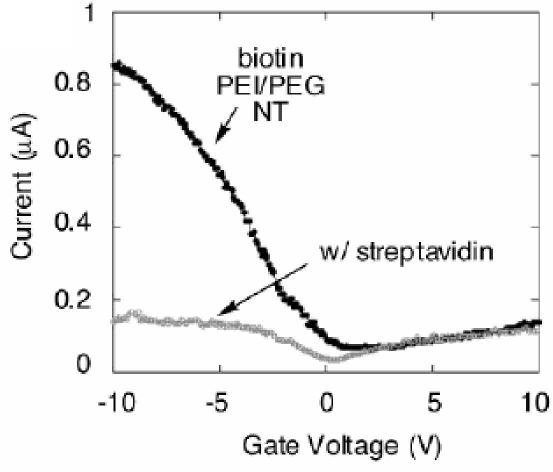
Nanoscale sensing ?

Sensitiveness and selectivity / molecular adsorption

Interactions Proteines ,
pH, enzymatic activity,…

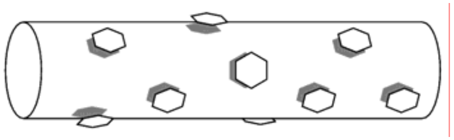
A. Star et al.,
Nanoletters 3, 459 (2003)





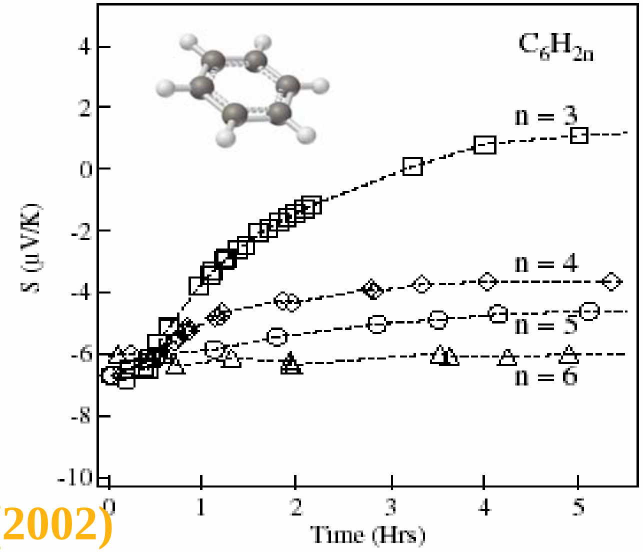
Physisorption

Any mesurable effects ?



Giant changes of electrical thermopower under benzene physisorption

$$S = -\frac{\pi^2 k_B}{3eG}\frac{dG(E)}{dE}\Big|_{E_F}$$

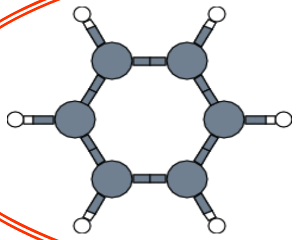


G. Sumanakera et al. **Phys. Rev. Lett. 89, 166801 (2002)**

Molecules

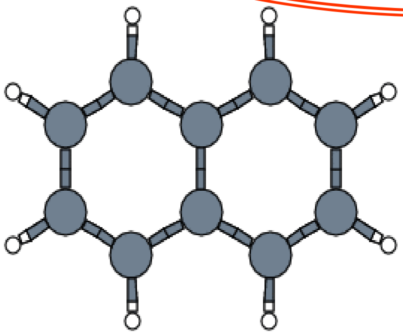
π-conjuguated

Cycle aromatic



Benzene (C_6H_6)

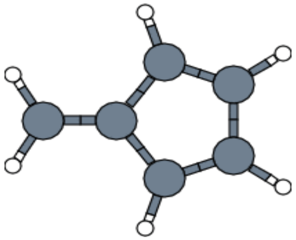
$E_g = 5.15$ eV



Naphtalene ($C_{10}H_8$)

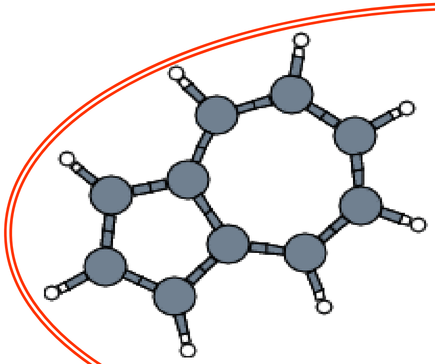
$E_g = 3.41$ eV

Non-aromatic



Fulvene (C_6H_6)

$E_g = 2.46$ eV



Azulene ($C_{10}H_8$)

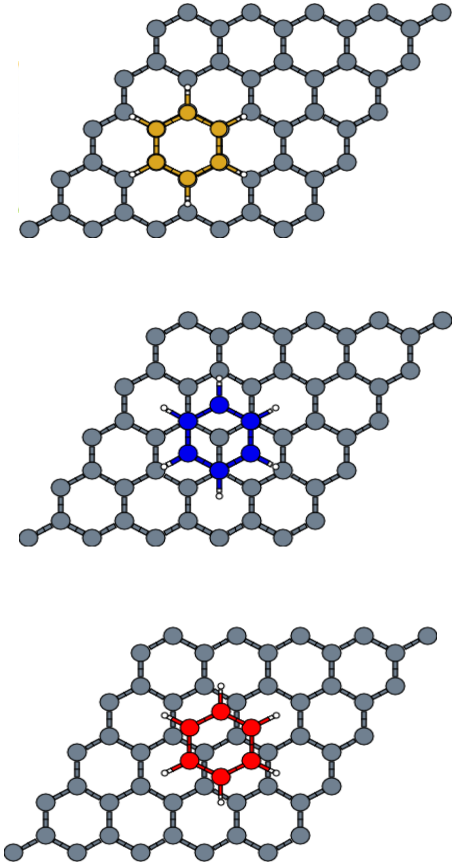
$E_g = 2.07$ eV

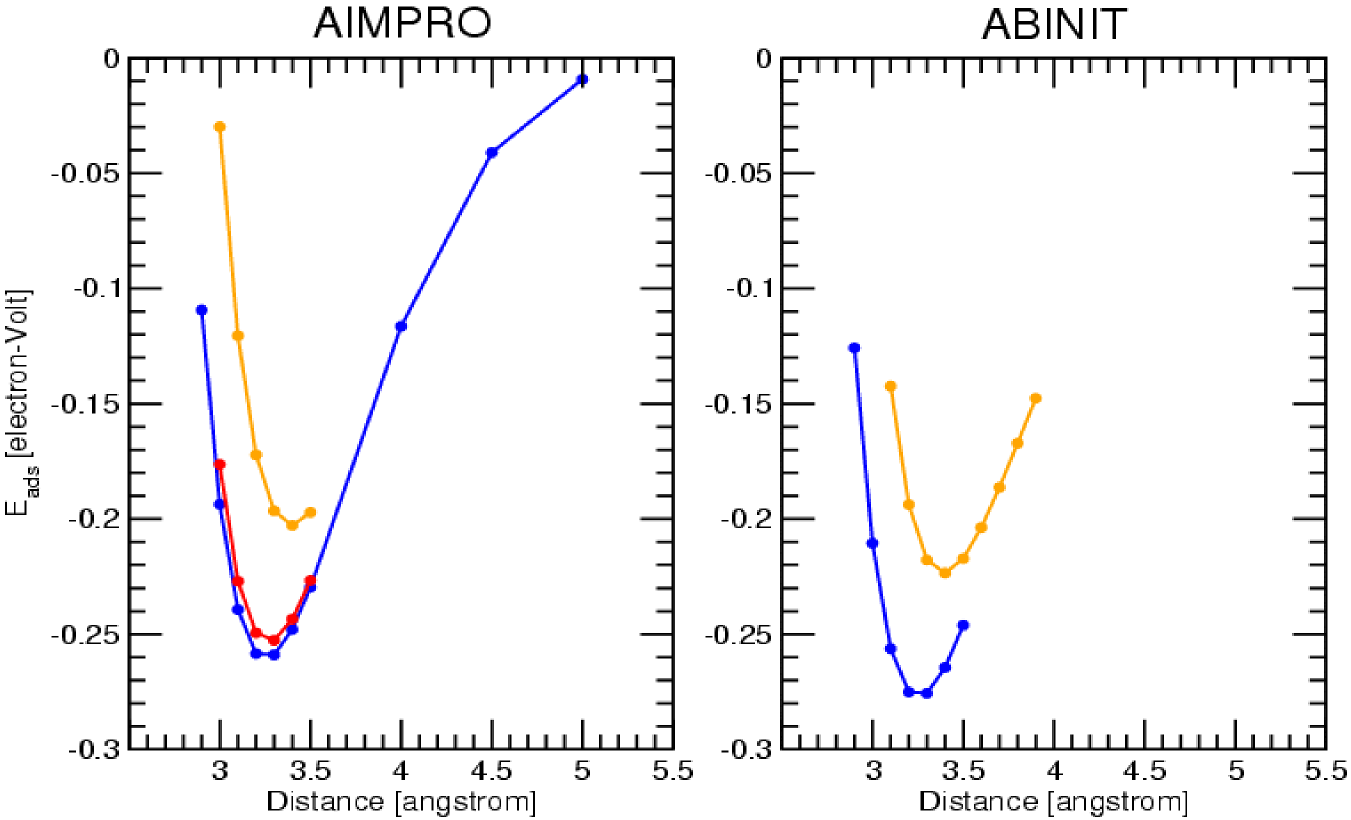
Ab-initio calculation

DFT-LDA (structure + electronic properties)

Structure

Equilibrium positions



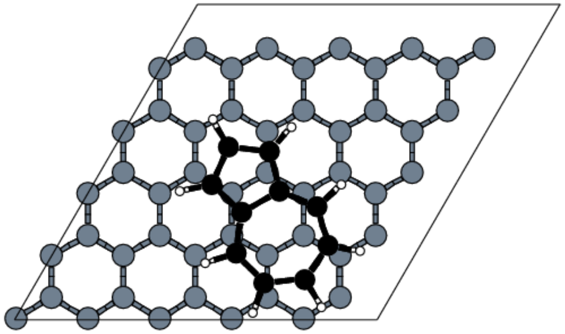


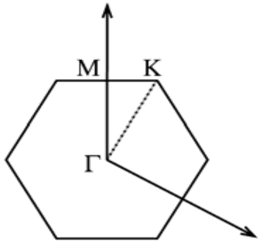
http://aimpro.ncl.ac.uk **http://www.abinit.org**

S. Latil (Univ. Namur)

Electronic properties : multiscale method

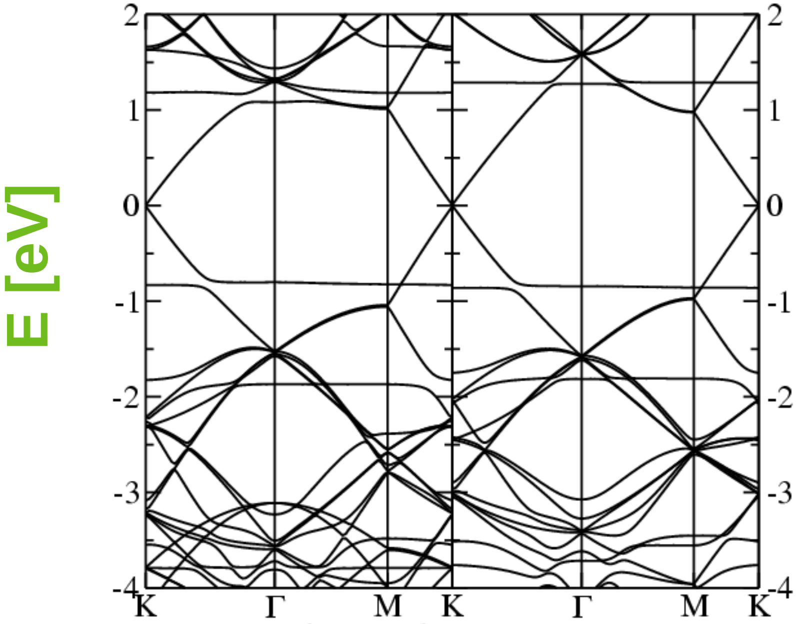
ab-initio (DFT)





DFT

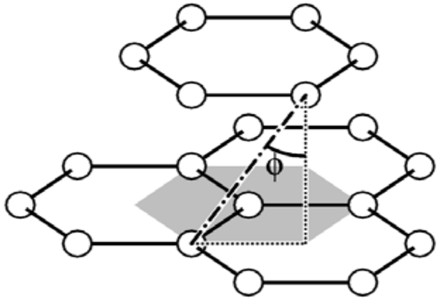
Tight-binding
parametrization



Effective model

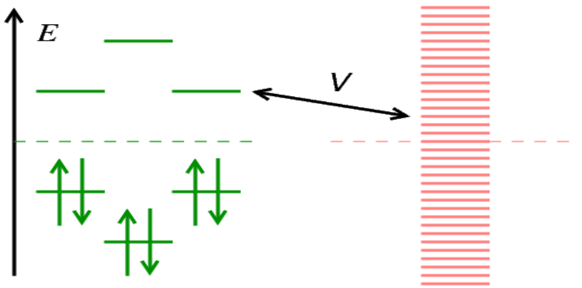
$|\pi_i\rangle =$ onsite orbital i, $energy = \varepsilon_i$

$$H = \sum_{\langle i,j \rangle} \varepsilon_i |\pi_i\rangle\langle\pi_i| - \gamma_0 \sum_{\langle i,j \rangle} |\pi_j\rangle\langle\pi_i| - \sum_{\langle i,j \rangle} \beta_{ij} |\pi_j^{mol}\rangle\langle\pi_i^{CNT}| + C.C$$



$$\beta_{ij} = \gamma_0 \cos(\phi_{ij}) e^{-(d_{ij}-\delta)/L}$$

Electronic properties of hybrid systems

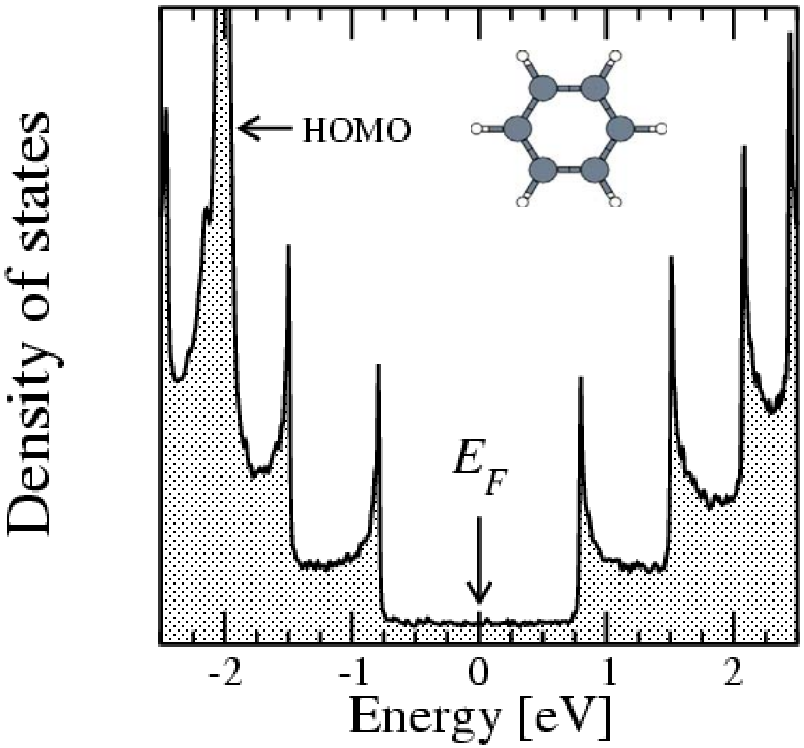


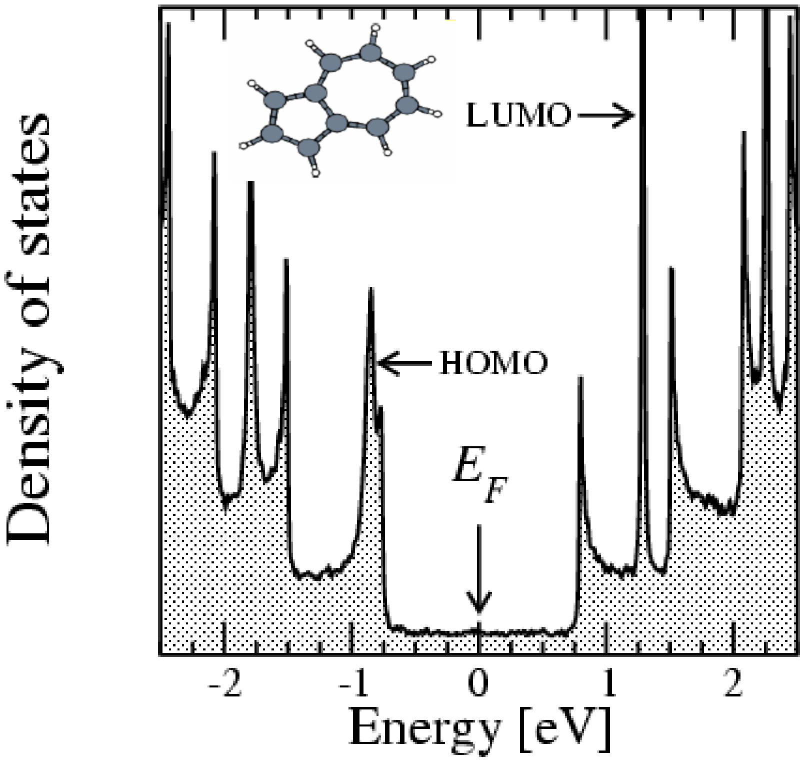
Molecules

LUMO

HOMO

Nanotube



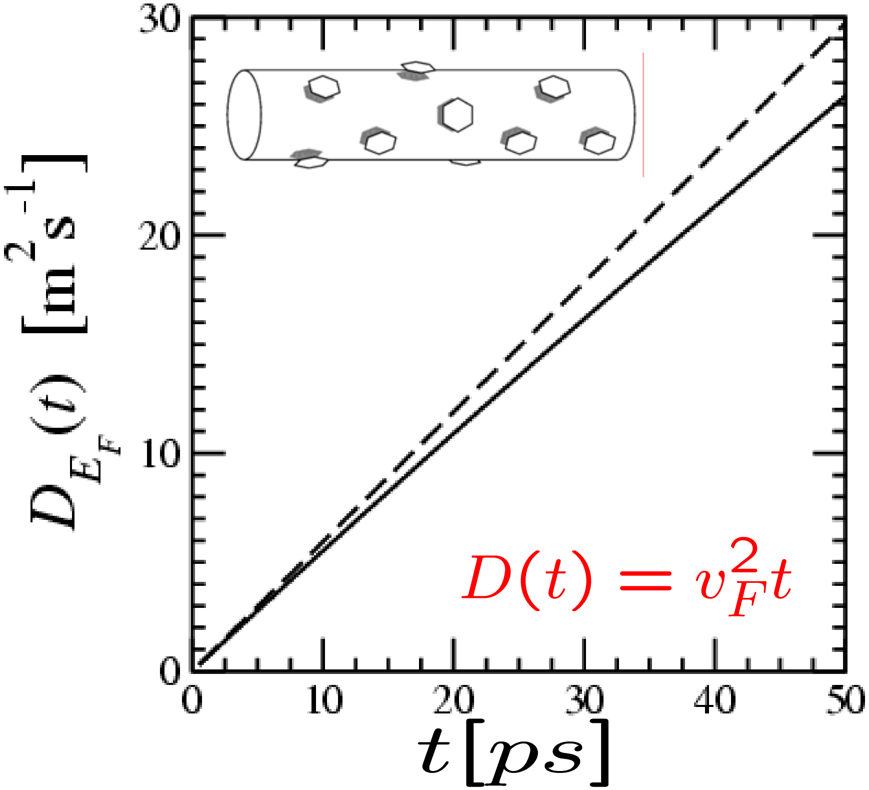


Molecular dependent transport scaling properties

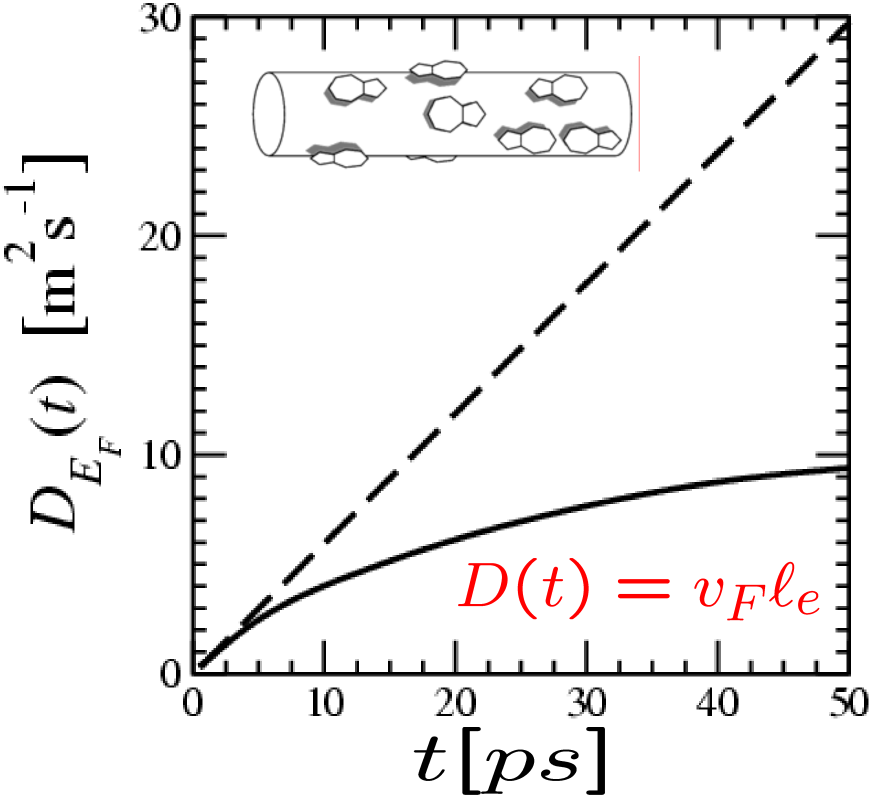
Random coverage of physisorber molecules C_6H_6 et de $C_{10}H_8$

$$D(E,t) = \frac{1}{t}\langle(\hat{X}(t) - \hat{X}(0))^2\rangle_E$$

Ballistic conduction

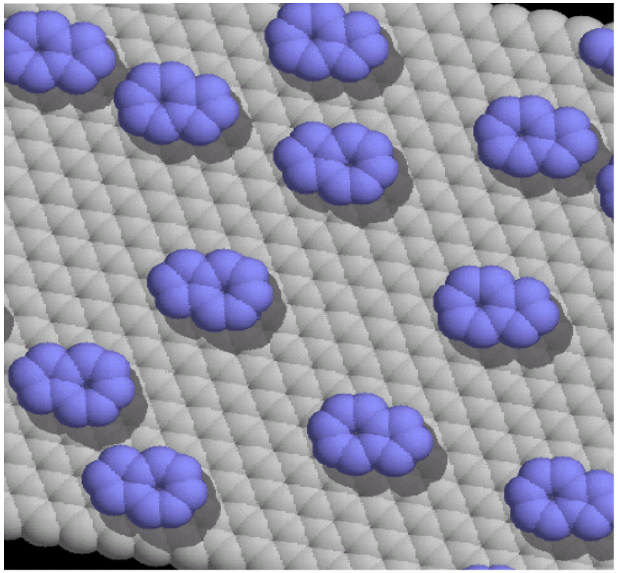


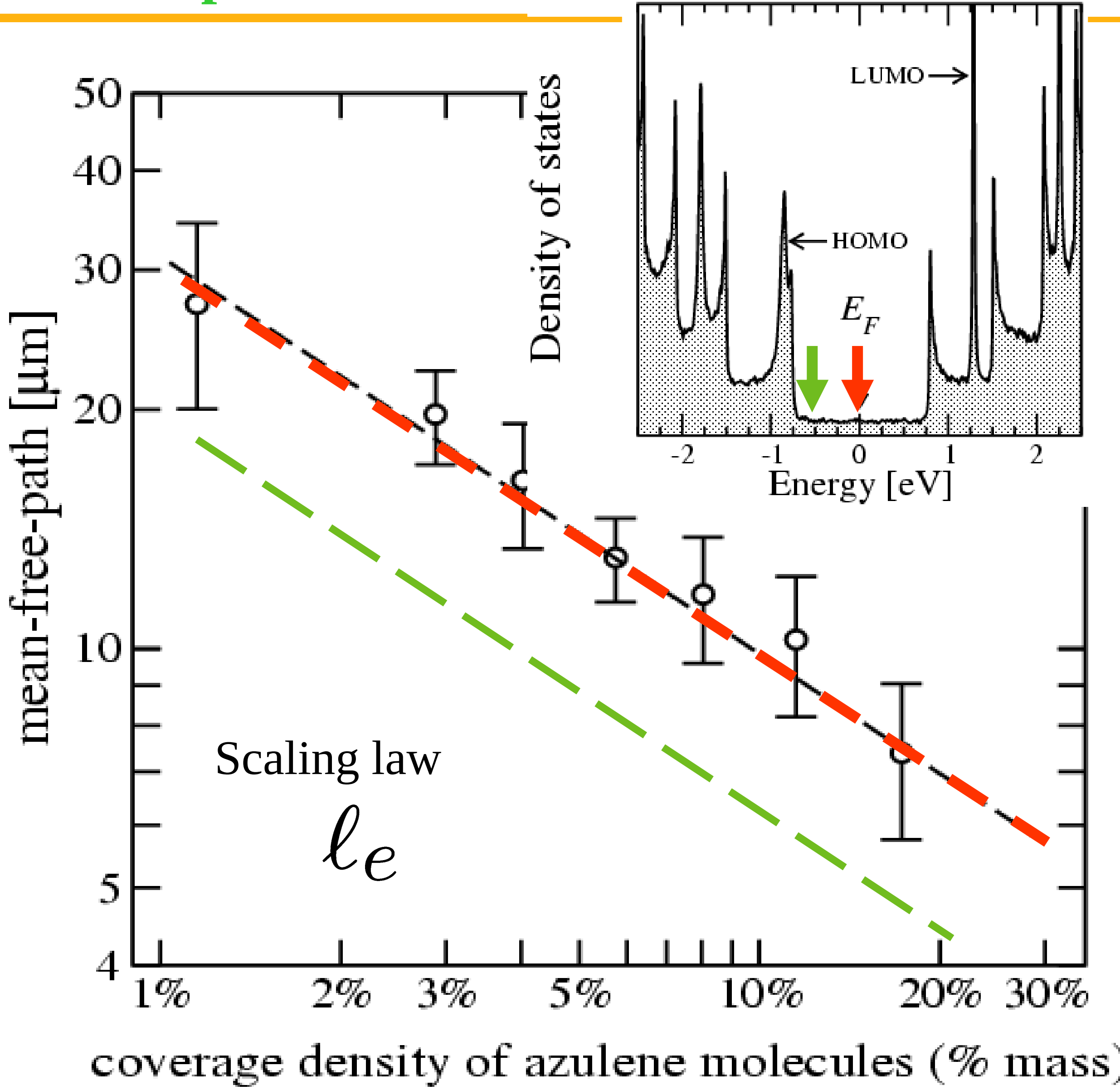
Diffusive conduction



Azulene case: mean free path

Random coverage
$C_{10}H_8$





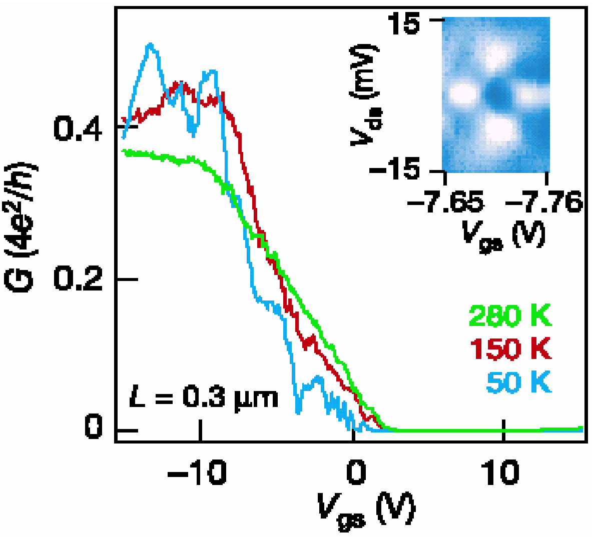
Scaling law
ℓ_e

downscaling of
MFP as FL approaches
HOMO resonance

ℓ_e

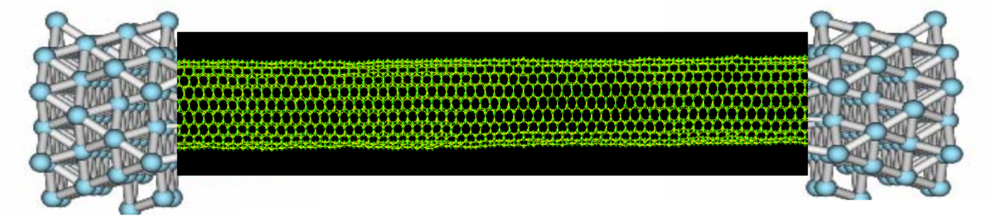
S. Latil, S.R., JC. Charlier, Nano letters 5(11), 2216 (2005)

Ballistic transport limitations (high bias conditions)



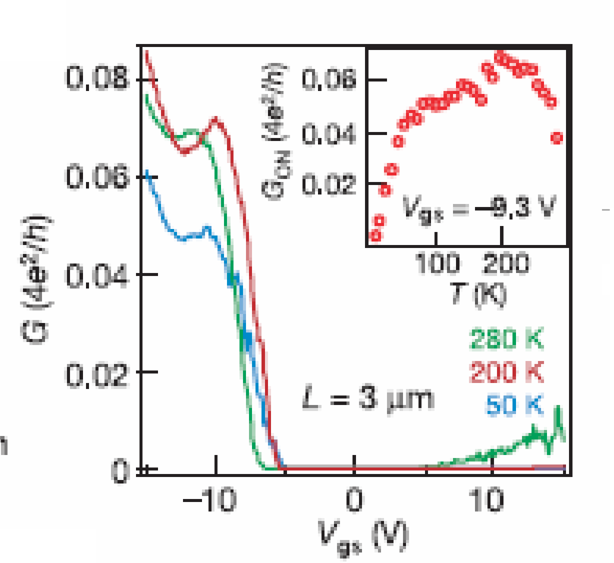
Electron-phonon coupling

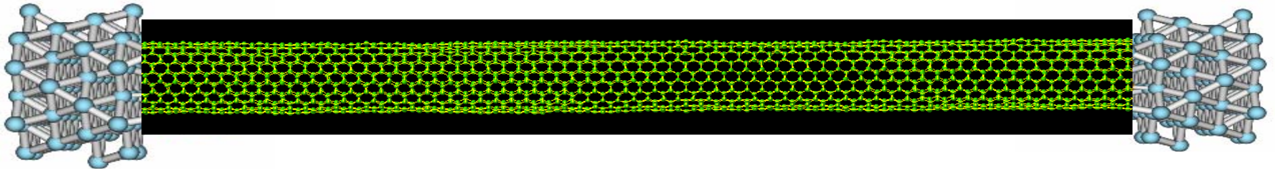
(high energy-optic vibrational modes)



$L=0.3\mu m > L_{el-ph}$

Balistic regime





$L=3\mu m < L_{el-ph}$

« ohmic-like regime ? »

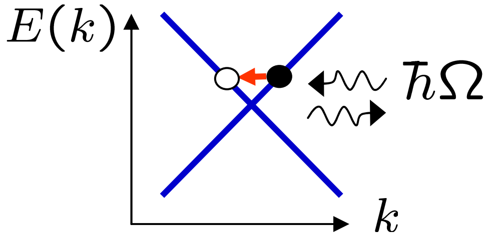
A. Javey, J; Guo, Q. Wang, M. Lundstrom & H.J. Dai

Nature 424, 654 (2003)

Electron-Phonon coupling in Carbon Nanotubes

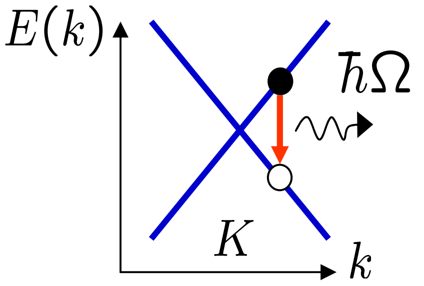
Acoustic Phonons

$q \sim 0, \hbar\Omega \ll k_B T$



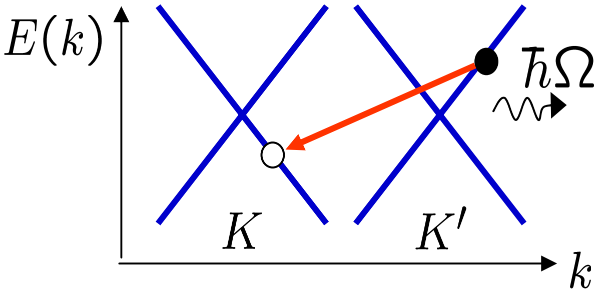
Optical phonon

$q \sim 0, \hbar\Omega > k_B T$

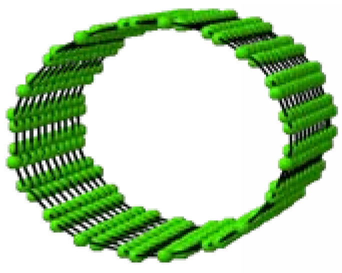


Zone boundary phonon

$q > 0, \hbar\Omega > k_B T$

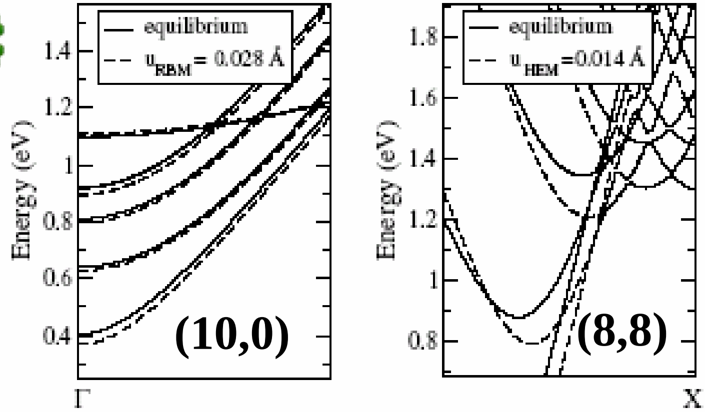


Atomic displacements & electronic structure



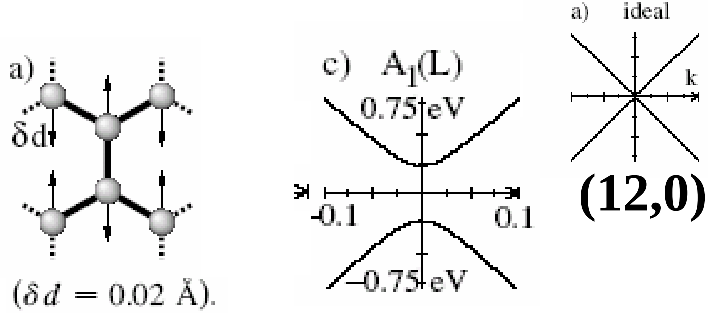
Ab-initio calculations

RBM mode : change in diameter



M. Machon, S. Reich et al., Phys. Rev. B 71, 035416 (2005)

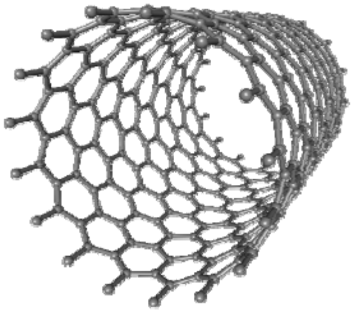
Optic modes A_1(L)



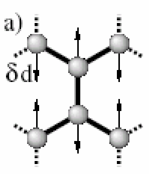
Gap opening

O. Dubay, G. Kresse, H. Kuzmany,
Phys. Rev. B 88, 235506 (2002)

Quantum Transport in presence of el-ph coupling



Hamiltonian

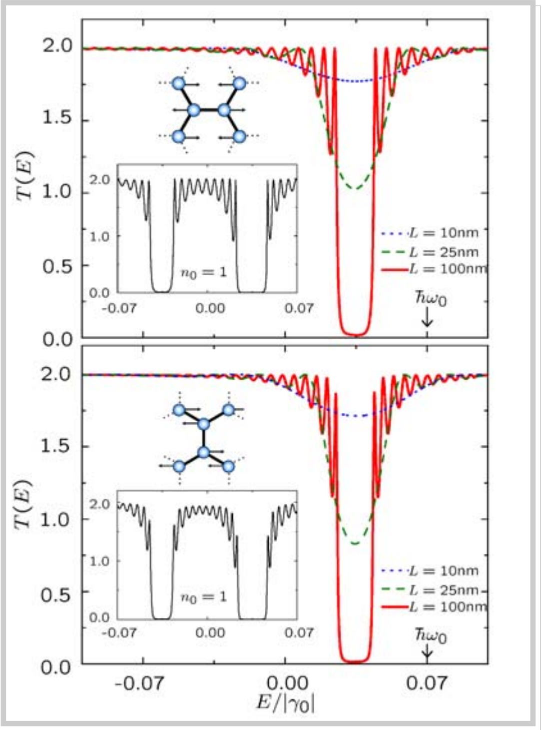


A$_1$(L)

$$H_e = -\gamma_0 \sum_{\langle i,j\rangle} \left[c_i^+ c_j + h.c.\right],$$

$$H_{ph} = \hbar\omega_0 b^+ b,$$ ***Mode LO (1580cm^{-1})***

$$H_{e-ph} = \sum_{\langle i,j\rangle_{vib}} \left[\gamma_{i,j}^{e-ph} c_i^+ c_j (b^+ + b) + h.c.\right]$$



Inelastic transport computed from
a many-body treatment of e-p in Fock space

Bonca and Trugman, PRL 75, 2566 (1995)

Peierls-type mechanism
when the electrons gain enough energy (bias source) to emit optic phonons…
Backscattering probability =1

Luis Foa-Torres and SR, Phys. Rev. Lett. 97, 076804 (2006)

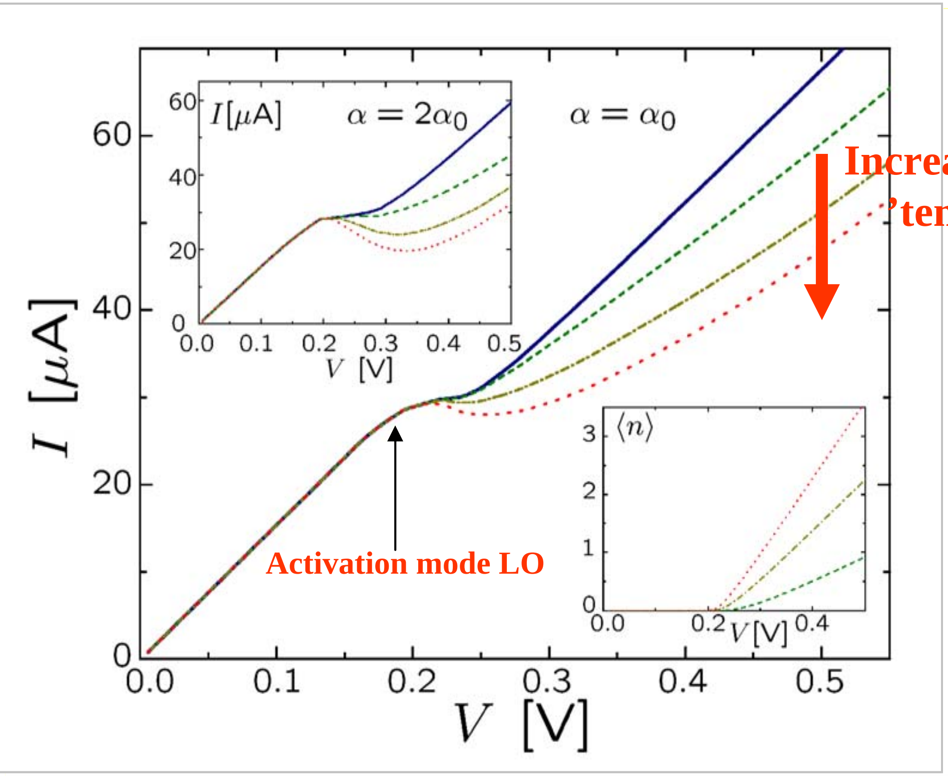
Peierls type mechanism & onset of current saturation

Ballistic regime

$$I = \frac{4e^2}{h}V$$

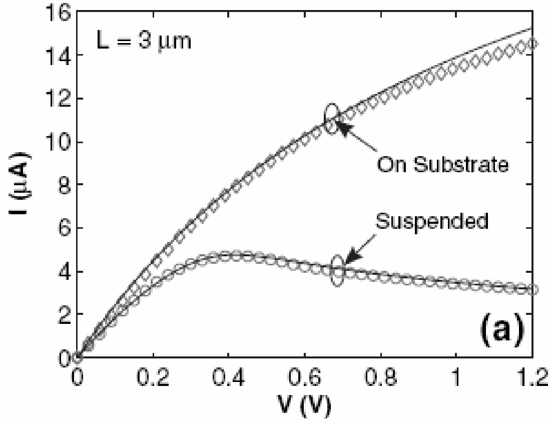
Onset of current saturation at $V = \hbar\omega_0$

$$I_{sat} = \frac{4e}{h}\hbar\omega_0$$



Activation mode LO

Increasing phonon 'temperature'



E. Pop et al, **PRL 95, 155505 (2005)**

These mechanisms are beyond the scope of a Fermi Golden rule-type description of inelastic backscattering

L.F. Foa-Torres and S.R., **Phys. Rev. Lett. 97, 076804 (2006)**

Thank you for your attention!

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