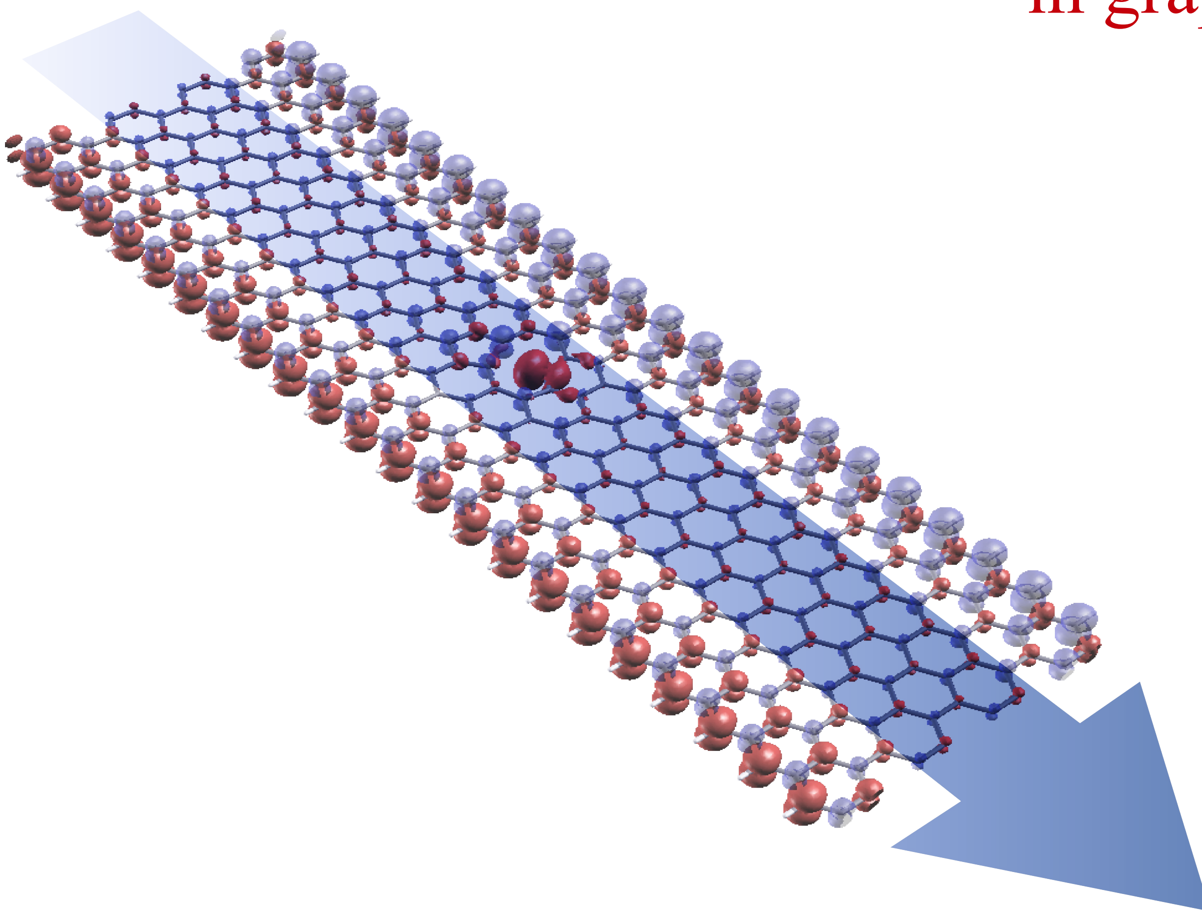
Quantum Transport

in graphene nanostructures

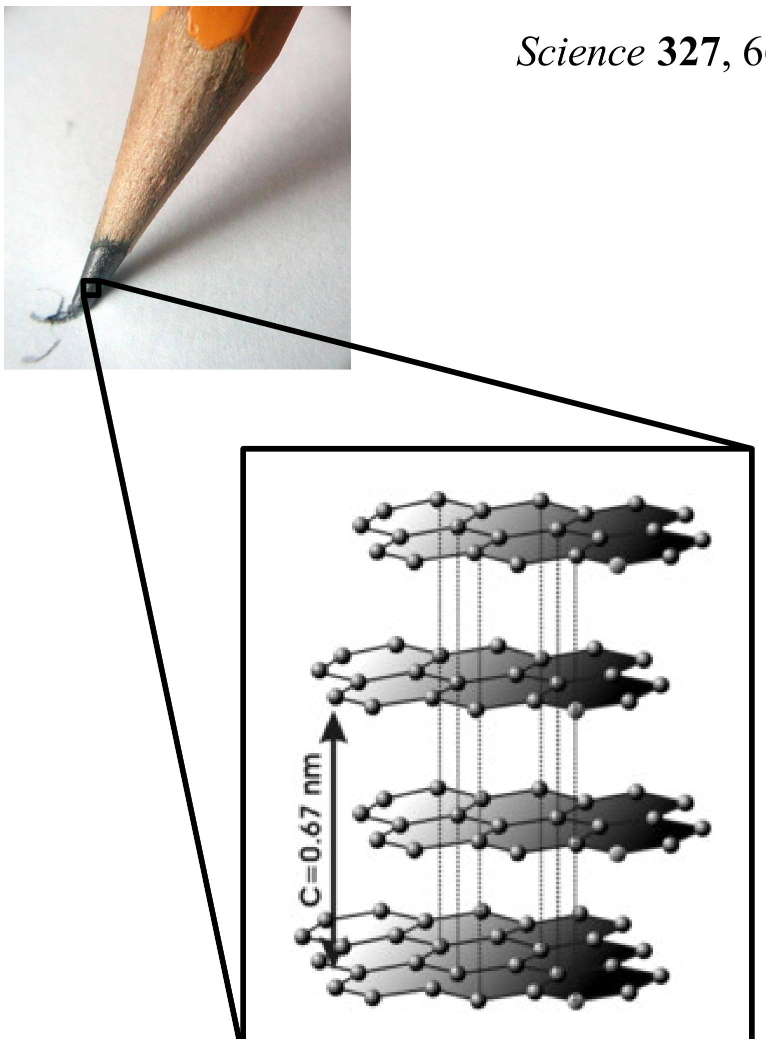


Simon Mutien-Marie Dubois

University of Cambridge
Cavendish Laboratory

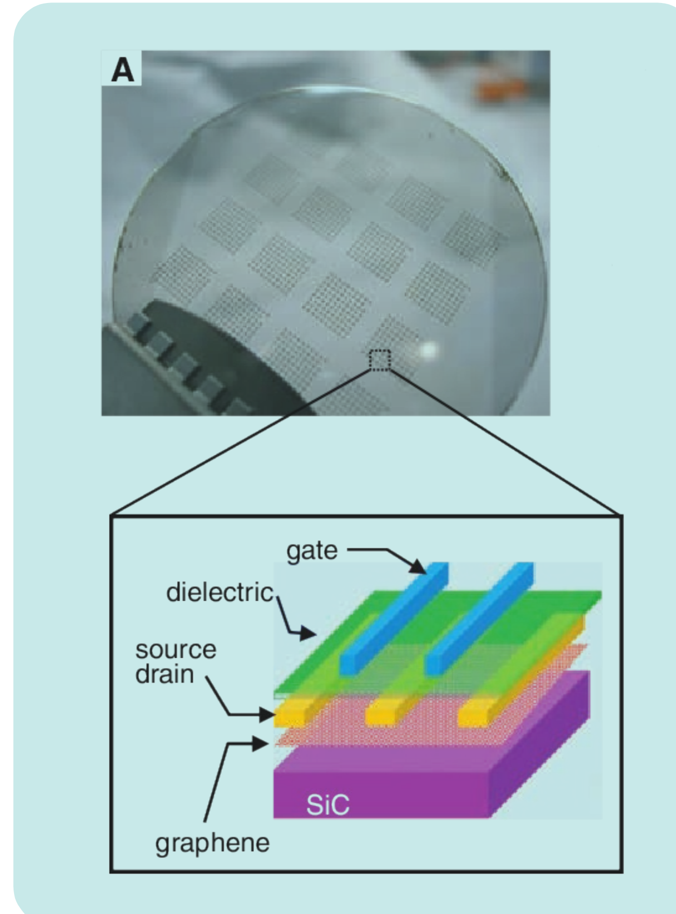
Onetep Spring School,
April, 17th 2010

Graphene wonderland....



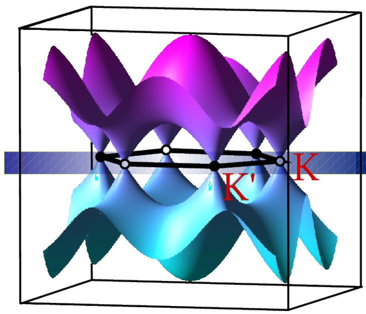
IBM 100-GHz Transistors
from epitaxial Graphene !

Science **327**, 662 (2010)

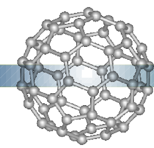


... show extremely high carriers mobilities and hold great promises for applications in electronics such as ultrahigh-speed transistors !

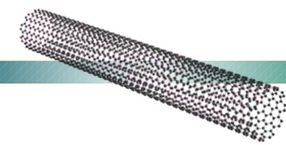
Graphene wonderland....



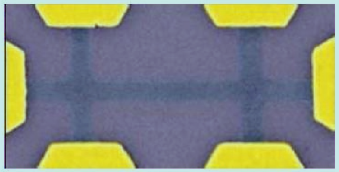
1947:
Graphene band-structure
Wallace

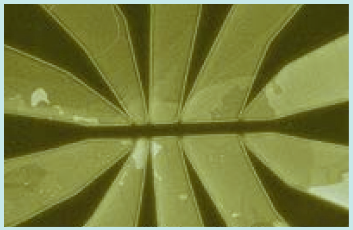


1985:
Fullerenes
Kroto, Curl, Smalley

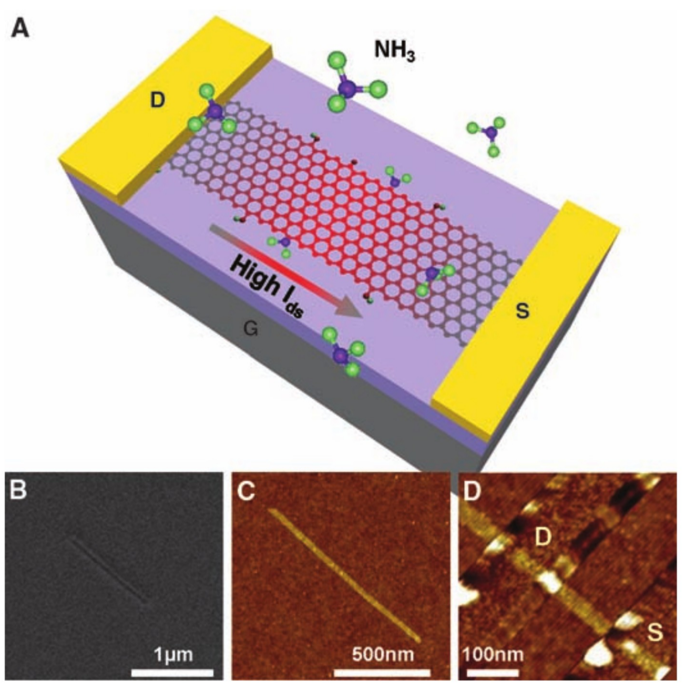


1991:
Nanotubes
Ijima





2004:
Contacted graphene
Novoselov, Geim
Berger, de Heer



X. Wang et al. Science 324, 768 (2009)

Well defined smooth GNRs
X. Li et al., Science 319, 1299 (2008)
M.Y. Han et al., PRL 98, 206805 (2007)

Half-metallicity of GNRs in electric fields
Son et al., Nature 444, 347 (2006)

Very large magnetoresistance in GNRs
W.Y. Kim and K.S. Kim, Nature Nanotech. 3, 408 (2008)

P- and n-type graphene FET
X. Wang et al., Science 324, 768 (2009)

Outline of presentation

- Graphene : its structure and properties

  → why do we consider graphene nanoribbons for application in nano-electronics ?

- Graphene nanoribbons

  → electronic confinement, reconstruction of the edge, stability of point-defects

- Electronic transport in defective nanoribbons

  → conductance patterns of point-defects, conductance scaling in mesoscopic samples

- Onetep future capabilities regarding quantum transport

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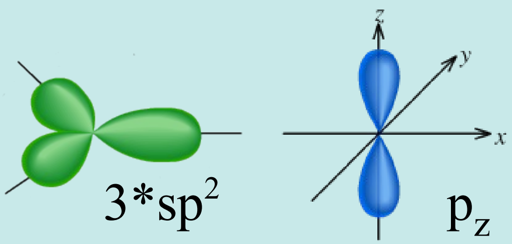
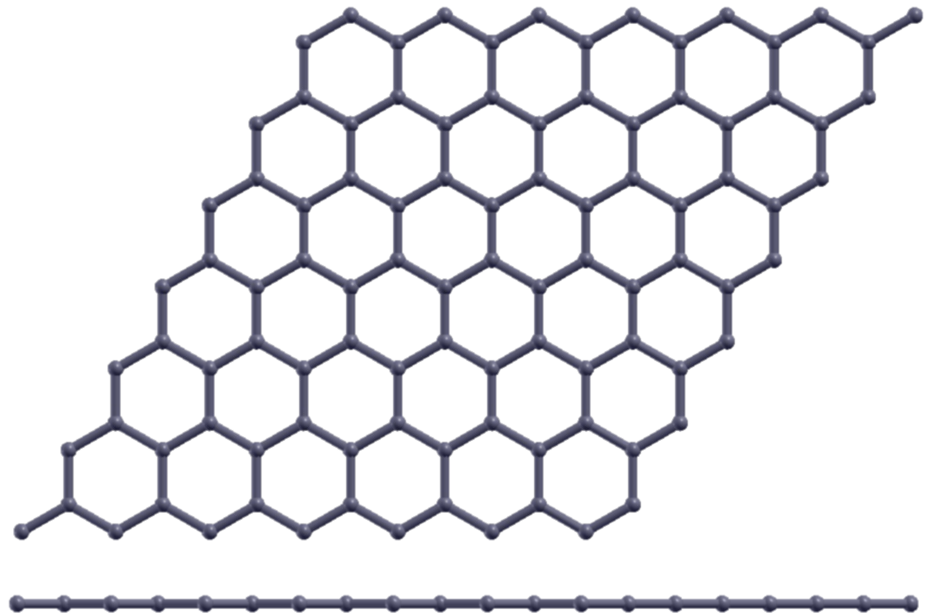
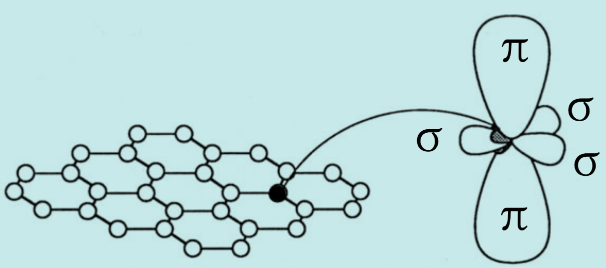
Graphene, the thinnest of all materials....

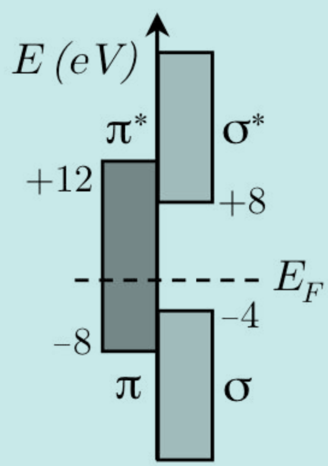




Graphene :

2D plane in which carbon atoms are periodically arranged in an hexagonal network.





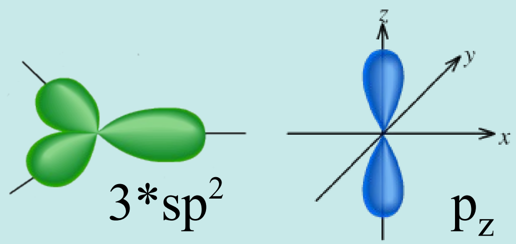
sp^2 → strong σ-bonds

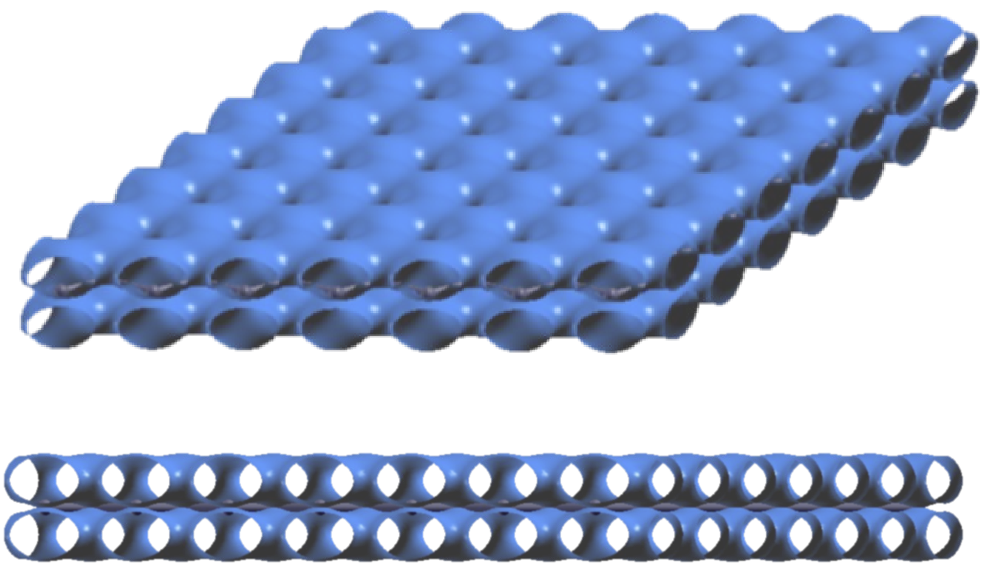
→ network structure

p_z → delocalized π-bonds

→ low energy electronic structure

Graphene, the thinnest of all materials....





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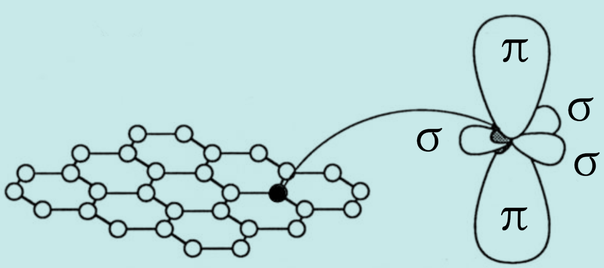

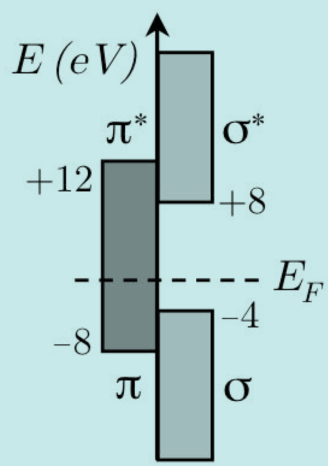

sp^2 → strong σ-bonds

→ network structure

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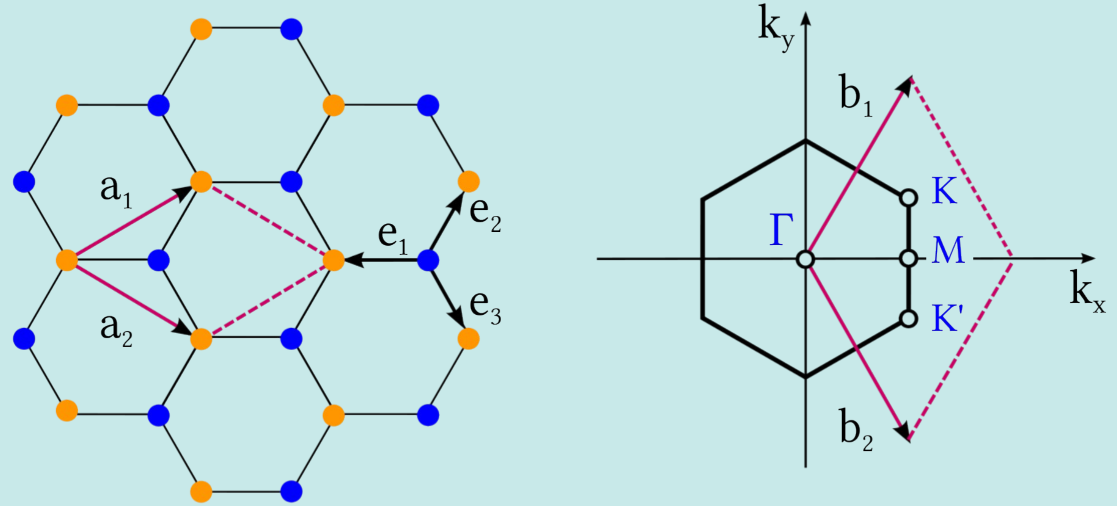
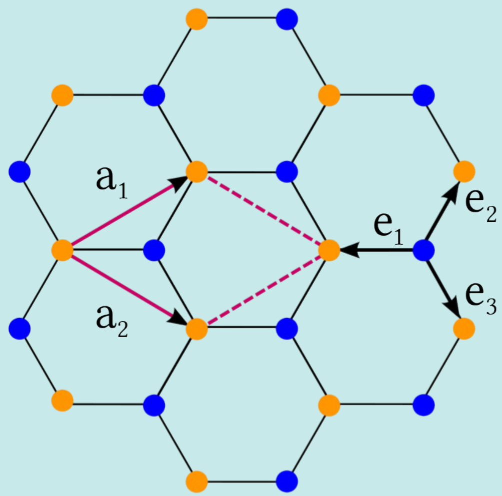
Peculiar energy-momentum relation :

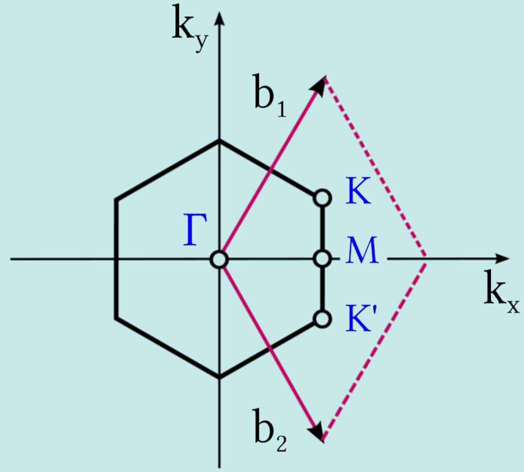


Band structure :

$$\hat{H} = \sum_{\mathbf{R}} \left(\epsilon_a \, \hat{a}^\dagger_{\mathbf{R}} \hat{a}_{\mathbf{R}} \, + \, \epsilon_b \, \hat{b}^\dagger_{\mathbf{R}+\mathbf{e}_1} \hat{b}_{\mathbf{R}+\mathbf{e}_1} \right) \, + \sum_{\mathbf{R}} \sum_{i=1,3} -t \, \left(\hat{b}^\dagger_{\mathbf{R}+\mathbf{e}_i} \hat{a}_{\mathbf{R}} \, + \, \hat{a}^\dagger_{\mathbf{R}} \hat{b}_{\mathbf{R}+\mathbf{e}_i} \right)$$

Peculiar energy-momentum relation :



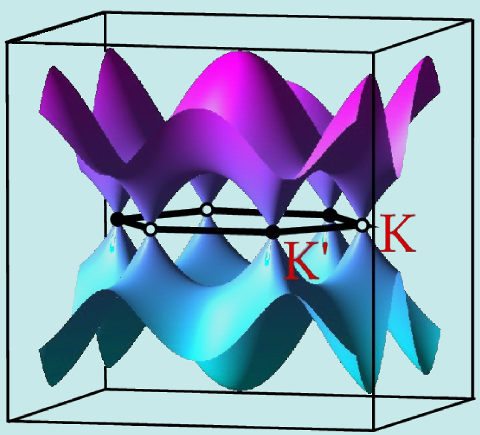


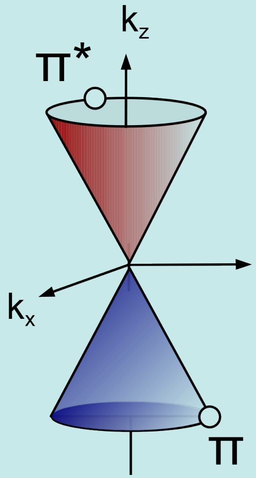
$$\epsilon_{\mathbf{k},c/v} = \pm t \left| \sum_{i=1,3} e^{i\mathbf{k}.\mathbf{e}_i} \right|$$

Band structure :

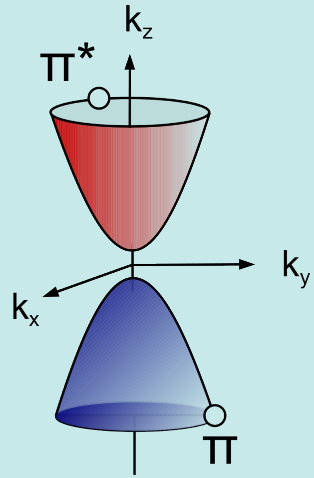
- Zero gap
- Electron-hole symmetry
- Linear dispersion

Graphene





Semi-conductors

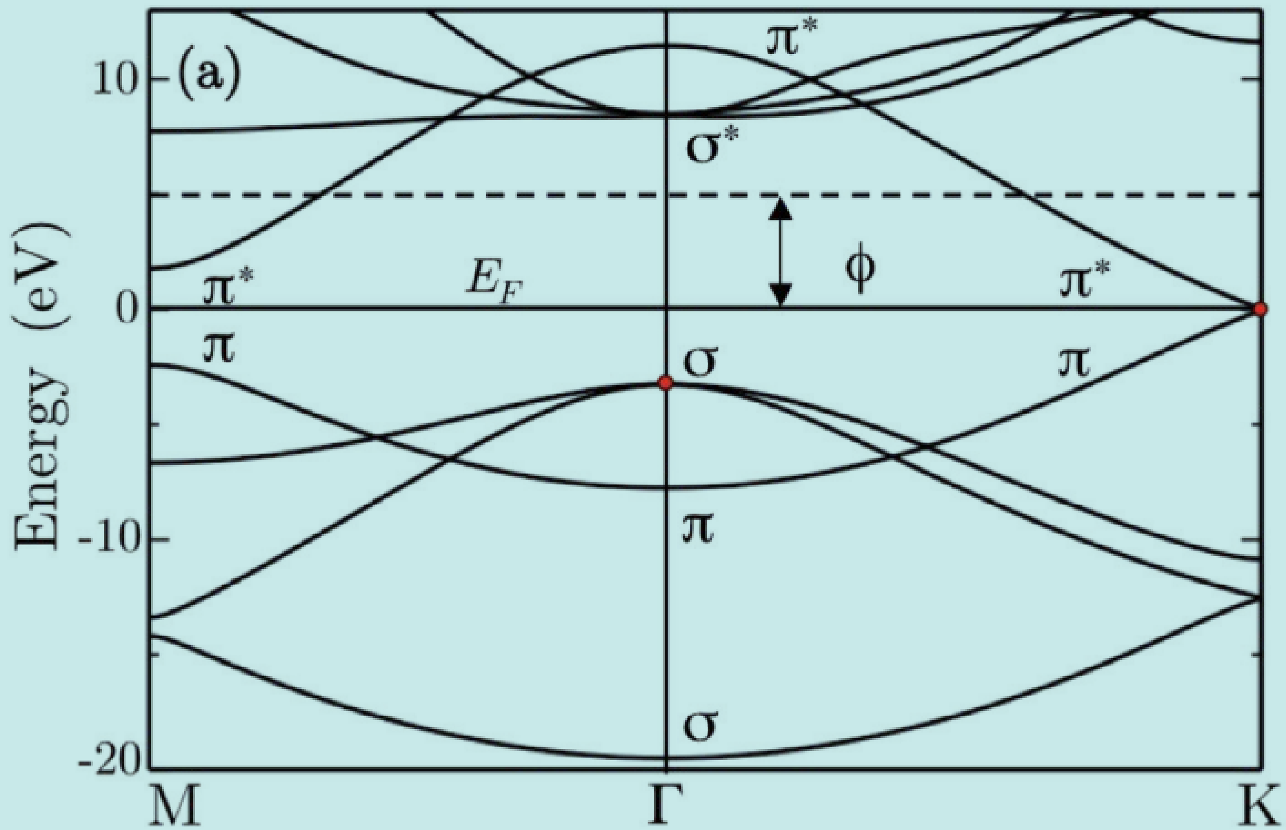


The remarquable properties of graphene :

- Peculiar energy-momentum relation

DFT calculation ....

- Zero gap
- Broken electron-hole
- Linear dispersion



J.-C. Charlier et al. Rev. Mod. Phys. 79, 677 (2007)

Many remarquable properties :

- Peculiar energy-momentum relation
  - → connection with the 2D massless Dirac equation
  - → anomalous quantum Hall effect, Klein paradox, ...

- High thermal conductivity (up to 5300 [W/m.K] at room temp)

  Diamond : up to 2000 [W/m.K] Cu : ~ 400 [W/m.K]

- Ultra high carriers mobilities (up to 200.000 [cm^2/V.s] at room temp)

  Silicon : 1400 [cm^2/V.s] and InSb : 78000 [cm^2/V.s]

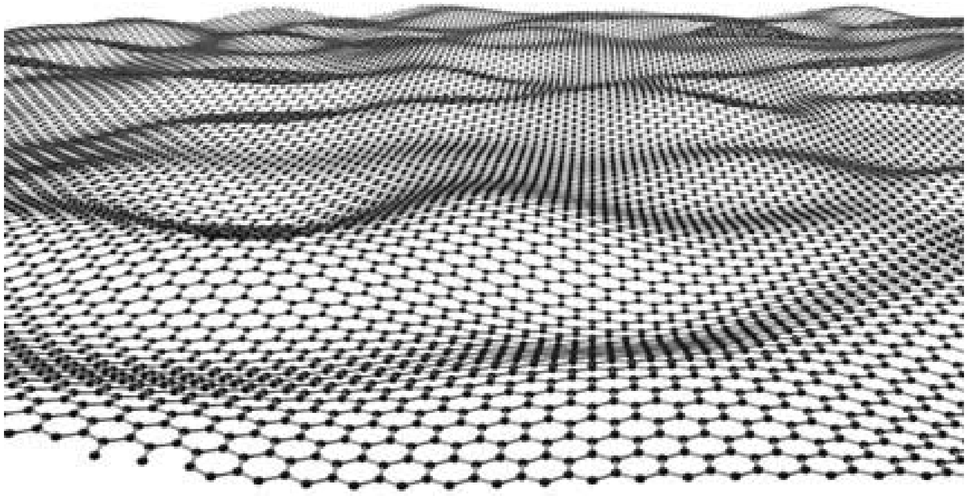
- Spin coherence length up to 1 μm

- Strongest material ever measured

  (extremely high Young modulus and breaking stress)

- Chemically inert, thermally stable, optically transparent

Great promises for application in electronics....



Spintronic applications

Micro-electro-mechanical devices (MEMS)

Field emitters

Ultrafast transistor

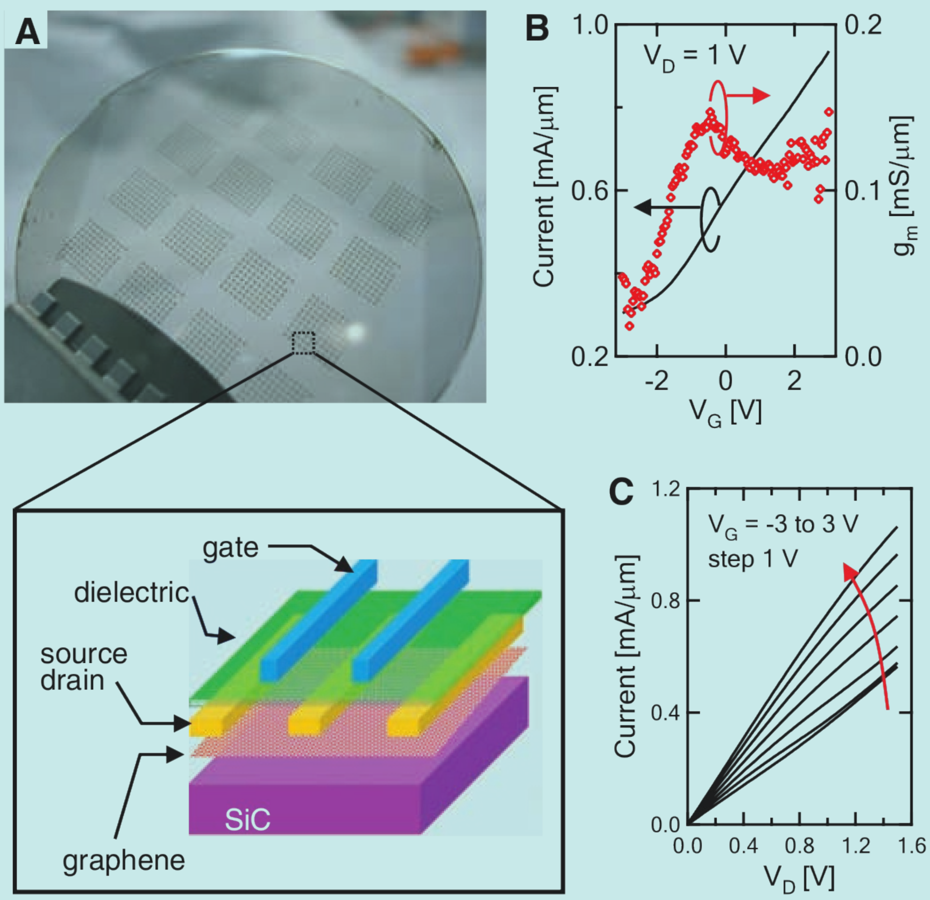
Devices in extreme conditions

Transparent electrodes for LEDs, improved solar cells?

Gas and molecules sensors

Nanoscale electric connections

A bit too conductive for FET....



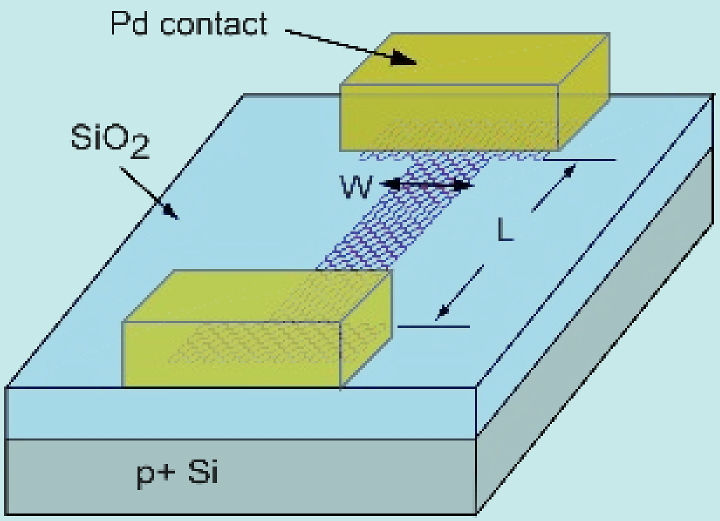
IBM 100-GHz Transistors
from epitaxial Graphene
Science **327**, 662 (2010)

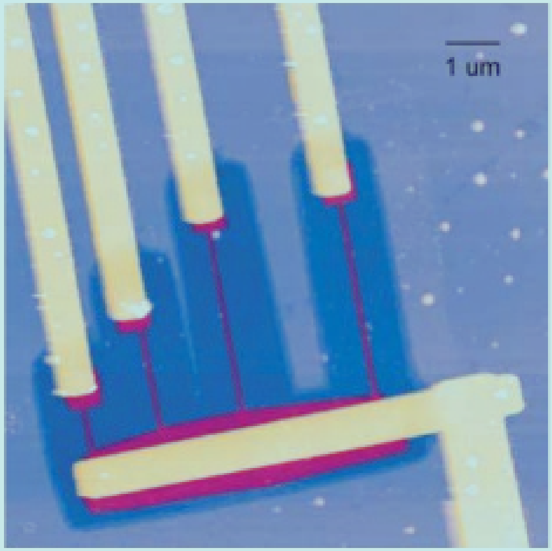
No energy gap !

Poor I_{on}/I_{off} ratio, not convenient for digital applications.

→ Graphene nanoribbons !

Energy gaps in graphene nanoribbons ?





Schematic representation of a GNR-FET and AFM image of actual GNR-FET devices.
Y.-M. Li et al., PRB 78, 161409(R) (2008).

→ High I_{on}/I_{off} ratio (> 10^5)

→ Carriers mobilities ~1000 cm^2/V.s
(<< 10^5 cm^2/V.s in graphene)

→ Poor signal to noise ratio

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- Onetep future capabilities regarding quantum transport

Theoretical framework.....

siesta

→ Pseudopotentials
→ LDA, GGA, Hybrid functionals
→ Localized basis set : NAOs
→ Atomic forces, stress tensor, (phonon)

+ efficient basis → high speed
+ direct interface with NEGF
+ extraction of adjusted TB parameters
+ lack of systematic variational convergence

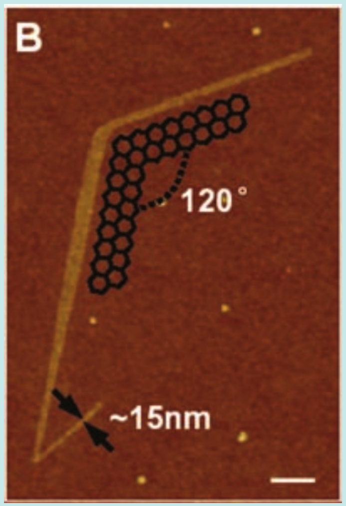
abinit.org

→ Pseudopotentials
→ LDA, GGA, Hybrid functionals
→ Plane Waves, PAW, (wavelets)
→ Atomic forces, stress tensor
→ Response functions (1^{st}, 2^{nd}, 3^{th} deriv)
→ GW approximation

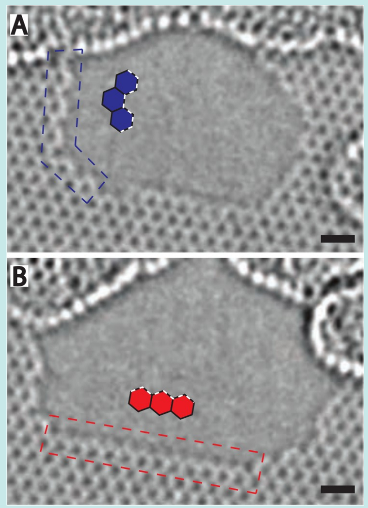
+ Complete basis sets
+ Lots of capabilities
+ Very robust
+ Lower speed
+ Indirect interface with NEGF via Max. Loc. Wannier Functions

Energy gaps in graphene nanoribbons?

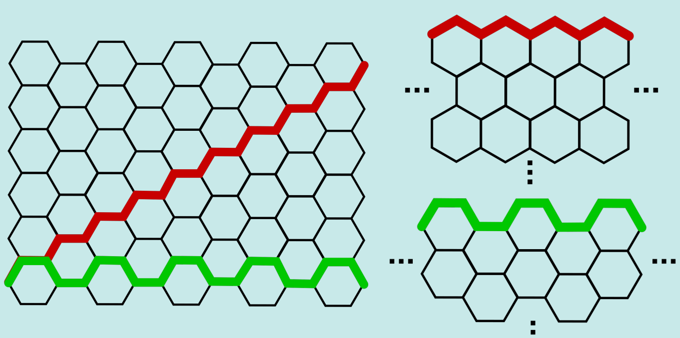
Experimental evidence of 2 main edge directions in graphene :



Afm image from X. Li et al. Science 319, 1229 (2008)



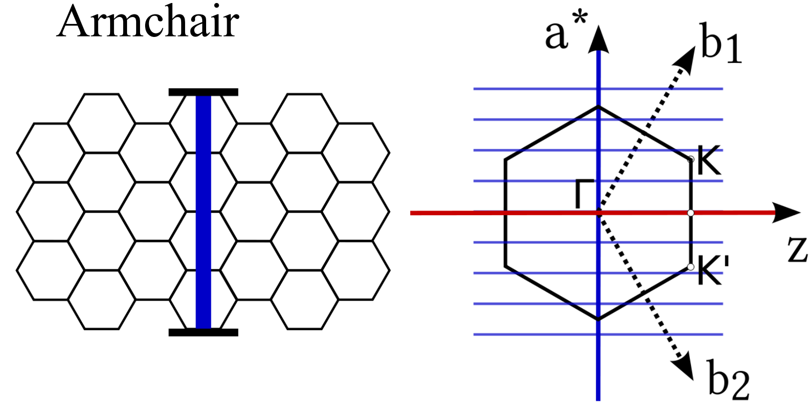
Aberration-corrected TEM images from C.O. Girit et al. Science 323, 1705 (2009)



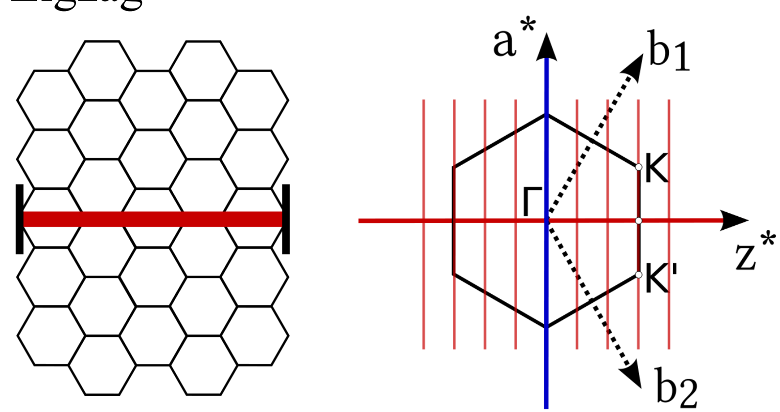
Two prototypical cutting directions with 30° of relative orientations, giving rise to the zigzag and armchair GNRs

Electronic confinement :

Armchair



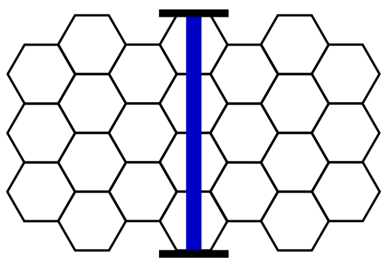
Zigzag

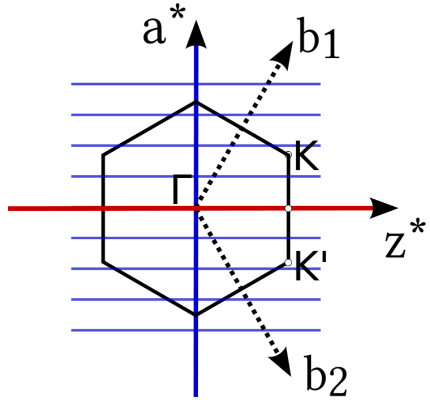


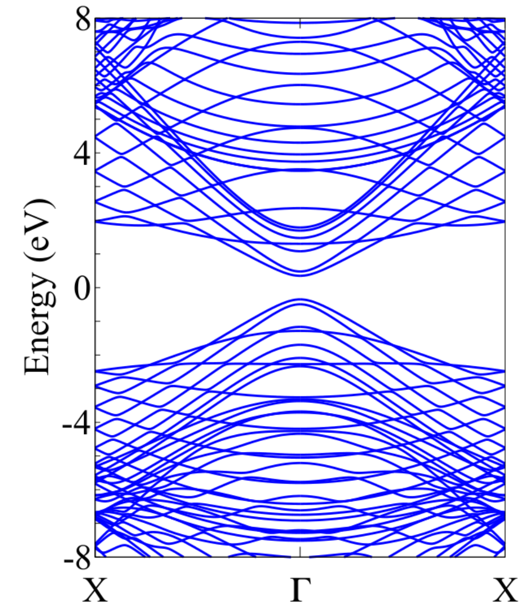
K. Nakada et al., Phys. Rev. B 54, 17954 (1996)

Electronic confinement in GNRs :

Armchair

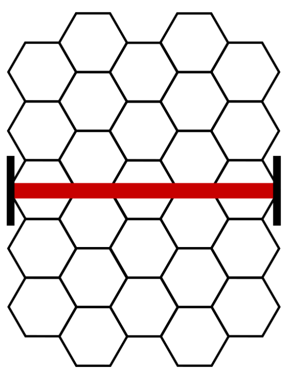


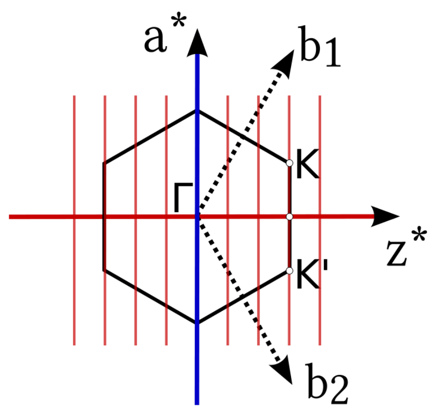


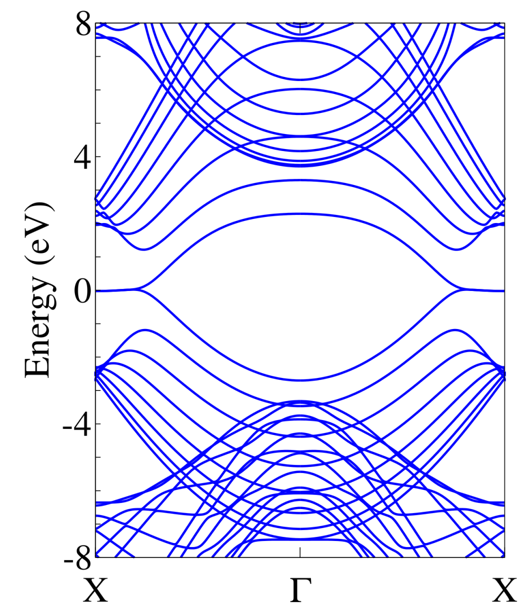


DFT

Zigzag

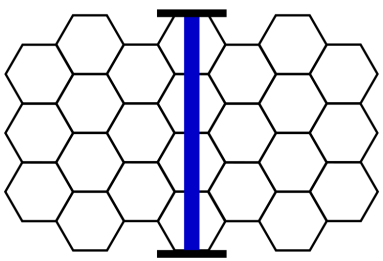


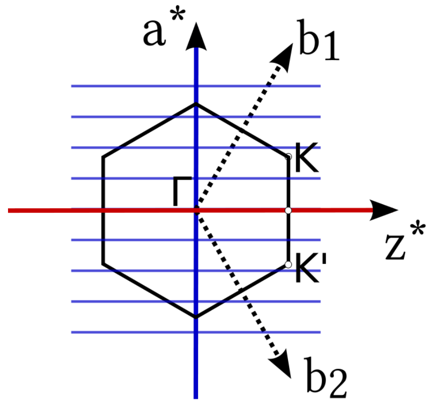


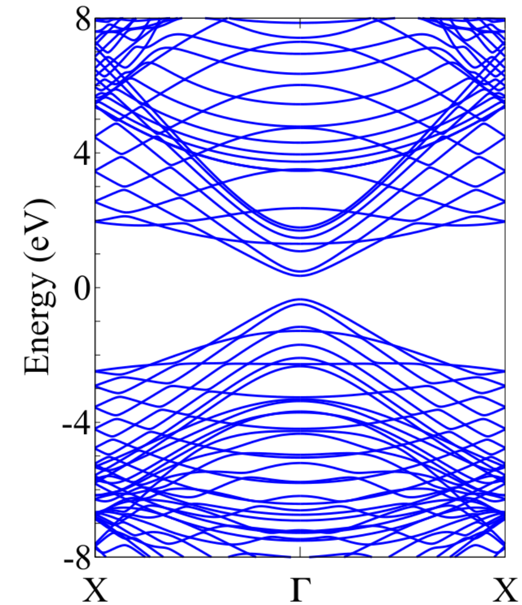


Electronic confinement in GNRs :

Armchair

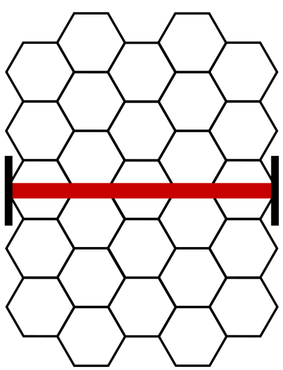


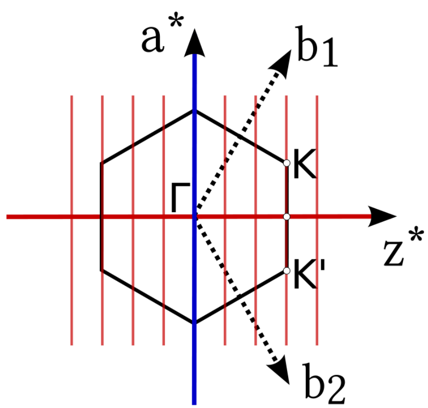


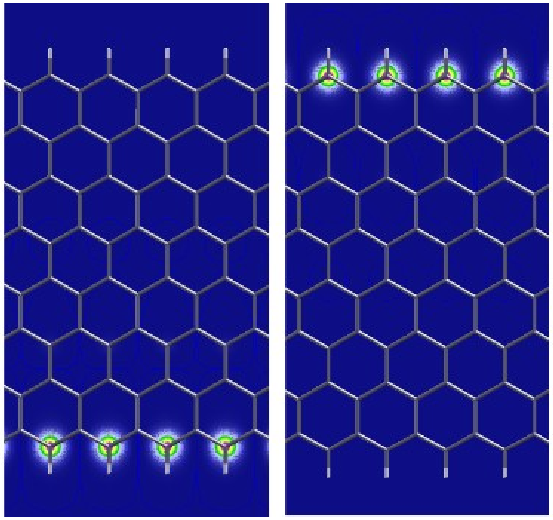


DFT

Zigzag



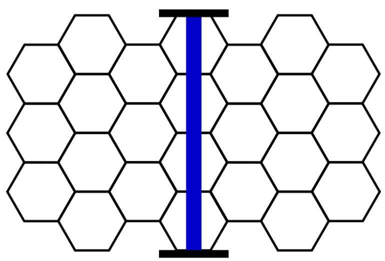




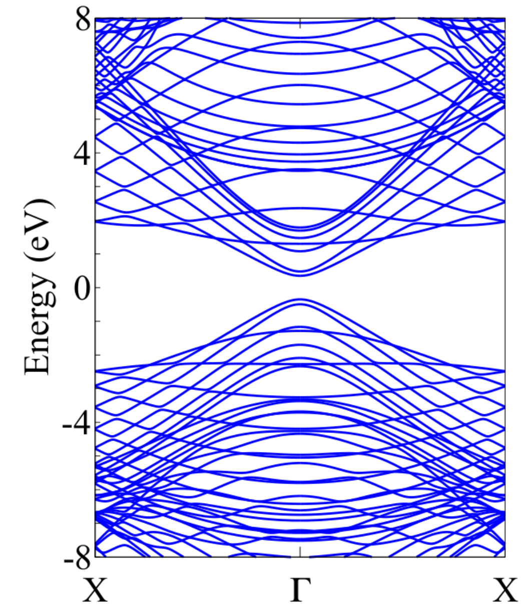
For more info. See :
Y.-W. Son et al., Phys. Rev. Lett. 97, 216803 (2006)
S. M.-M. Dubois et al., Eur. Phys. J. B 72, 1 (2009)

Electronic confinement in GNRs :

Armchair

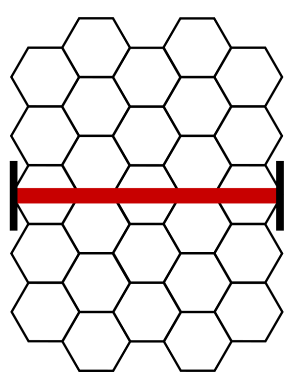


→

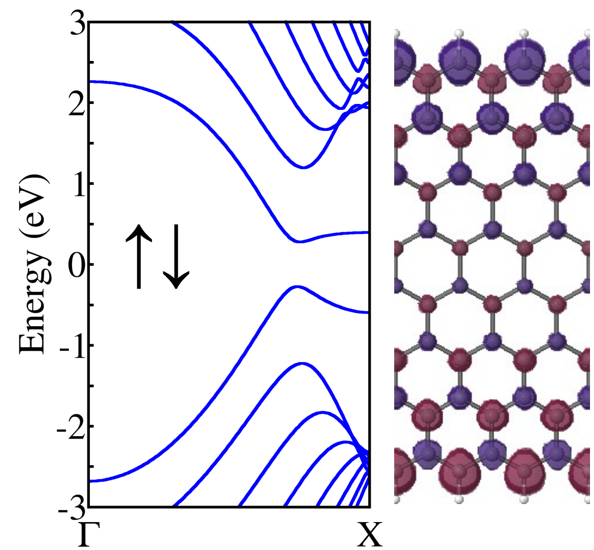


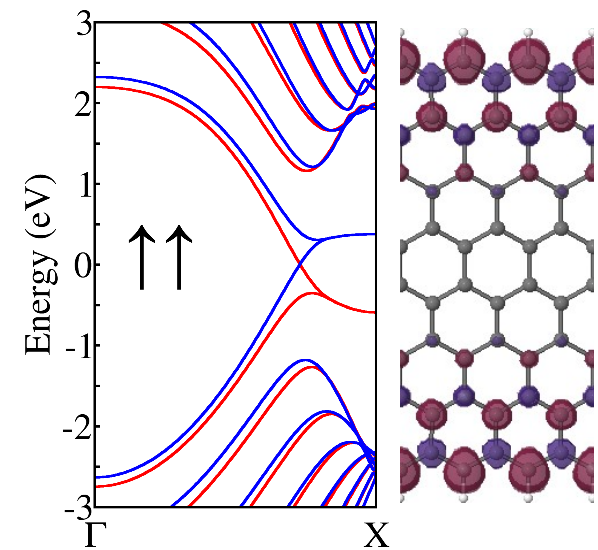
DFT spin-polarized

Zigzag



→





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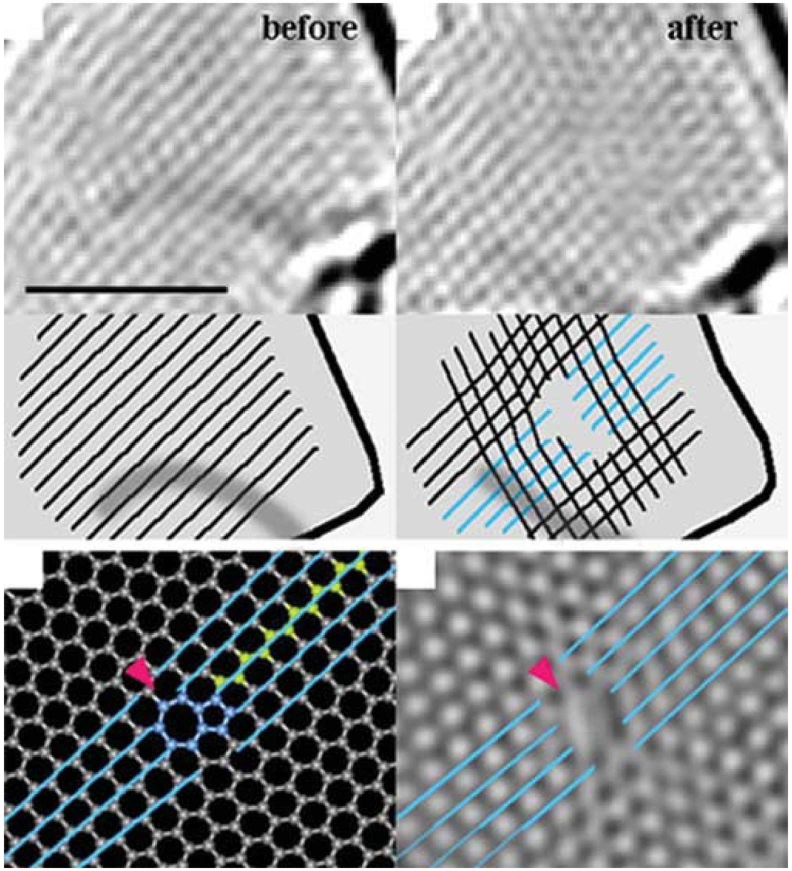
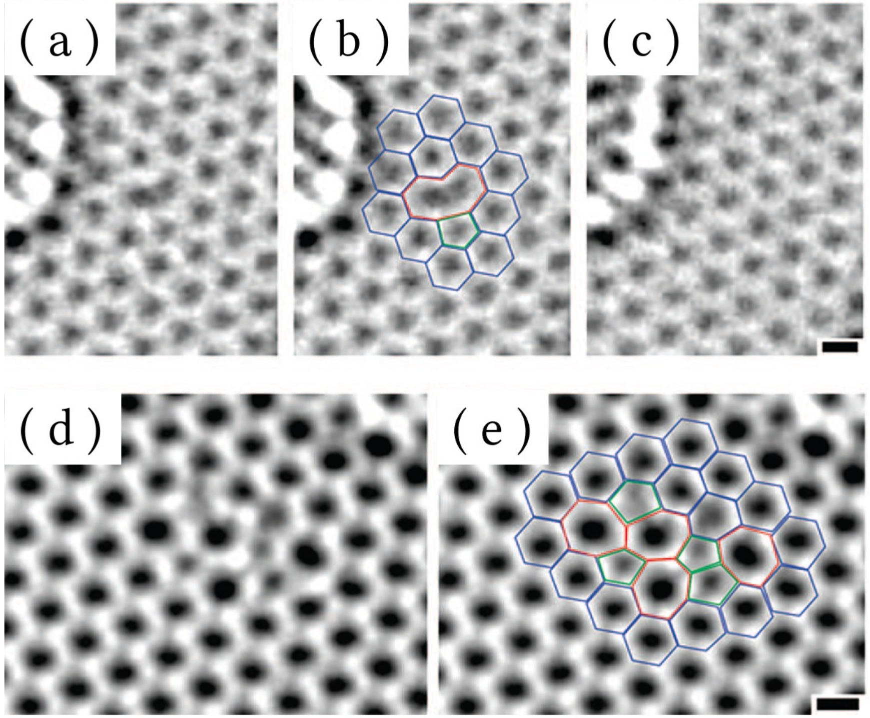
Local reconstruction of the GNRs : Point-defects



Irradiation induced defects observed with HRTEM
from A Hashimoto et al., Nature 430, 870 (2004)

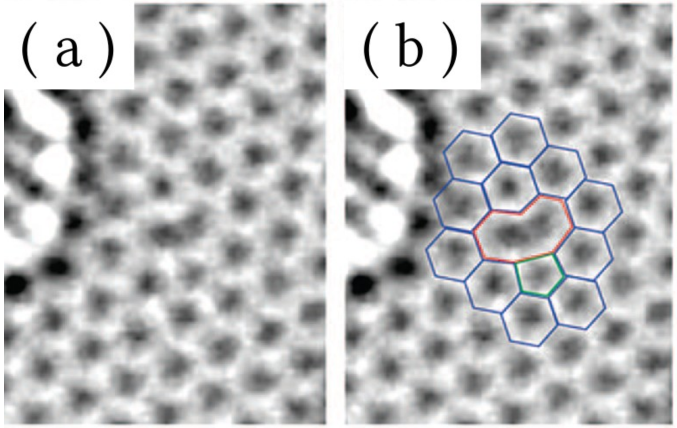


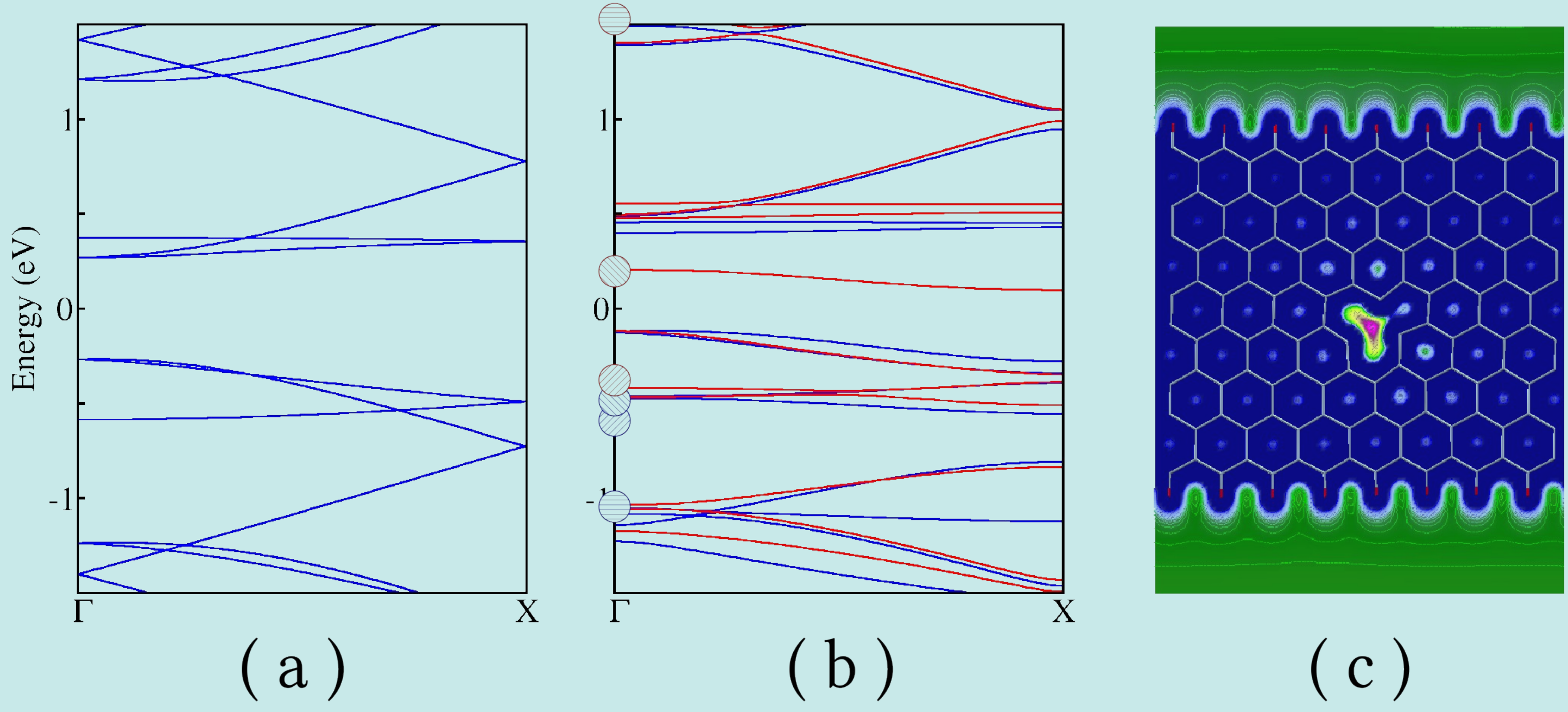
Metastable defects found in HRTEM image sequences
from J.C. Meyer et al., NanoLetters 8, 3582 (2008)

→ Defects are ubiquitous in graphene and is always expected in actual samples

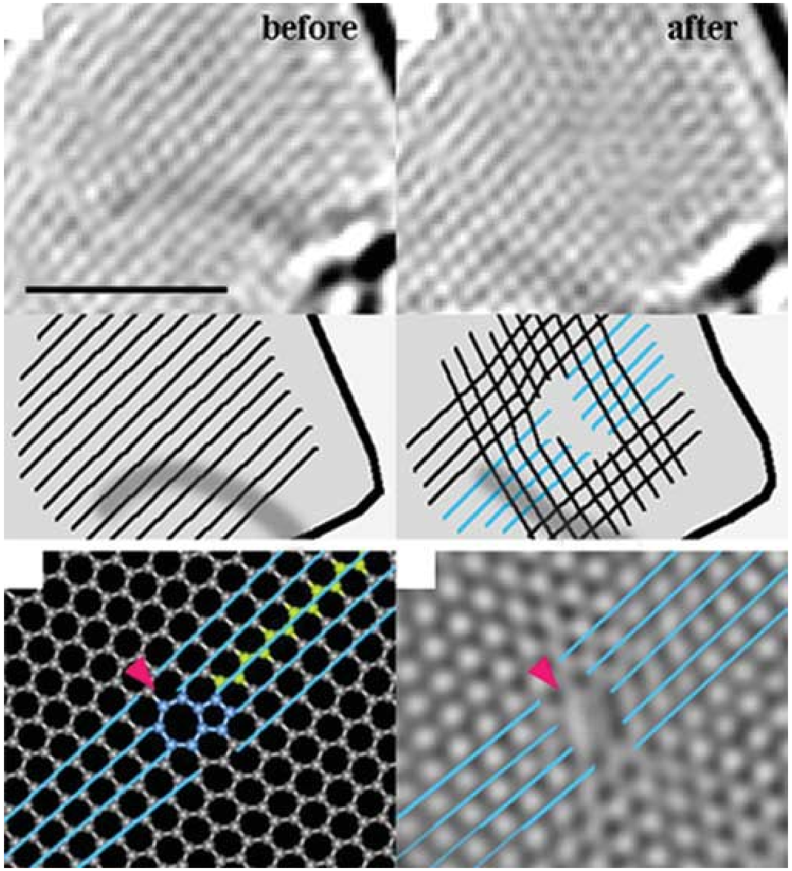
→ The introduction of defects also offer the opportunity to tailor the electronic properties in many different ways....

Impact of point-defects on the electronic structure





Point-defects : stability analysis...



Irradiation induced defects observed with HRTEM
from A Hashimoto et al., Nature 430, 870 (2004)

→ Here we focus on the vacancies and ad-atoms. Not only they are intrinsic in graphene but their concentration can be tuned by irradiation.

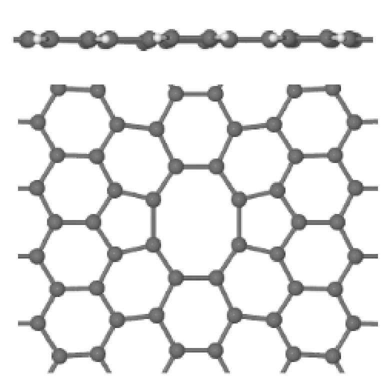
→ Point-defects are highly mobile and likely to recombine together or with the edges.

→ All the defects configuration have been considered (vacancy, di-vacancy, adatom, carbon dimer)

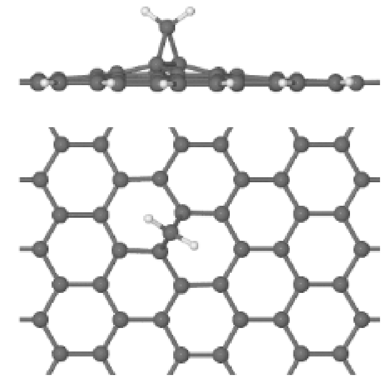
→ Hydrogenation of the defect has been used to assess the defect chemical reactivity

Most stable defects configurations....

Within the *bulk* :



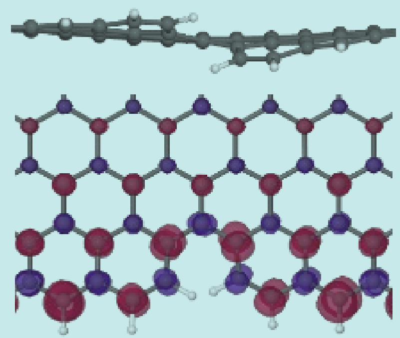
ξ^{def} = **7.6eV**



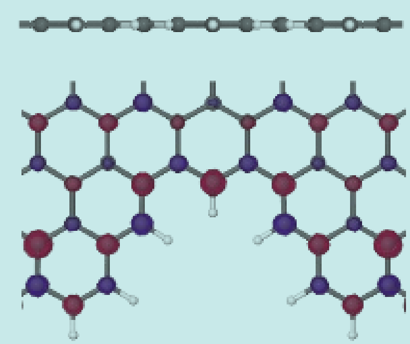
ξ^{def} = **2.0eV**

At the *edge* :

zigzag

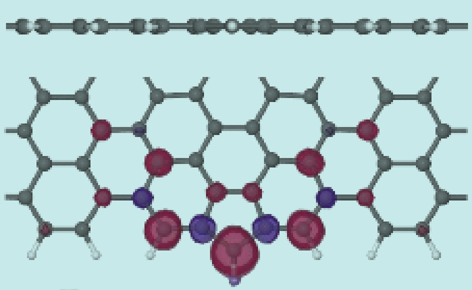


ξ^{def} = **0.01eV**

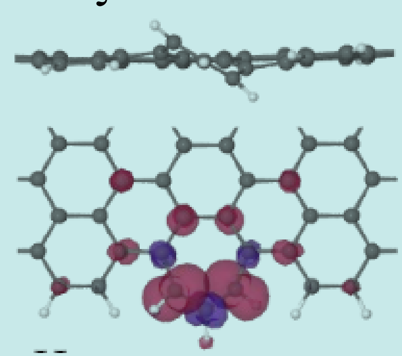


ξ^{def} = **-0.7eV**

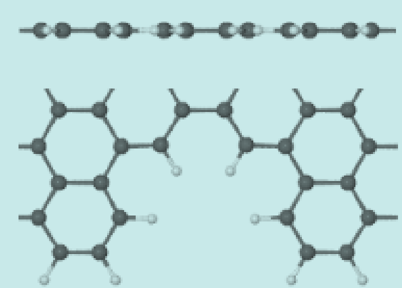
armchair



ξ^{def} = **0.6eV**



ξ^{def} = **0.8eV**



ξ^{def} = **0.2eV**

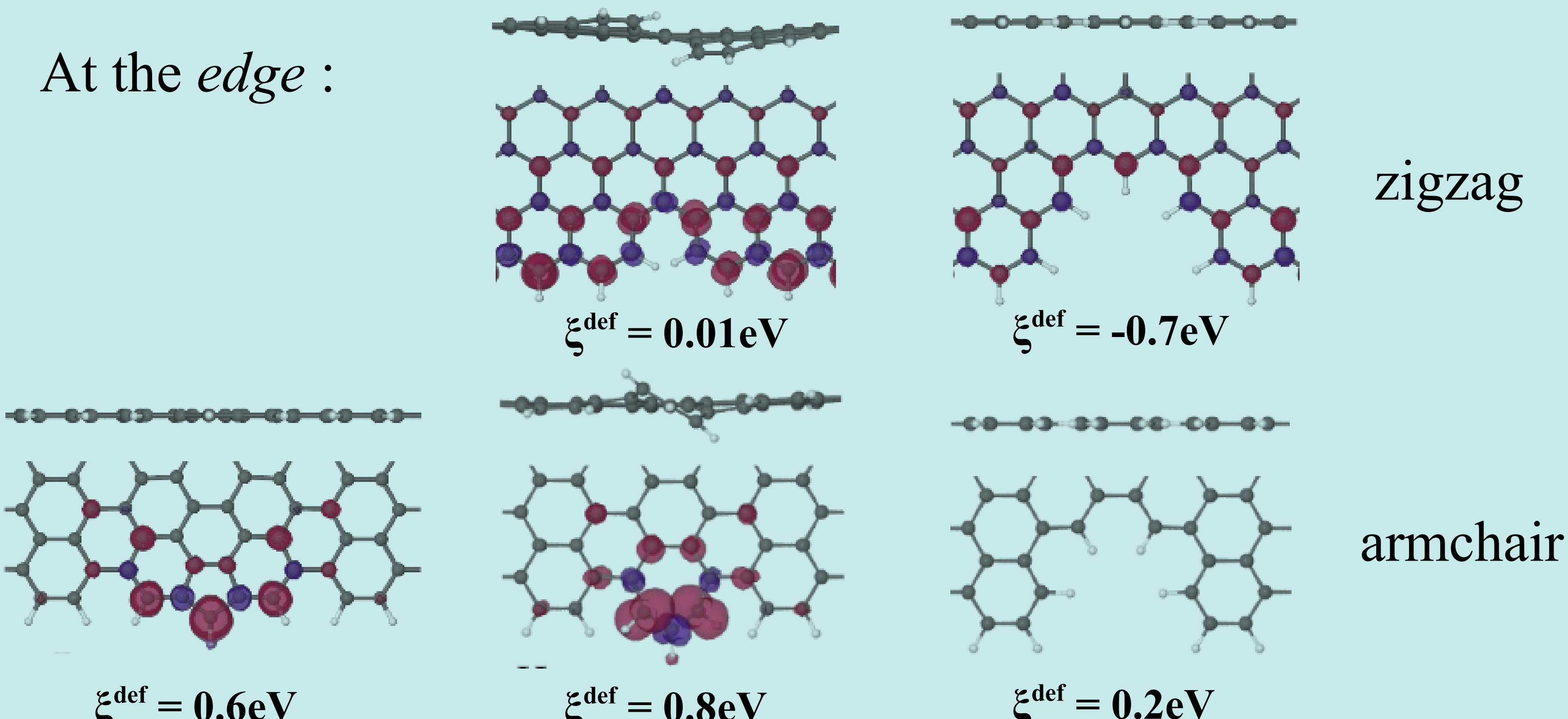
Most stable defects configurations....

→ In GNRs, the point defects are likely to migrate and recombine at the edge

→ Point-defects therefore contribute to the edge reconstruction (roughness, odd-membered ring)

→ zGNRs are less robust than aGNRs with respect to the introduction of defects at the edges

At the *edge* :



Outline of presentation

- Graphene : its structure and properties
  → why do we consider graphene nanoribbons for application in nano-electronics ?

- Graphene nanoribbons
  → electronic confinement, reconstruction of the edge, stability of point-defects

- Electronic transport in defective nanoribbons
  → conductance patterns of point-defects, conductance scaling in mesoscopic samples

- Onetep future capabilities regarding quantum transport

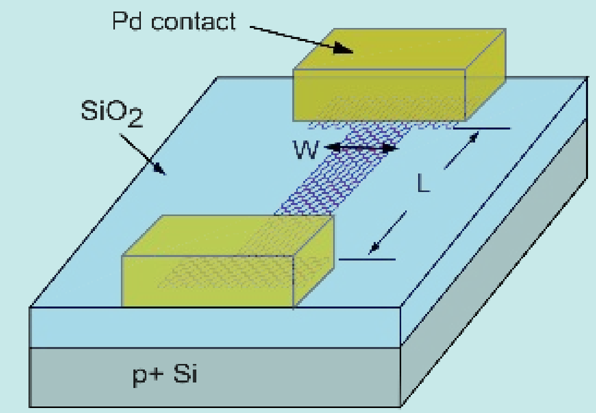
Quantum computational tools...

The transport problem :

siesta

\+ Smeagol

Non-equilibrium Electronic Transport



Schematic representation of GNR-FT

→ Intrinsic properties (i.e. no-contact, gate, substrate)

→ Coherent transport only

→ Leads at thermal equilibrium

→ Green's functions to describe the carriers propagation across the device :

$$[(E + i\delta) - \mathcal{H}]\,\mathcal{G}^r(E) = \mathcal{I}$$

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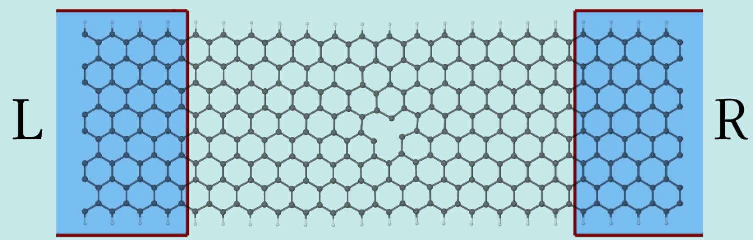

- → Intrinsic properties (i.e. no-contact, gate, substrate)
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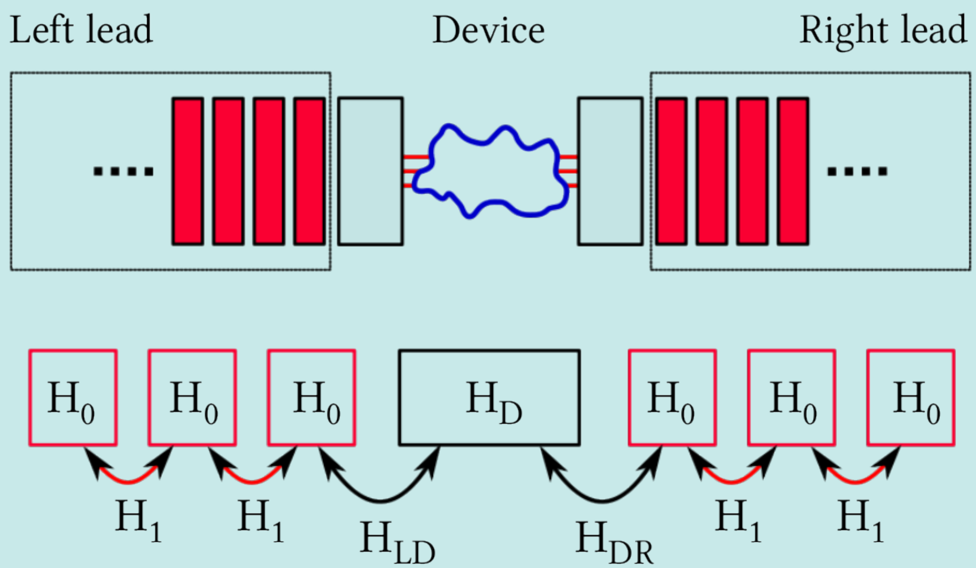
The transport setup

Decomposition of system into principal layers (Pls) :



Tridiagonal structure of the Hamiltonian within LCAOs representation :

$$\mathcal{H} = \begin{pmatrix} \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & & & & & \\ \ldots & 0 & H_{-1} & H_0 & H_1 & 0 & \ldots & & & & \\ & \ldots & 0 & H_{-1} & H_0 & H_{LD} & 0 & \ldots & & & \\ & & \ldots & 0 & H_{DL} & H_D & H_{DR} & 0 & \ldots & & \\ & & & \ldots & 0 & H_{RD} & H_0 & H_1 & 0 & \ldots & \\ & & & & \ldots & 0 & H_{-1} & H_0 & H_1 & 0 & \ldots \\ & & & & & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \end{pmatrix}$$

The transport setup

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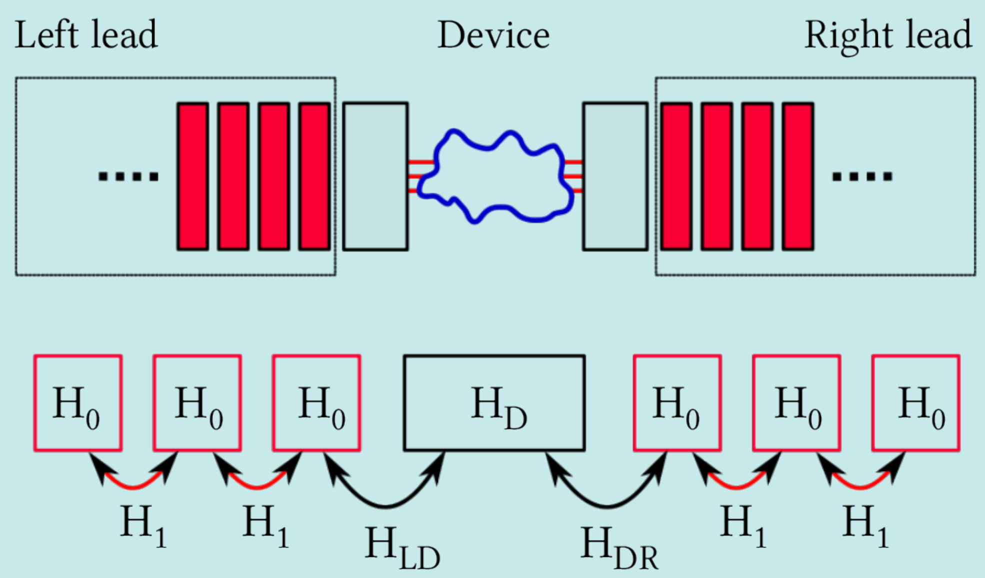


Retarded Green function :

$$[(E + i\delta) - \mathcal{H}]\, \mathcal{G}^r(E) = \mathcal{I}$$

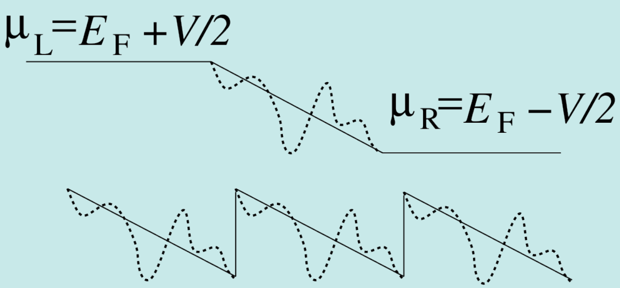
→ description of the electrons propagation

Retarded Green function of the single particle Hamiltonian :

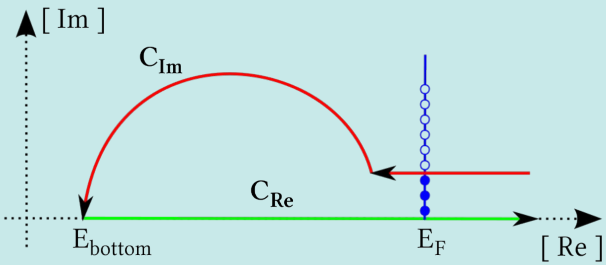
$$\begin{pmatrix} \epsilon^+ \mathcal{S}_L - \mathcal{H}_L & \mathcal{S}_{LD} - \mathcal{H}_{LD} & 0 \\ \mathcal{S}_{DL} - \mathcal{H}_{DL} & \epsilon^+ \mathcal{S}_D - H_D & \mathcal{S}_{DR} - \mathcal{H}_{DR} \\ 0 & \mathcal{S}_{RD} - \mathcal{H}_{RD} & \epsilon^+ \mathcal{S}_R - \mathcal{H}_R \end{pmatrix} \cdot \begin{pmatrix} \mathcal{G}_L & \mathcal{G}_{LD} & \mathcal{G}_{LR} \\ \mathcal{G}_{DL} & G_D & \mathcal{G}_{DR} \\ \mathcal{G}_{RL} & \mathcal{G}_{RD} & \mathcal{G}_R \end{pmatrix} = \mathcal{I}$$

Out-of-equilibrium density and the electric current (DFT + NEGF)

Periodic recasting of the electrostatic problem :



Contour integration for the density matrix :



Semi-analytic calculation of $\Sigma_{L/R}$

Preliminary DFT calculation :

GS electronic density of the system (lead-device-lead).

Preliminary DFT calculation :

Bulk Hamiltonians of the left and right leads.

Contacts self-energies :

$$\Sigma^r_L(E),\ \Sigma^r_R(E),\ \mathcal{G}^{0r}_{L/R}$$

SCF

Electronic Hamiltonian :

$$\hat{H}^e = \hat{T}^e + \sum_i \hat{V}_i^{pseudo}(\mathbf{r}) + \hat{V}^{Hart} + \hat{V}^{xc}(\mathbf{r})$$

Retarded Green's function :

$$G^r_D(E) = \left[\epsilon^+ S_D - H_D - \Sigma^r_L(E) - \Sigma^r_R(E)\right]^{-1}$$

Out-of-equilibrium density matrix :

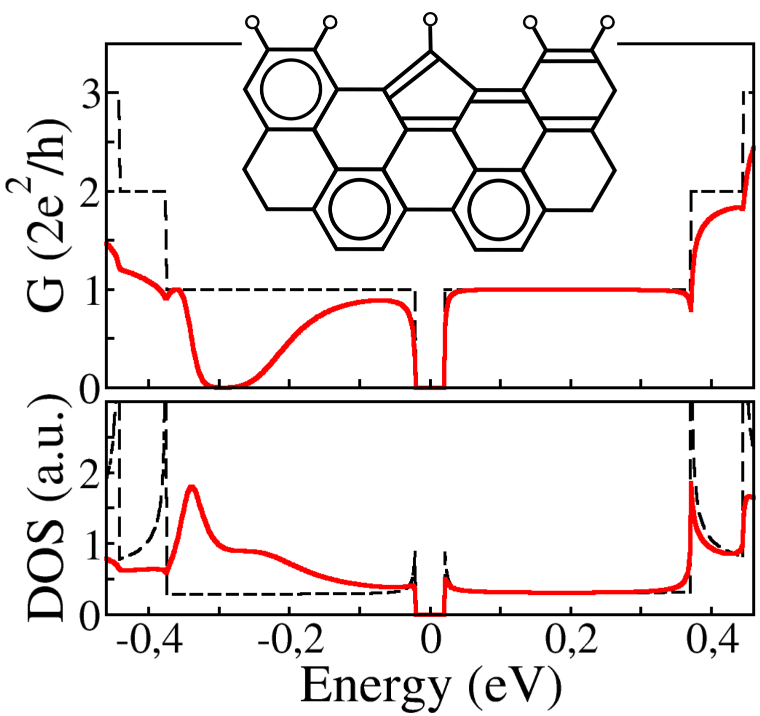
$$\rho = \frac{1}{2\pi}\int dE\ \left[A_L f(E-\mu_L) - A_R f(E-\mu_R)\right]$$

Electric current :

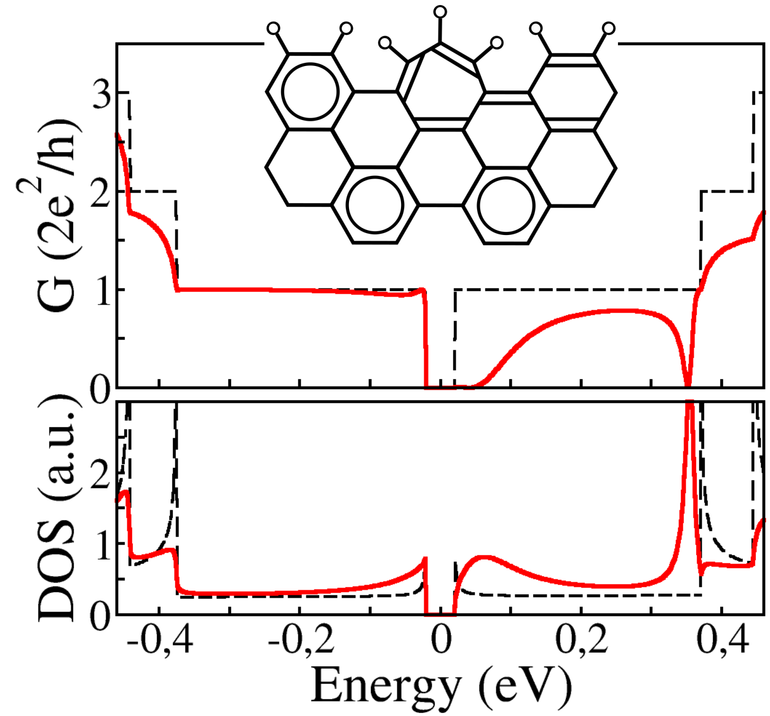
$$I = \frac{e}{h}\int dE\, Tr\left[\Gamma_L G^{r\dagger}_D \Gamma_R G^r_D\right]\left[f(E-\mu_L) - f(E-\mu_R)\right]$$

Electronic transport in *edge* defective aGNRs

Pentagon



Heptagon



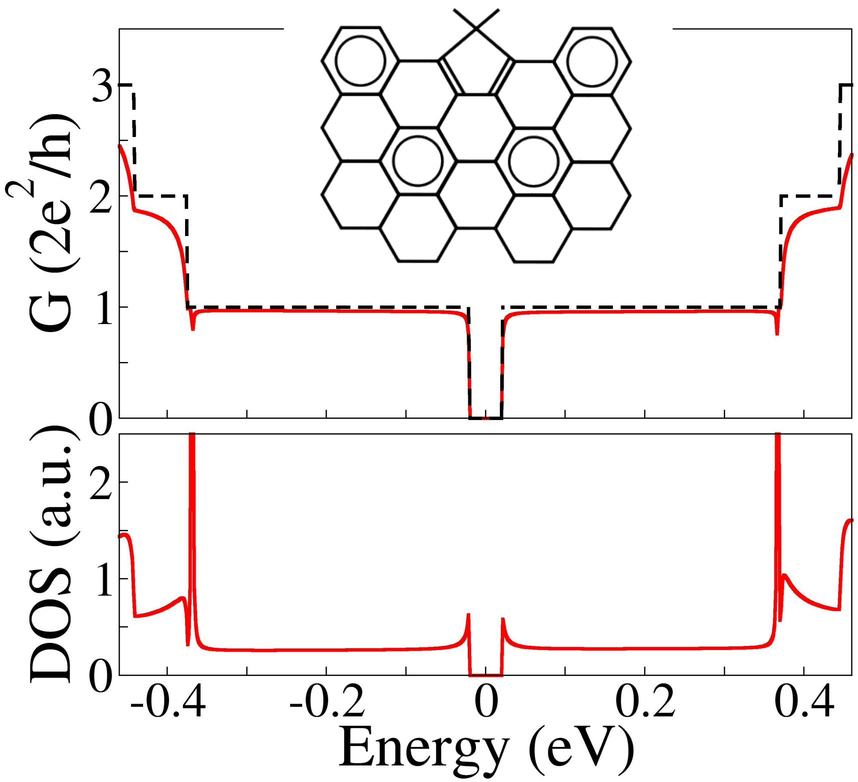
→ Excess of electron on the pentagon
→ Defect state at -0.3 eV
→ Acceptor character

→ Deficit of electron on the heptagon
→ Defect state at 0.05 eV
→ Donor character

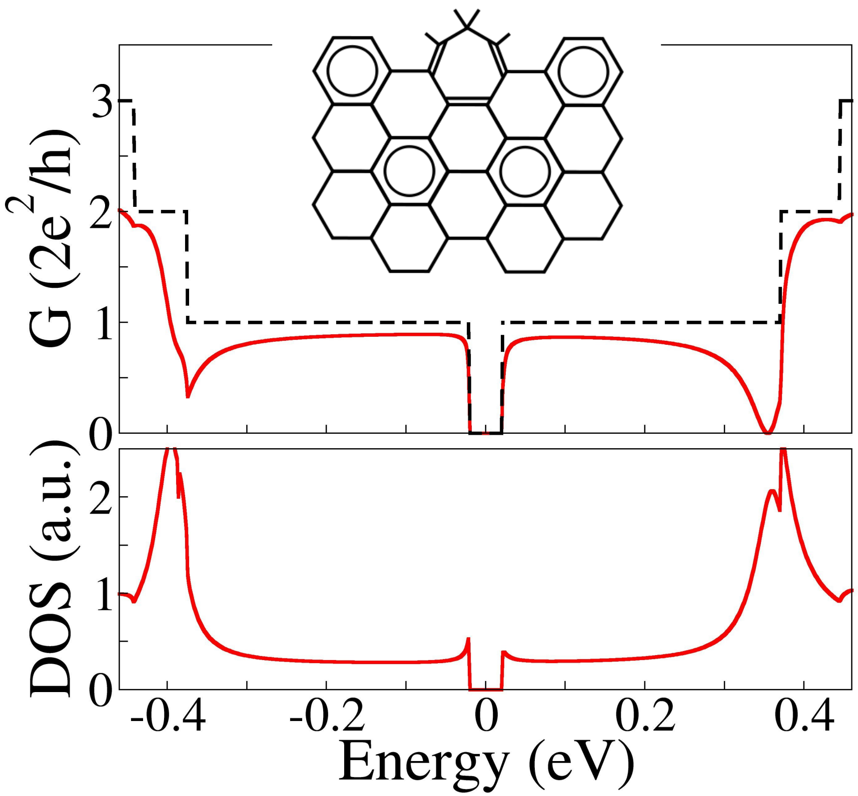
S.M.-M. Dubois, A. Lopez-Bezanilla, A. Cresti, F. Triozon, B. Biel, J.-C. Charlier, and S. Roche
ACS Nano, DOI: 10.1021/nn100028q

Electronic transport: hydrogenation of the defects

Pentagon hydro



Heptagon hydro



S.M.-M. Dubois, A. Lopez-Bezanilla, A. Cresti, F. Triozon, B. Biel, J.-C. Charlier, and S. Roche
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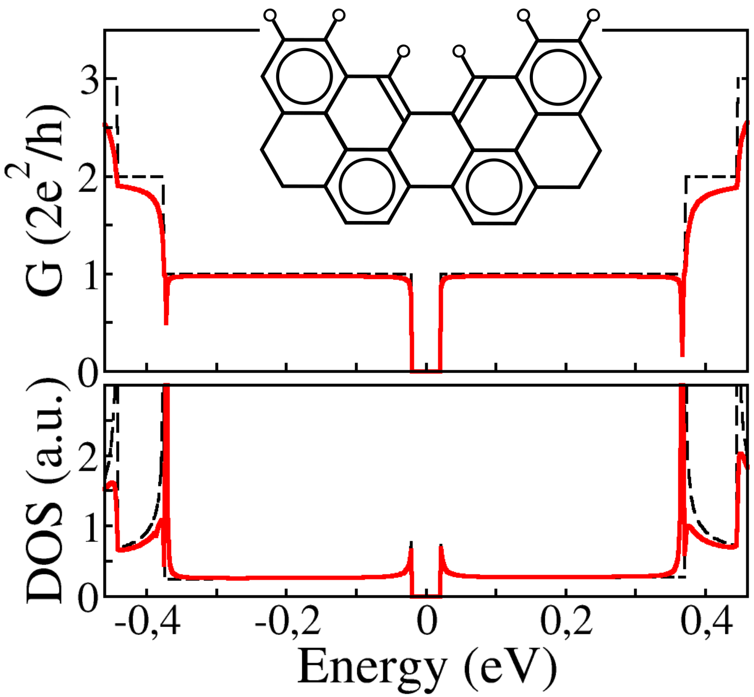
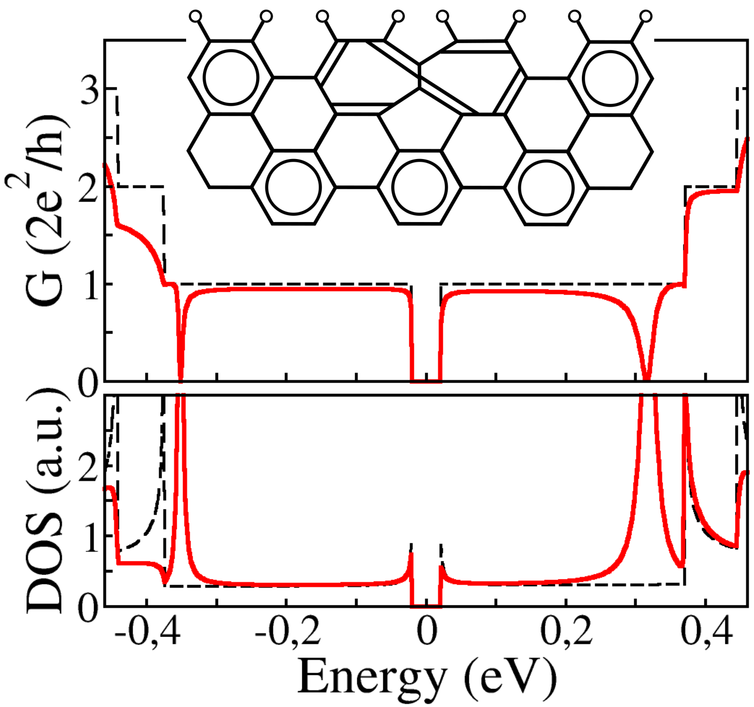
Electronic transport : benzenoid-like defects

Dip defect



757 reconstruction



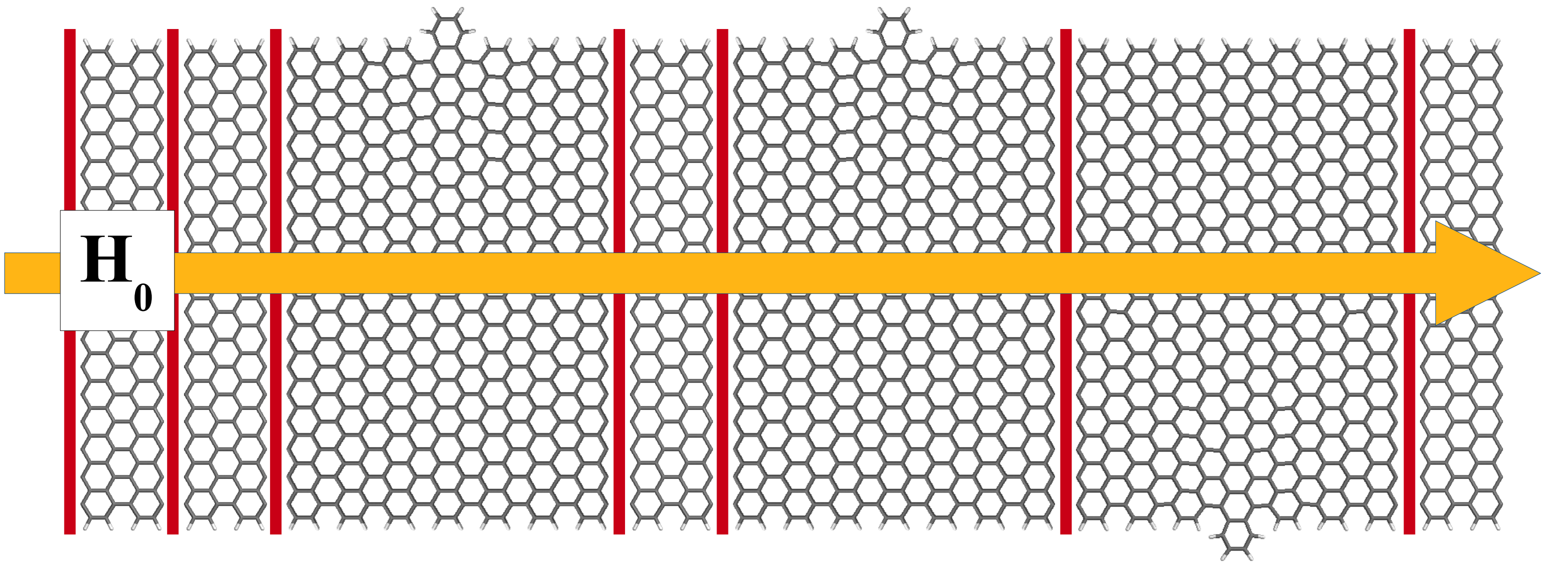
→ Benzenoid-like defects are likely to have a weak impact on T(E)

→ Hydrogenation tends to restore the benzenoid character of the ribbon and the conductivity!

Electronic transport in long defective aGNRs

Transport at the mesoscopic scale :

F. Triozon et al., Nanotechnology 16, 230 (2005)



- Based on the GS hamiltonian
- Non-self consistent transport calculations
- Divide and conquer methodology
- Adjusted TB models

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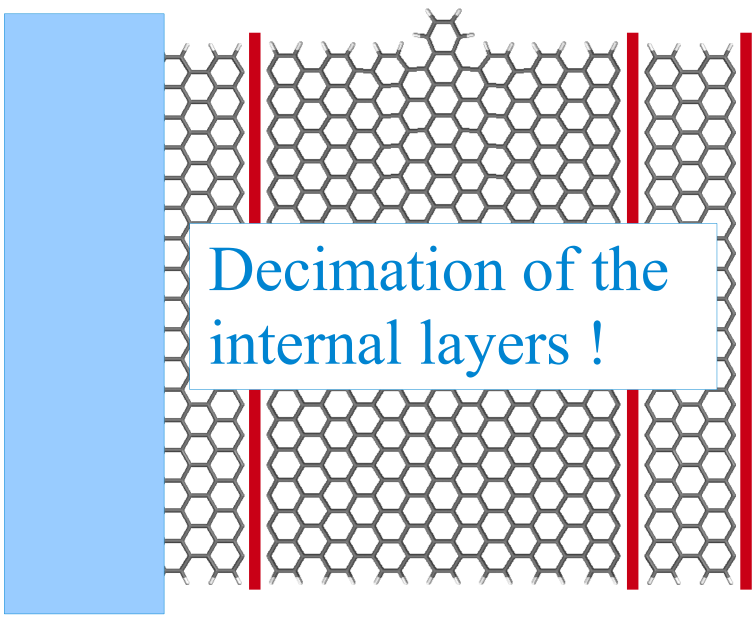


Full system :

$$[(E+i\delta)S - H]\,.G(E) = \mathcal{I}$$

$$K(E).G(E) = \mathcal{I}$$

$$\sum_{j=1}^{N} K_{ij}\,G_{jk} = \delta_{ik}$$

Isolation :

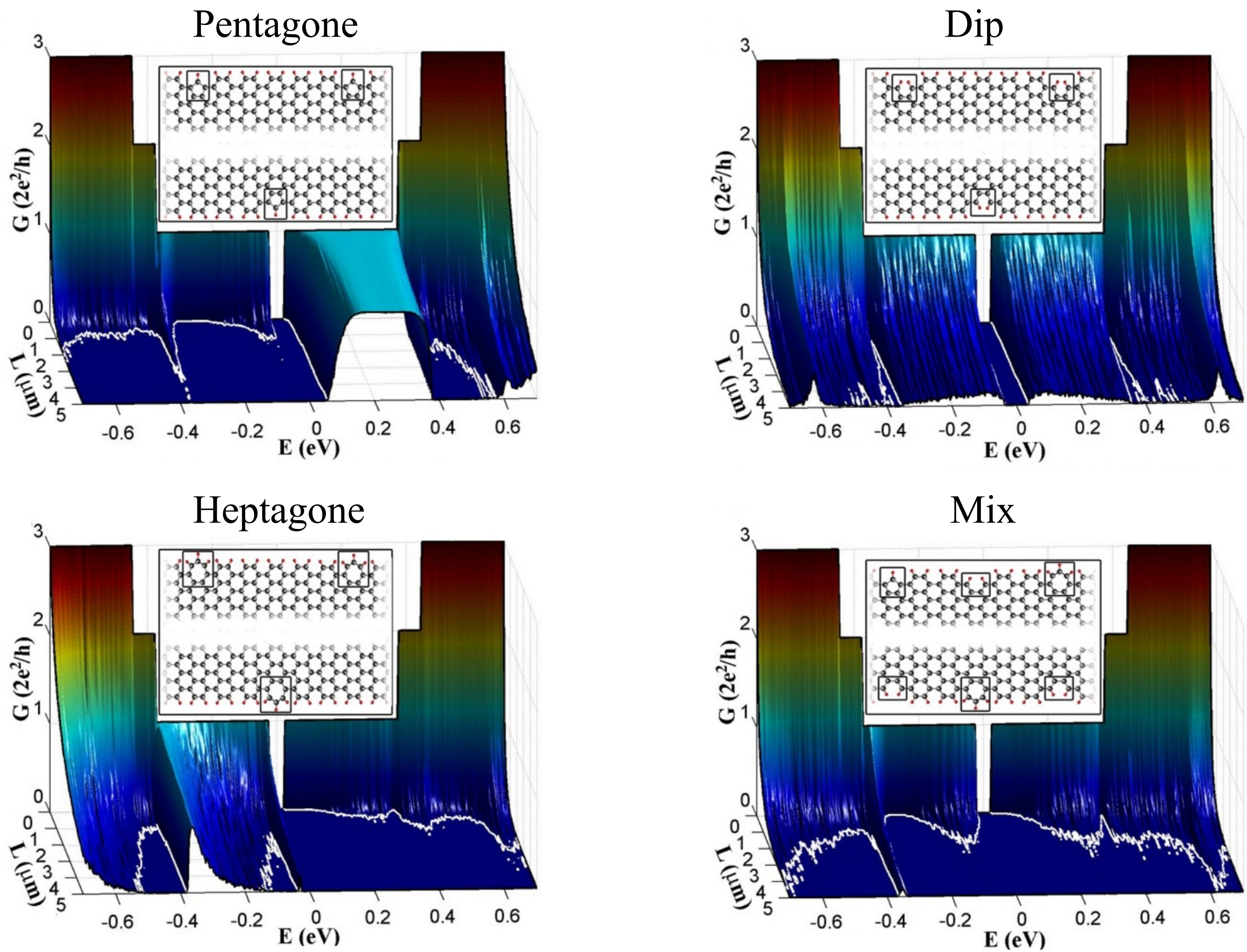
$$\sum_{j=1}^{N-1} K_{ij}\,G_{jk} + K_{iN}\,G_{Nk} = \delta_{ik}$$

$$G_{Nk} = \frac{\sum_{j=1}^{N-1} K_{Nj}\,G_{jk}}{K_{NN}} \quad (for k \neq N)$$

Elimination :

$$\sum_{j=1}^{N-1} \left[K_{ij} - \frac{K_{iN}\,K_{Nj}}{K_{NN}} \right] G_{jk} = \delta_{ik}$$

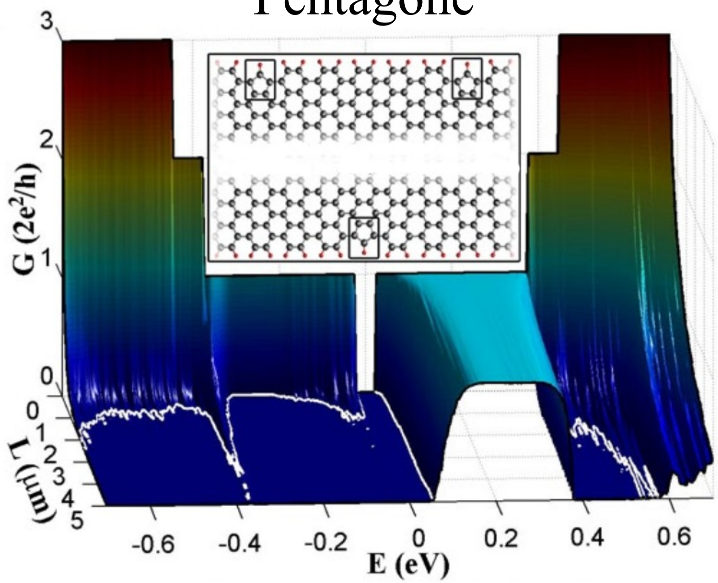
Electronic transport in long defective aGNRs



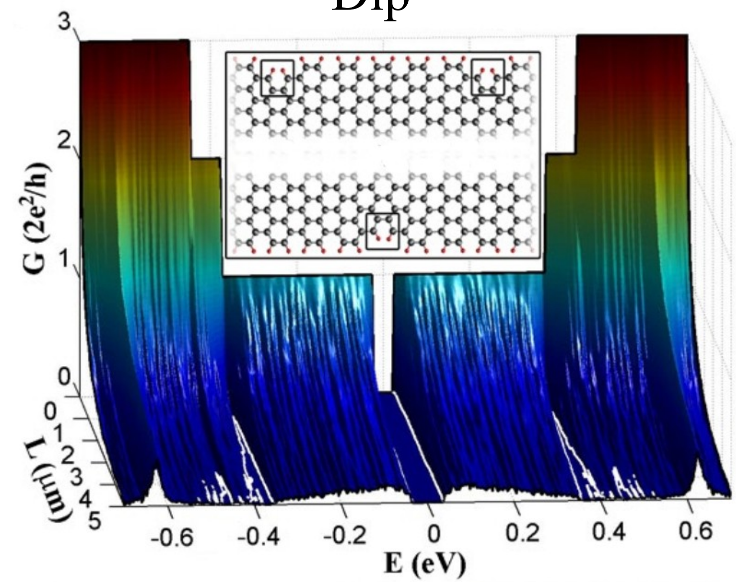
Long aGNRs (up to 5 μm) with a defect density of $6x10^{-2}$ nm^{-1}

Electronic transport in long defective aGNRs

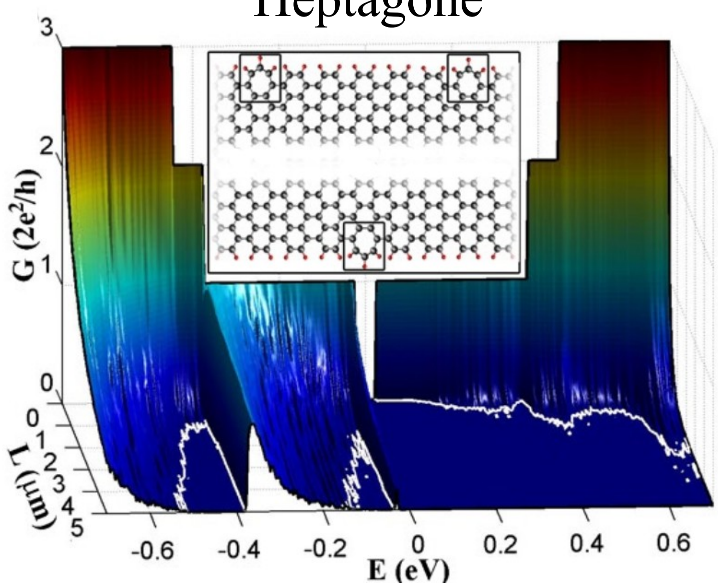
Pentagone



Dip



Heptagone



→ Strong impact of the edge roughness

→ Odd-membered rings
⇒ large electron-hole anisotropy

→ Transport ranging from ballistic to highly localized regimes

→ Benzenoid defects (or hydrogenation)
⇒ improved carriers propagation

S.M.-M. Dubois, A. Lopez-Bezanilla, A. Cresti, F. Triozon, B. Biel, J.-C. Charlier, and S. Roche
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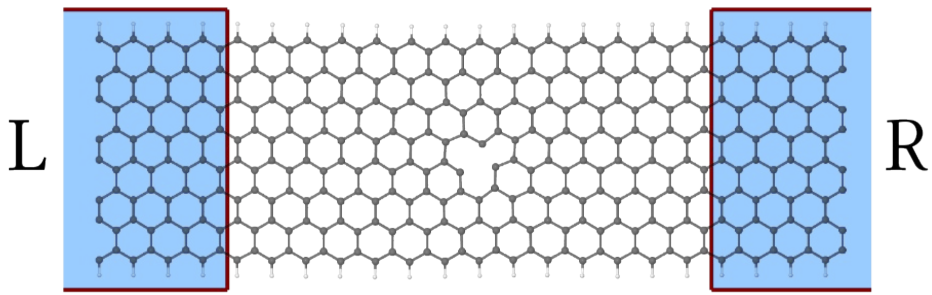
The transport problem :



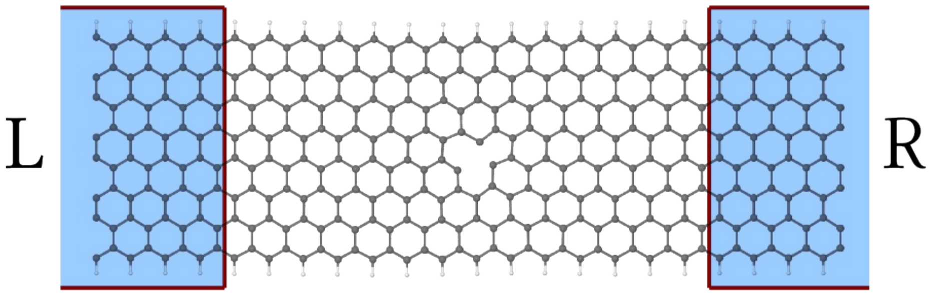
abinit.org

→ siesta + Smeagol Non-equilibrium Electronic Transport

→ Tight-binding

Transport calculation with ONETEP...

The transport problem :



→ Minimal basis set

→ More realistic defect patterns

→ Account for the defect-defect interaction (e.g. magnetic coupling)

→ Complete basis set
(→ controllable accuracy)
(→ non-coherent processes)

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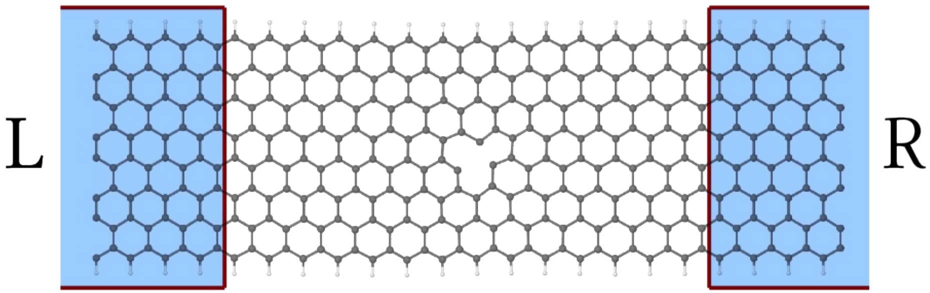

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GS denskern + NGWFs

↓

GS leads calculations :

$$\Sigma_L \,,\; \Sigma_R \,,\; \Gamma_{L/R} = i\left[\Sigma^R_{L/R} - \Sigma^{R\dagger}_{L/R}\right]$$

↓

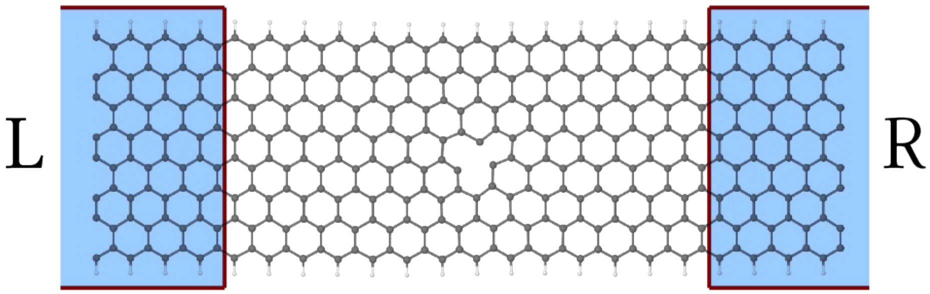
$$G^R_D(E) = \left[\epsilon^+ S_D - H_D - \Sigma^R_L - \Sigma^R_R\right]^{-1}$$

↓

$$G = \frac{2e^2}{h} Tr\left[\Gamma_L G^{R\dagger}_D \Gamma_R G^R_D\right]$$

Transport calculation with ONETEP...

The transport problem :



Future developments

→ Improve the current implementation
(sparsity patterns, parallelization, …)

→ Progress towards the O(N) scaling
(e.g. decimation of the Green's function)

→ Achieve self-consistency (with fixed NGWFs)

Conclusions

Electronic confinement in GNRs

- Edge relaxation and magnetic order ⇒ energy gaps in aGNRs and zGNRs
- Structure of the thermodynamically stable edges depends on P_{H2}
- The most stable edge topologies have been identified (a_{22}, a_{11}, $z(600)_{2222}$, z_{211}).

Topological defects in GNRs

- Vacancies and adatoms coalesce / recombine with the edges
- *Bulk* and *edge* defects are centers of high chemical reactivity
- Most stable *bulk* defects : di-vacancy and adatom+H_2
- Most stable *edge* defects : Dips (and odd-membered rings in aGNRs)

Quantum transport in defective GNRs

- Quasi-localized states and backscattering ⇒ reduction of the conductance
- Bonding energies and conductance patterns strongly depend on the defect position
- Edge-states strongly impact the T(E) of zGNRs ⇒ ballistic channels around E_F

- Full hydrogenation helps in preserving the conduction in defective GNRs
- Impact of defect range from weak scattering to full suppression of conduction channels
- Conductance scaling of aGNRs strongly depends on the edge profile

Acknowledgment

→ My previous supervisors :
Jean-Chritophe Charlier and **Gian-Marco Rignanese**

→ **Mike Payne**

→ The mesoscopic transport calculation have been done in collaboration with **Stephan Roche**, **François Triozon**, **Blanca Biel**, **Alejandro Lopez-Bezanilla** and **Alessandro Cresti** from the CEA Grenoble

→ I acknowledge **Nick**, **David**, **Daniel**, **Arash**, **Peter**, **Chris**, **Tonatiuh**, **Aurélien** and **François** for interesting and valuable discussions.....