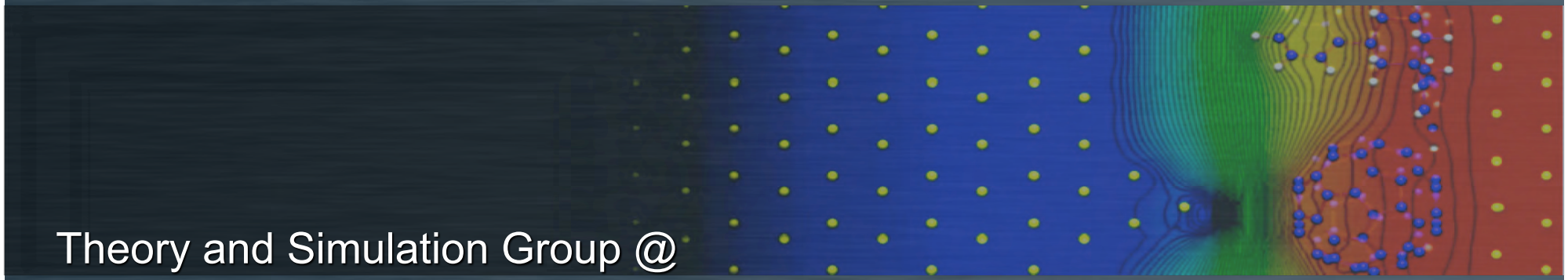
Beating the Size Limits of First-Principles Calculations in Nanoscale Systems

Pablo Ordejón



Theory and Simulation Group @

CSIC

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CENTRE D'INVESTIGACIÓ EN NANOCIÈNCIA I NANOTECNOLOGIA

CAMPUS UAB. BELLATERRA. BARCELONA

OUTLINE:

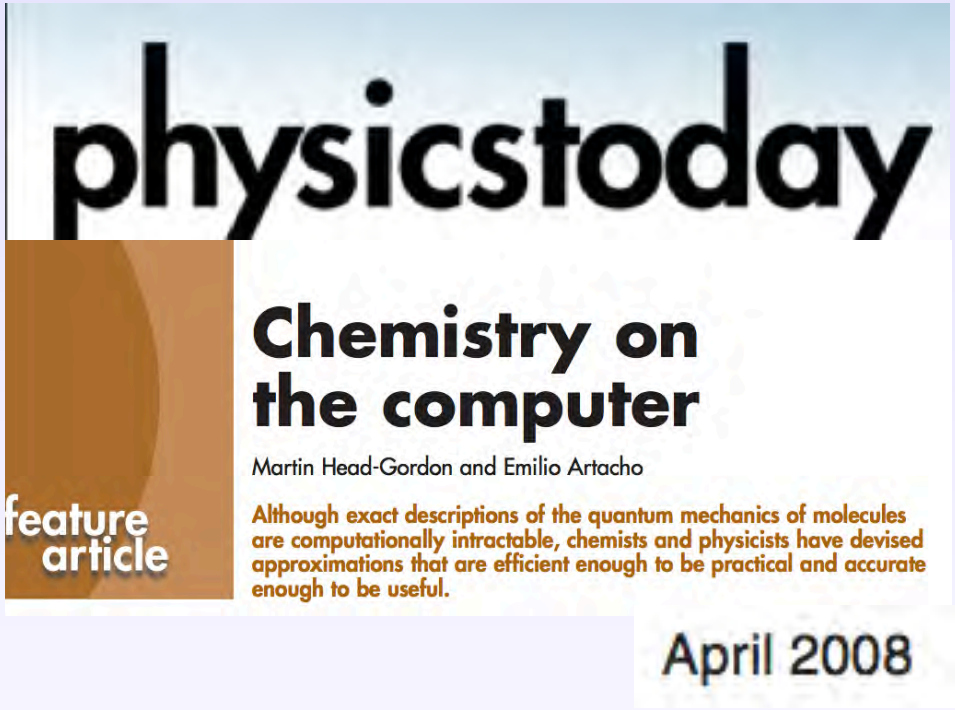
- Some reflexions on atomistic simulations and HPC: What are the limits?
- SIESTA: a DFT code
- Transport from DFT: TranSIESTA
- One example of DFT (including transport): CNT-linked graphene layers
- Going to larger systems:
  - Transport in the meso-scale: O-functionalized graphene
  - QM/MM for MD simulations: Proteins, Au nanoparticles and graphite

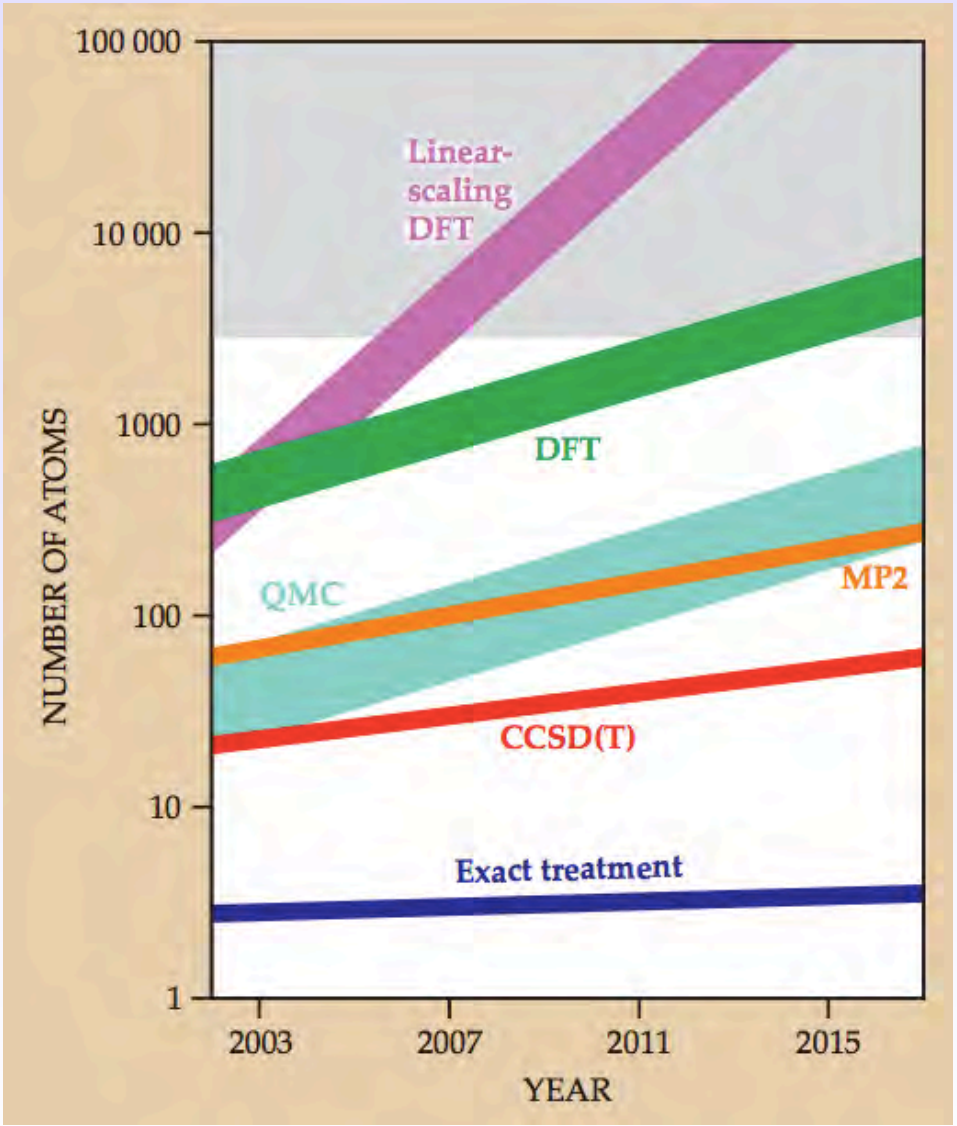
“Complexity” of a Simulation

The relation between computing time T (CPU)
and degrees of freedom N (number of atoms, electrons, length…)

$T \propto O(N)$	in the best (simplest) cases - linear scaling (classical force fields)
$T \propto O(N^3)$	quantum mechanics - DFT (Matrix diagonalisation and inversion)
$T \propto e^N$	complex problems (Quantum chemistry; multiple minima problems, etc)

“Complexity” of a Simulation





Estimate of accessible time and size scales

- Supercomputer with performance: F Flops (floating point operations per second)
- One week of CPU of the whole computer: $T_{CPU} \sim 6 \times 10^5$ seconds
- Number of operations in one week: $N_{ops} \sim 6 \times 10^5 \times F$
- Operations in a simulation: $\#ops \propto C \times N_{at}^{s} \times n_t$
  (Typicall, C ~ 10^3 --10^6 floating point operation per MD step)
- $N_{at} \propto$ Volume $\propto L^D$ (L = typical length scale, in units of atomic distances)

  D = dimension of the system (1,2,3).
- Time (n_t) scales, ***at least***, as L (for information to propagate across the system)
  $n_t \sim 100\ L$

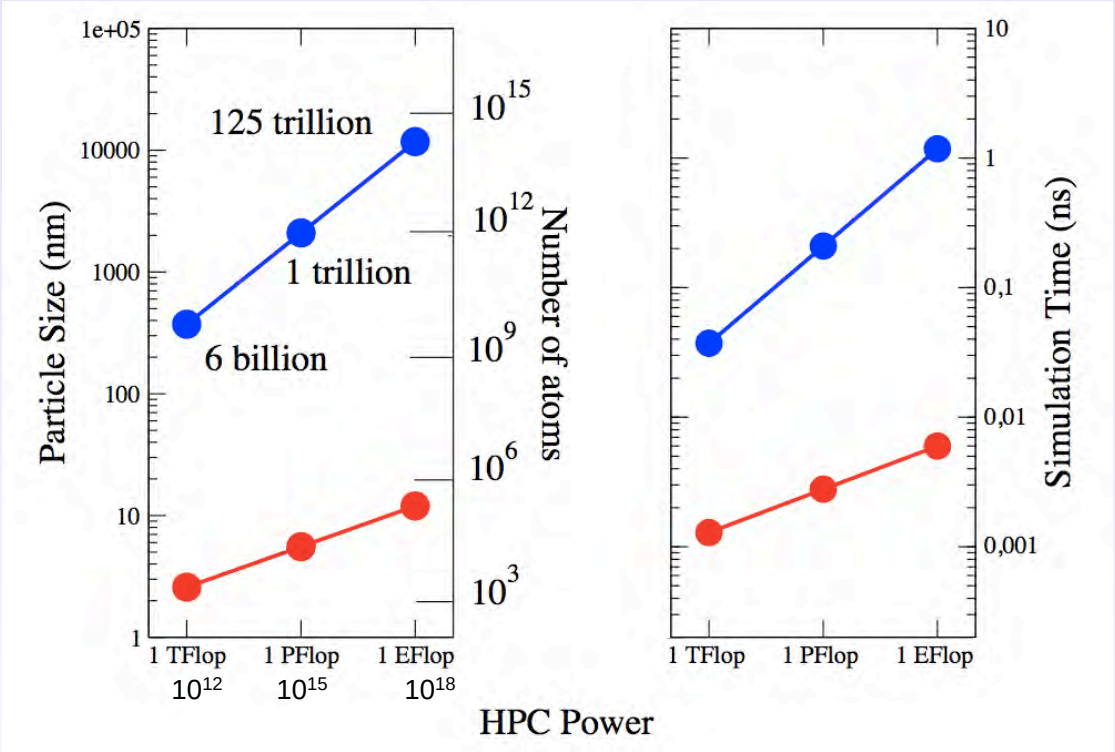
$$N_{at} \sim F^{D/(sD+1)}$$

$$n_t \sim L \sim F^{1/(sD+1)}$$

Example in 3D system
(one week of full usage)

Empirical potentials - O(N)

DFT - O(N^3)



Protein: 10 nm - 10^5 atoms
Virus: 100 nm - 10^8 atoms
Cell: 5 µm - 10^{14} atoms
Grain of salt: 0.5 mm - 10^{20} atoms

- Bridging length scales - Multiscale approaches
- Data analysis and handling becomes a hard problem!
- Time scales: often too short for relevant issues (new methods needed)

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TRILLION-ATOM MOLECULAR DYNAMICS BECOMES A REALITY

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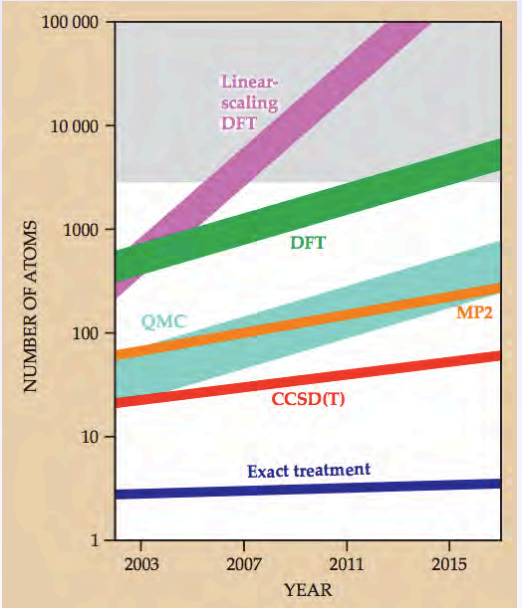
By utilizing the molecular dynamics code *SPaSM* on Livermore's BlueGene/L architecture, consisting of 212 992 IBM PowerPC440 700 MHz processors, a molecular dynamics simulation was run with one trillion atoms. To demonstrate the practicality and future potential of such ultra large-scale simulations, the onset of the mechanical shear instability occurring in a system of Lennard-Jones particles arranged in a simple cubic lattice was simulated. The evolution of the instability was analyzed on-the-fly using the in-house developed massively parallel graphical object-rendering code *MD_render*.

Keywords: Molecular dynamics; BlueGene/L; high performance computing; SPaSM; large-scale; trillion-atom; visualization.

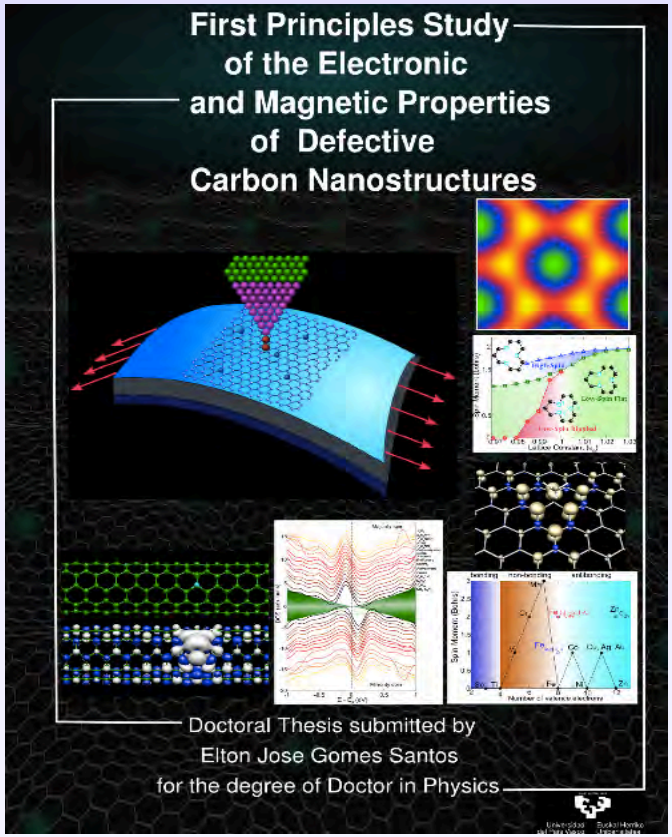
Soler, Artacho, Gale, García, Junquera, Ordejón and Sánchez-Portal
J. Phys.: Cond. Matt. **14**, 2745 (2002)

- Self-consistent DFT code (LDA, GGA, new VdW functionals...)
- Pseudopotentials (Kleinman-Bylander)
- LCAO approximation:
  Basis set:
  Confined Numerical Atomic Orbitals
  (Sankey's "fireballs")
  As complete as needed

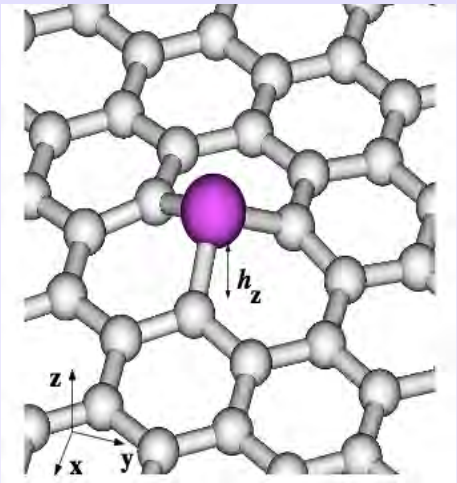


- Order-N methodology (in the calculation of the DFT Hamiltonian and --if required-- in the solution of the eigenvalue equation to obtain the WFs)

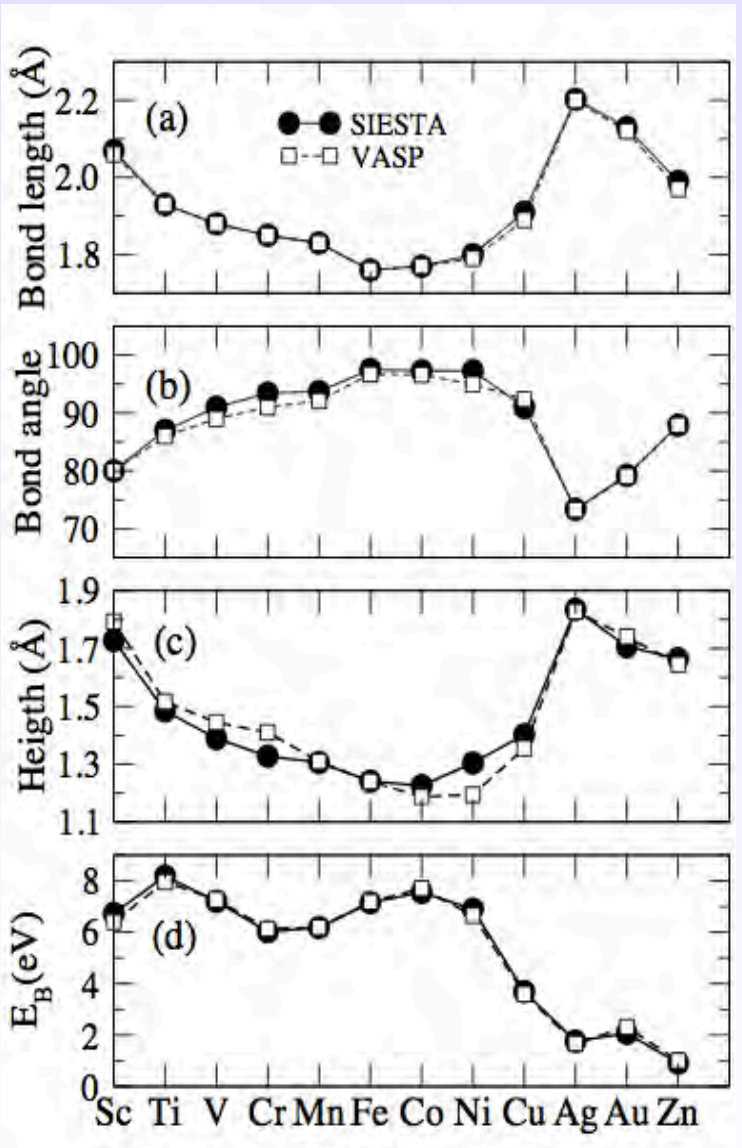
Example of Accuracy of standard DZP bases (in graphene)



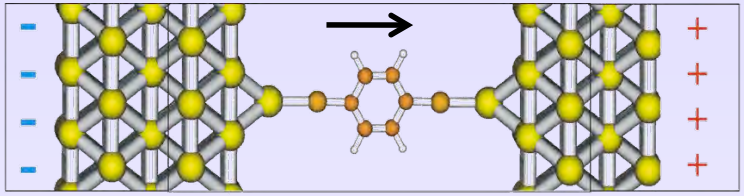
- DZP Basis
- E_{shift} = 50 meV
- r_c of TM increased to obtain converged E_B (variationally)

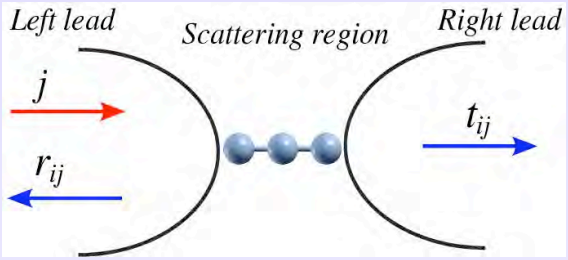


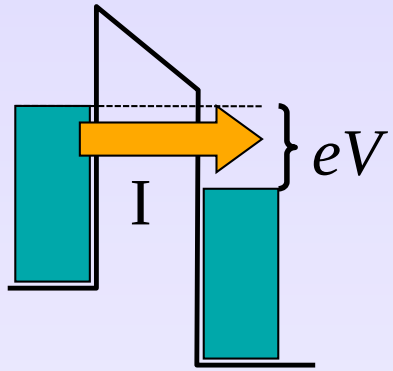
	r_{sp}^{NAO} (a_o)	r_d^{NAO} (a_o)
Co	8.00	4.73
Ni	10.94	6.81
Cu	8.87	5.52
Ag	10.48	6.52
Au	8.63	6.08
Zn	9.24	5.33



Electronic Transport from Scattering Theory (Buttiker-Landauer)



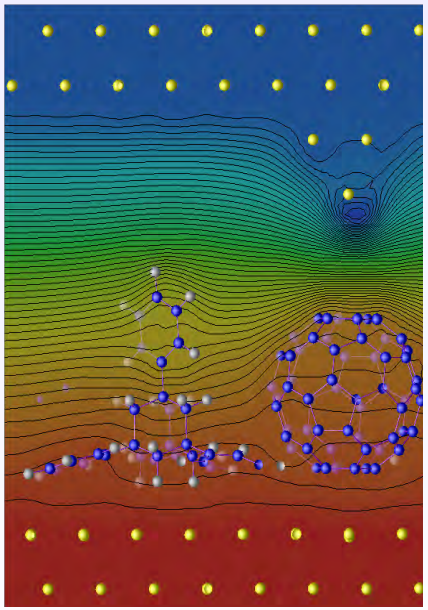


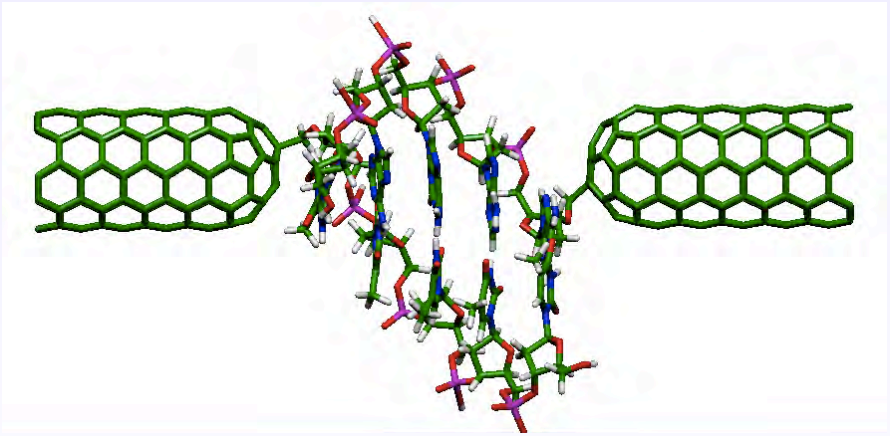


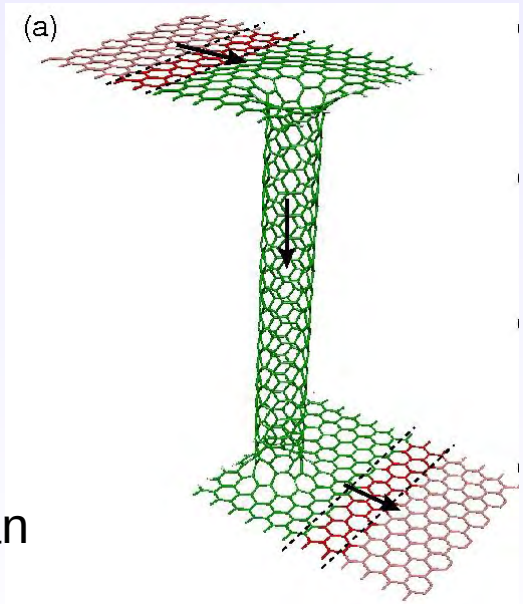
Atomistic; first-principles:
DFT + NEGF's -- TranSIESTA

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

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







(Other similar packages like SMEAGOL can also be linked to SIESTA)

An example: Graphene layers bridged by CNTs

Novaes, Rurali, Ordejón, ACS Nano 4, 7596 (2010)

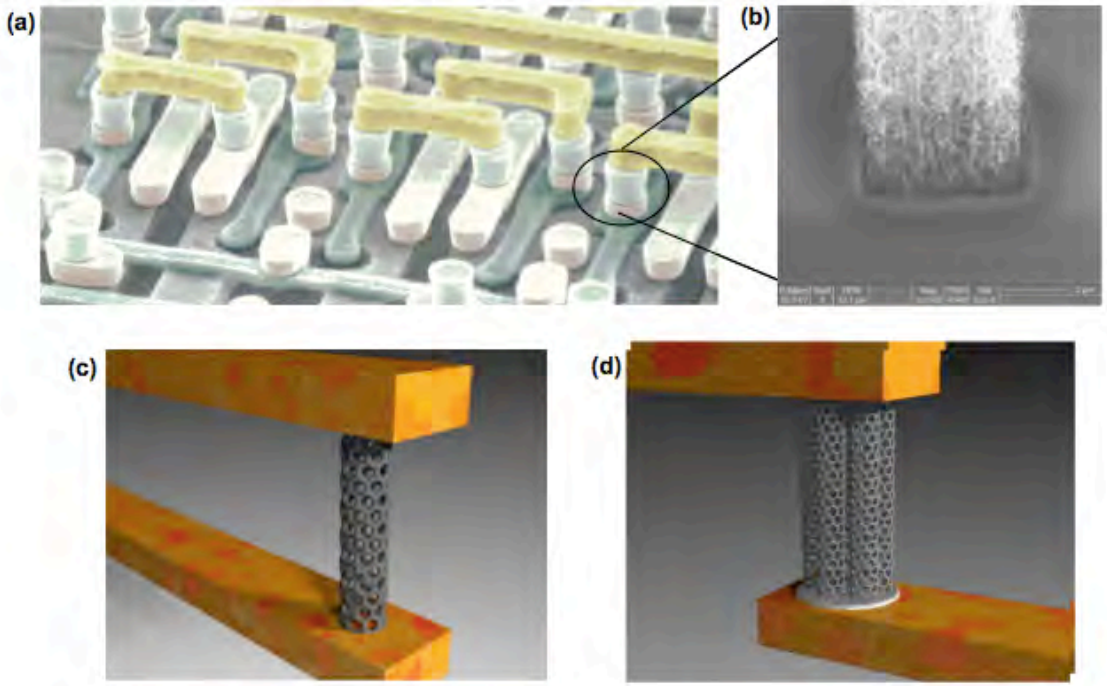
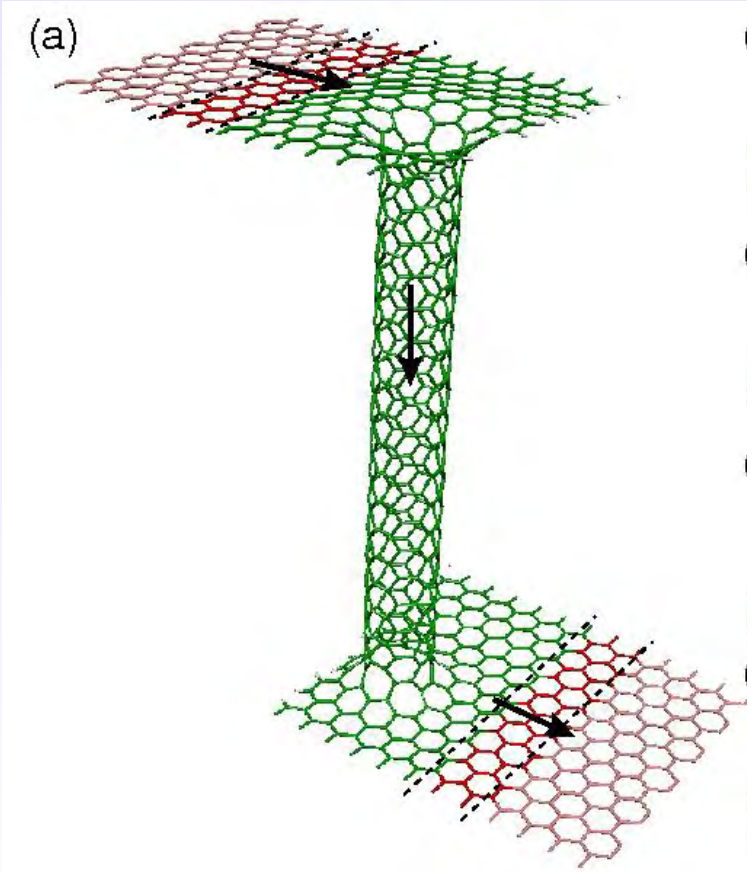
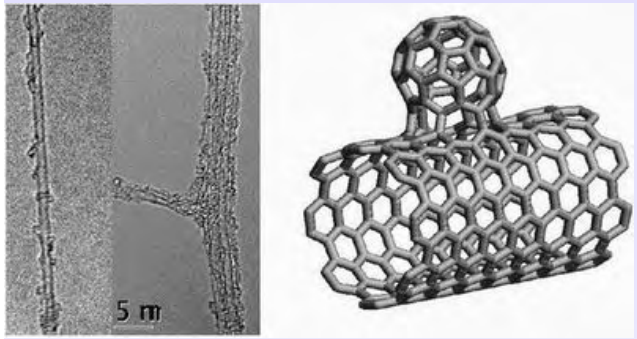


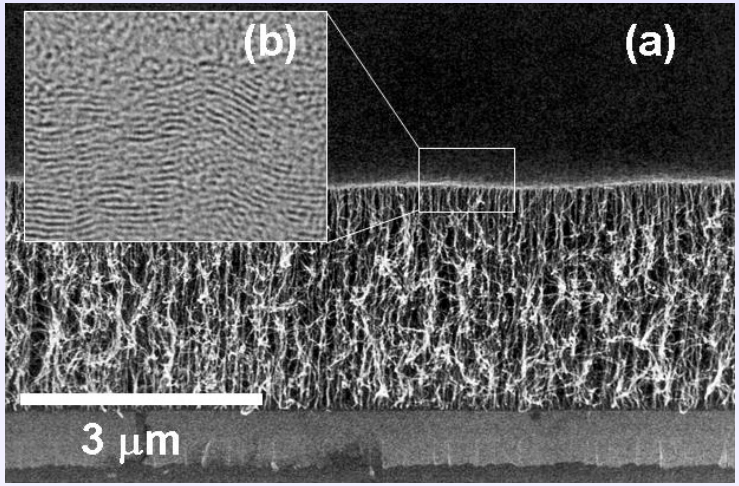
Figure 8. (*a*) A pictorial representation of the wiring in an integrated circuit. The horizontal interconnects are shown in yellow and the vertical interconnects are shown in grey. (*b*) An example of a MWNT array grown in a silicon oxide via, which can potentially be used as a vertical interconnect 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.)



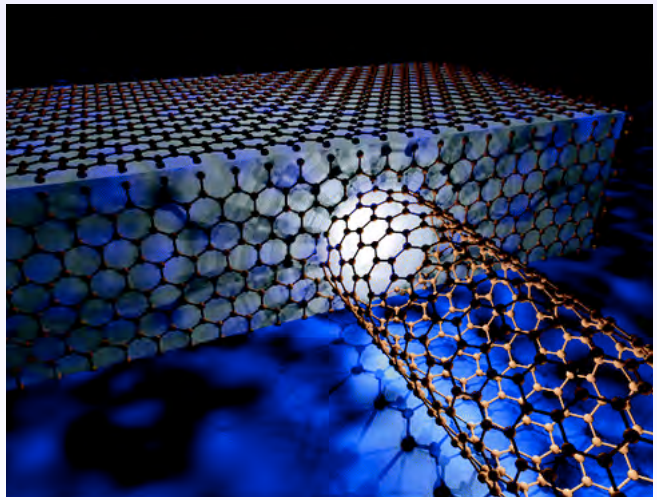
Related structures



Carbon “Nanobuds”
(nanotubes with fullerenes covalently attached)



Nanotube/Graphite composite
D. Kondo et al., Appl. Phys. Express **1**, 074003 (2008)



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

Covalent link of CNT's to graphene

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

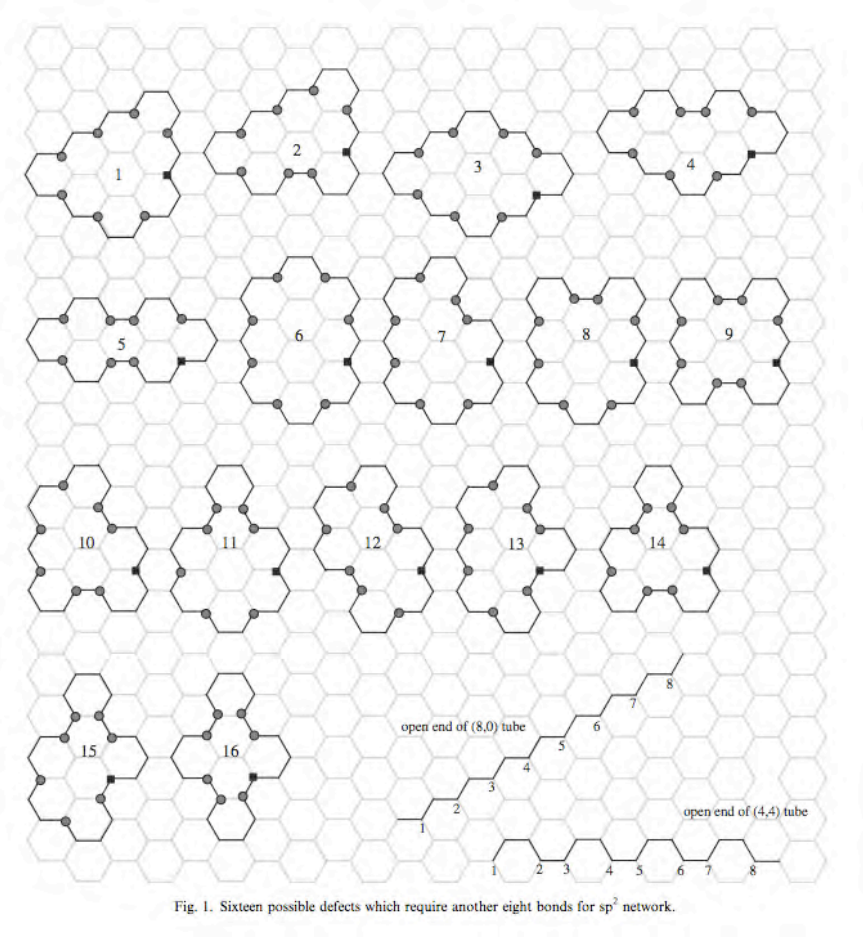
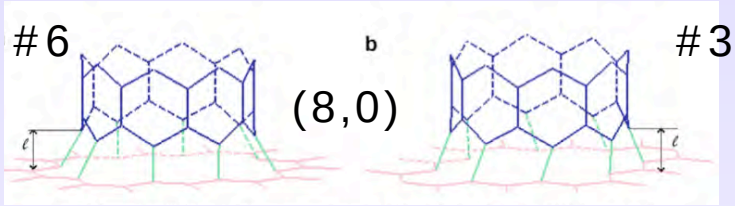
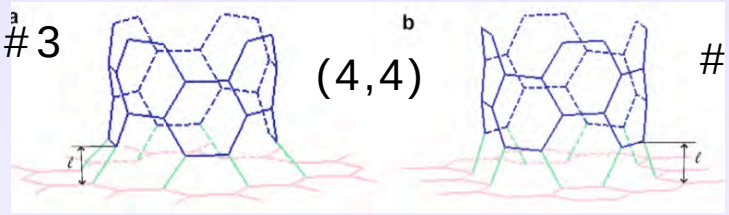
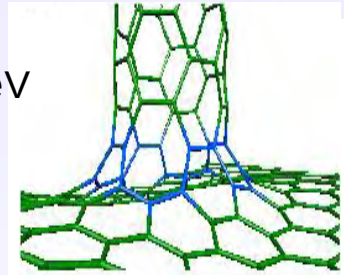


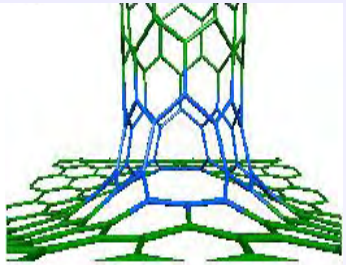
Fig. 1. Sixteen possible defects which require another eight bonds for sp^2 network.





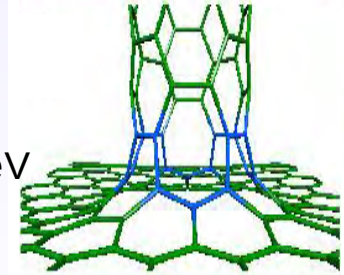
#3
8.13 eV

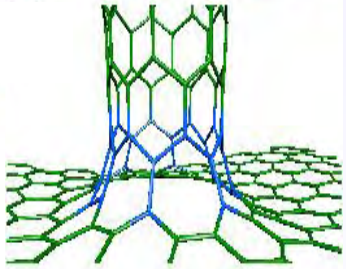




#3
10.68 eV

#9
9.77 eV

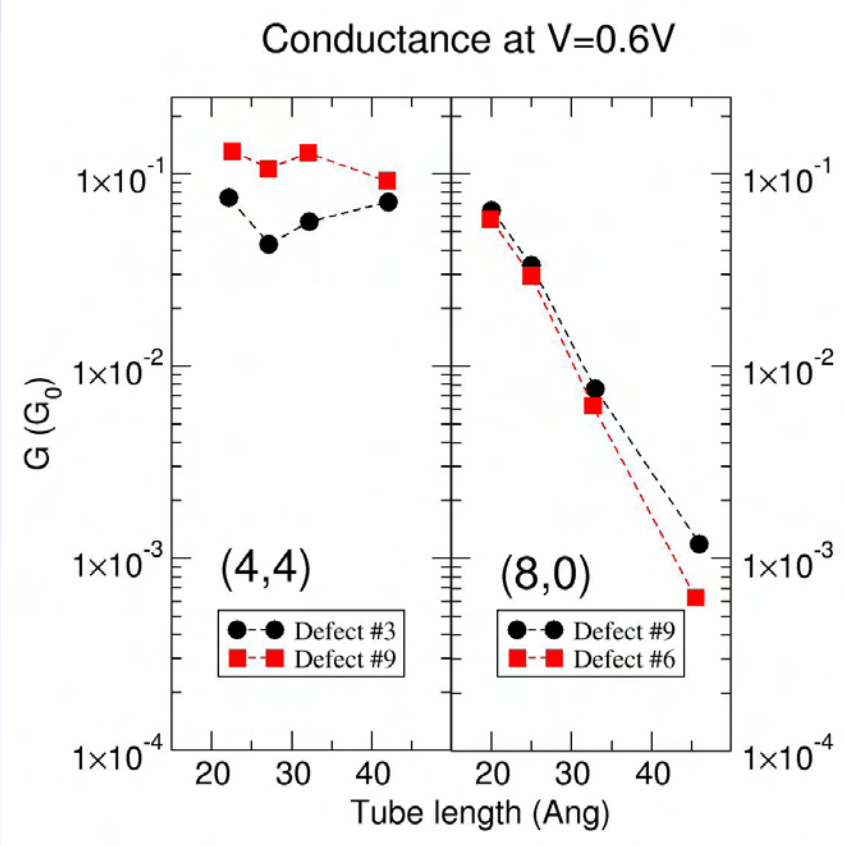


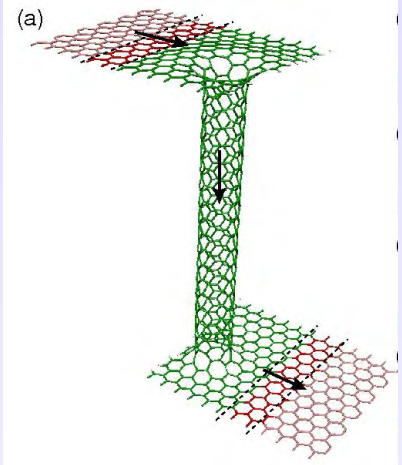


#6
11.05 eV

GGA (PBE); DZP Basis set

Covalent link of CNT's to graphene



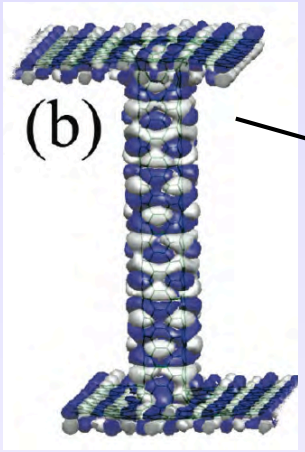


$$G = \frac{I}{V} = \frac{G_0}{V}\int_{-V/2}^{V/2} d\varepsilon\, T(\varepsilon)$$

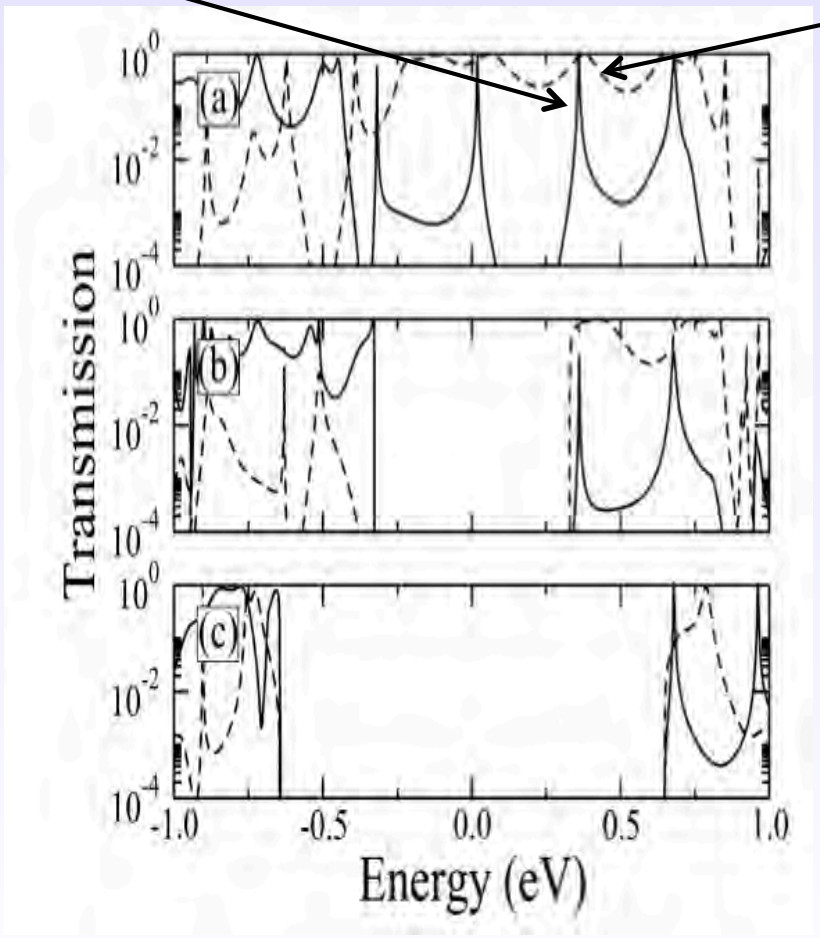
Metallic tubes: Extended states → G is roughly independent of tube length

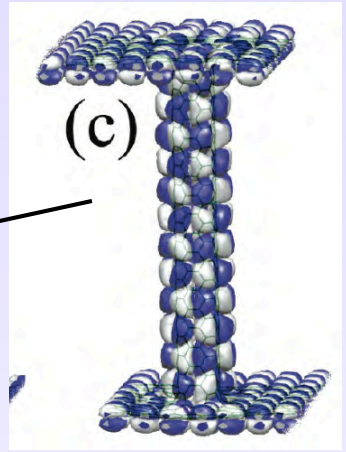
Semiconducting tubes: No states in the gap. Conduction by tunneling
→ G decreases exponentially with tube length

(k-resolved) Transmission Curves - Eigenchannel analisys



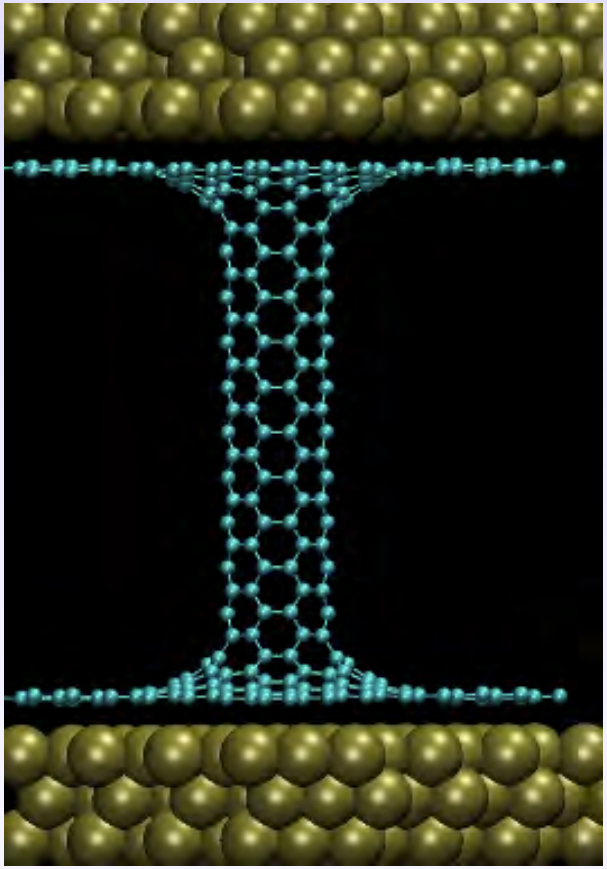
(8,0) CNT

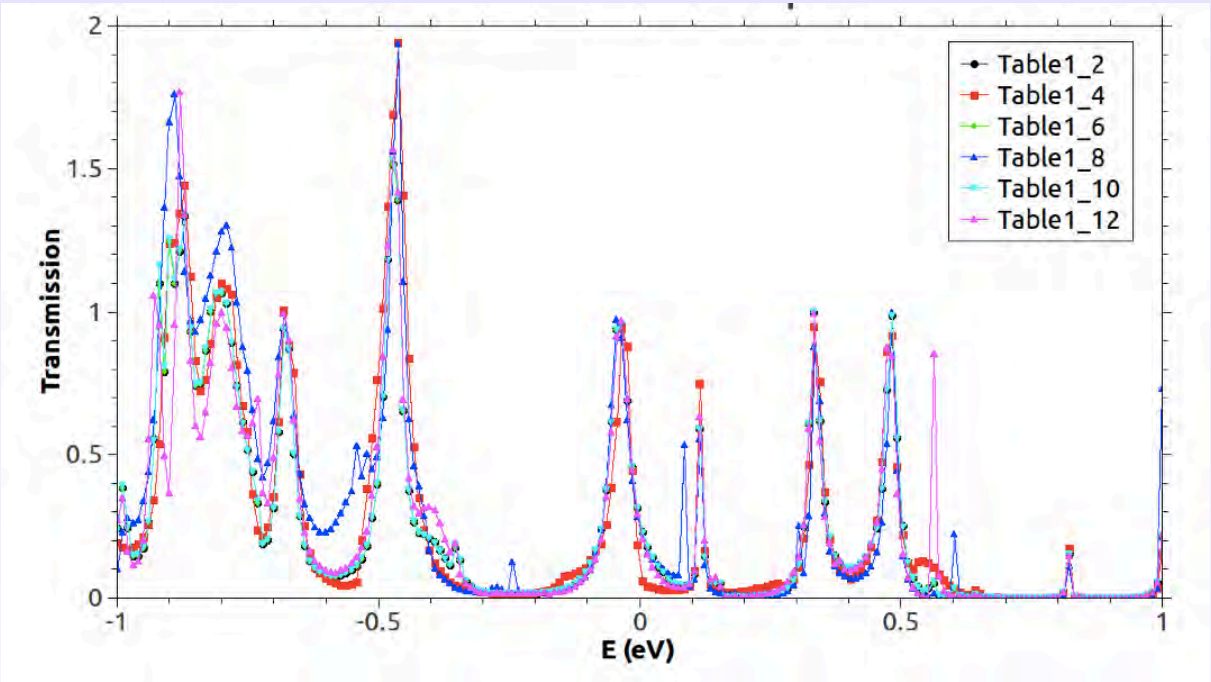




- CNT π and π* states couple differently to graphene
- Large (0.2 eV) band offset between CNT and graphene
- Influence of link structure on the band offset (specially for semiconducting CNTs).

Pt / Graphene /CNT contacts

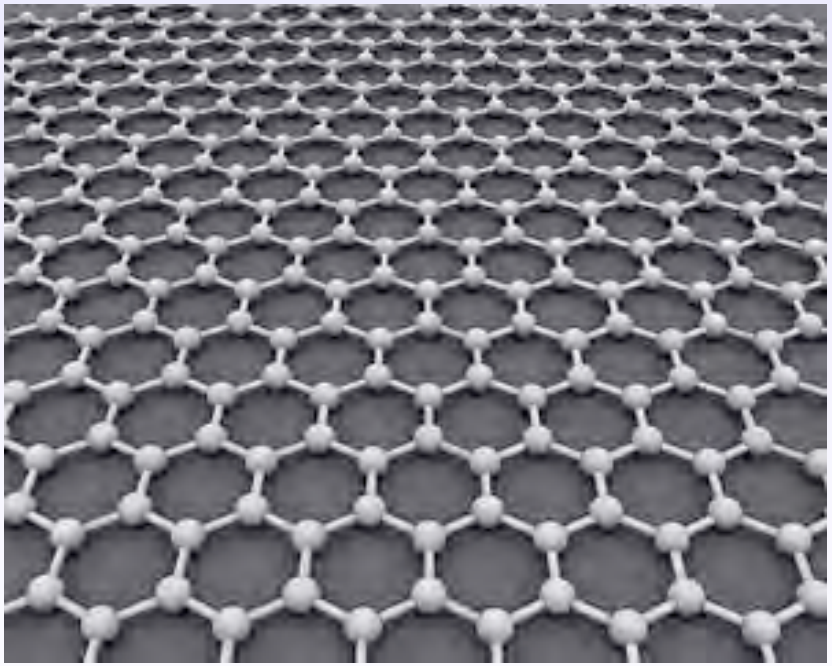


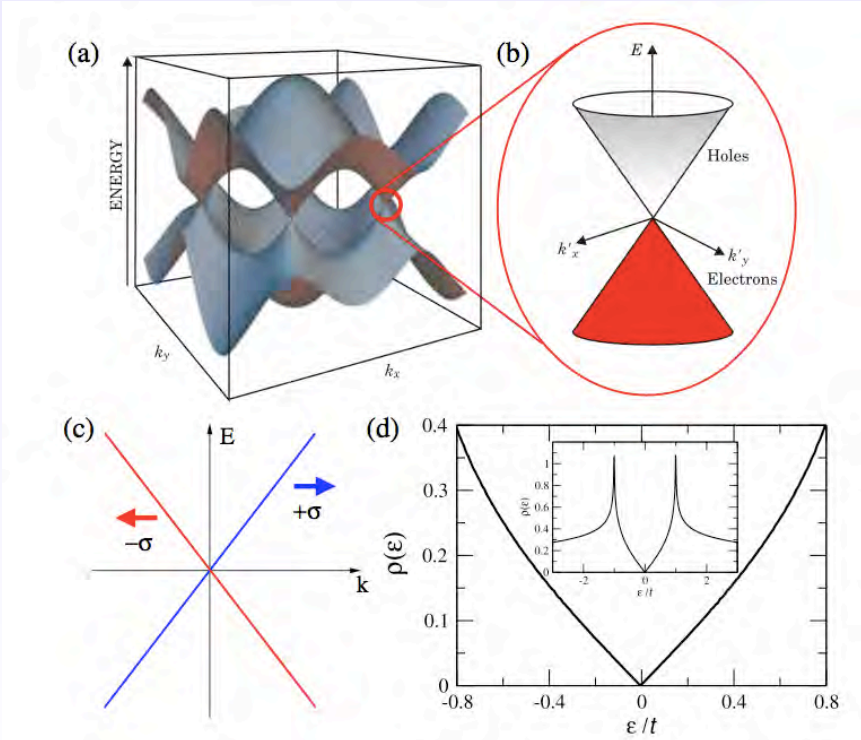


- Resonant transmission through the electronic states of the (short) CNT
- The presence of graphene does not seem to improve the coupling between CNT and Pt

Graphene

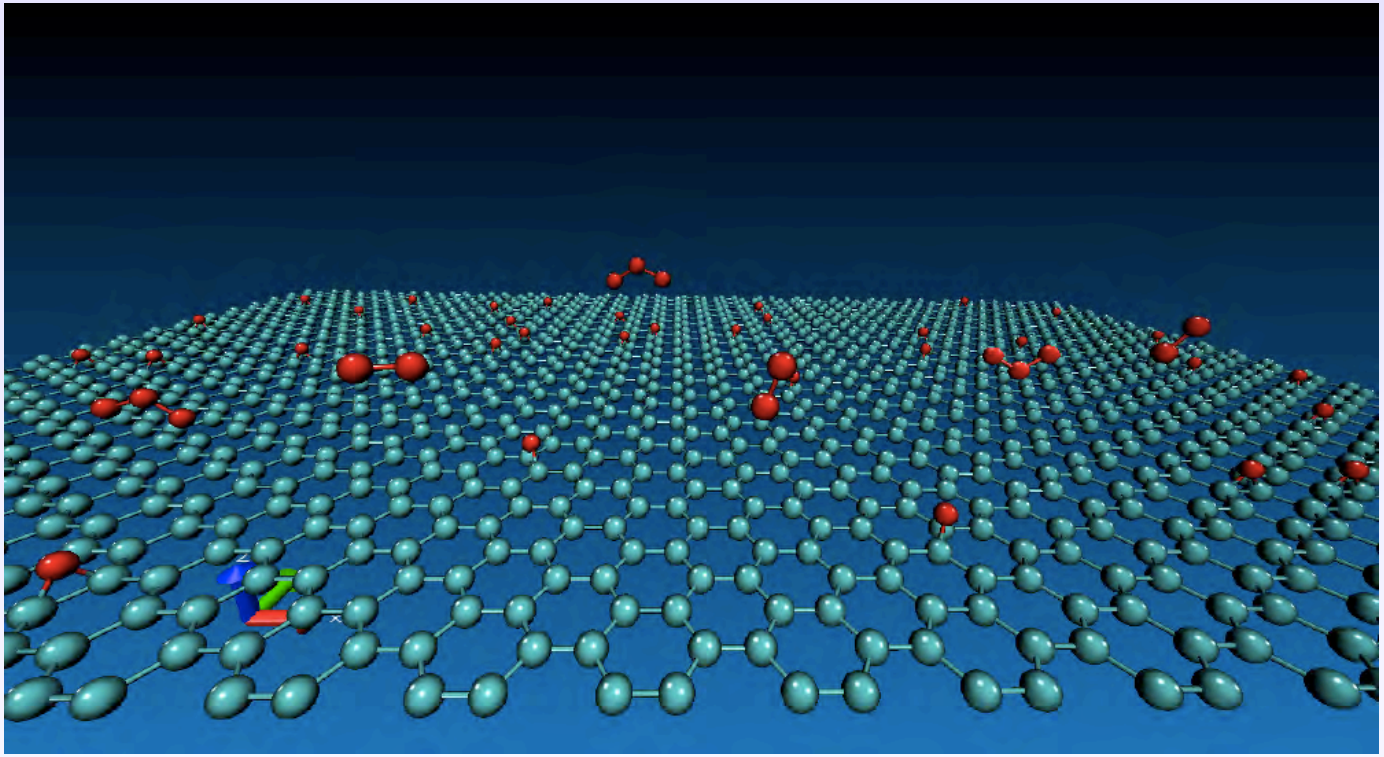
- One-atom thick sp^2 carbon material
- Many interesting physical properties (electronic, optical, mechanical, etc)
- Linear dispersion relations (electrons behave as massless Dirac Fermions)
- Zero-gap semiconductor
- Very large mobility (excellent for electronic devices)
- ***Modifiying the properties via chemical functionalization?***





Transport in chemically - modified graphene:

- Much larger scales involved: Very high mobility and mean free paths (microns!)
- Accurate description of effects of chemicals required, but straight DFT is not feasible!
- Intrinsic transport properties, instead of contact characteristics --> Landauer is not the best choice



- Experimentally: Ozone exposure (J. Moser, H. Tao, S. Roche, F. Alzina, C. M. Sotomayor Torres, and A. Bachtold, PRB 81, 205445 (2010))
- Exploring the possibility of driving a strong localization regime by introducing Oxygen impurities

From DFT to the mesoscale: "Poor-man's" multiscale approach:

DFT

Ab initio calculations to describe the local potential induced by the impurity

$\Downarrow$

DFT $\rightarrow$ TB

Extract sufficient TB parameters to reproduce the local potential

$\Downarrow$

TB-parametrized Kubo Formalism

Allows us to simulate mesoscopic-sized systems (10^6 atoms) :

- comparison with experiment
- calculate transport properties to visualize quantum effects

Kubo-Greenwood calculation for transport (Linear response; Fluctuation-dissipation)

Kubo conductivity

$$\sigma_{DC} = \frac{1}{2} e^2 \rho(E_F) \lim_{t\to\infty} \frac{\partial}{\partial t} \Delta X^2(E_F, t)$$

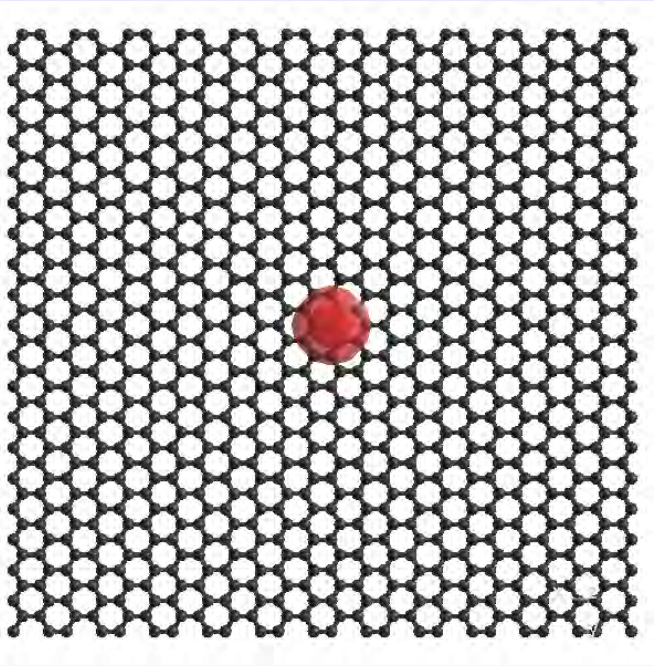
Wave packet : mean quadratic displacement

$$\Delta X^2(E,t) = \frac{Tr\left[[\widehat{X}, \widehat{U}(t)]^\dagger \delta(E-\widehat{H})[\widehat{X}, \widehat{U}(t)]\right]}{Tr\left[\delta(E-\widehat{H})\right]}$$

Diffusion coefficient

$$D_x(t) = \frac{\Delta X^2(t)}{t}$$

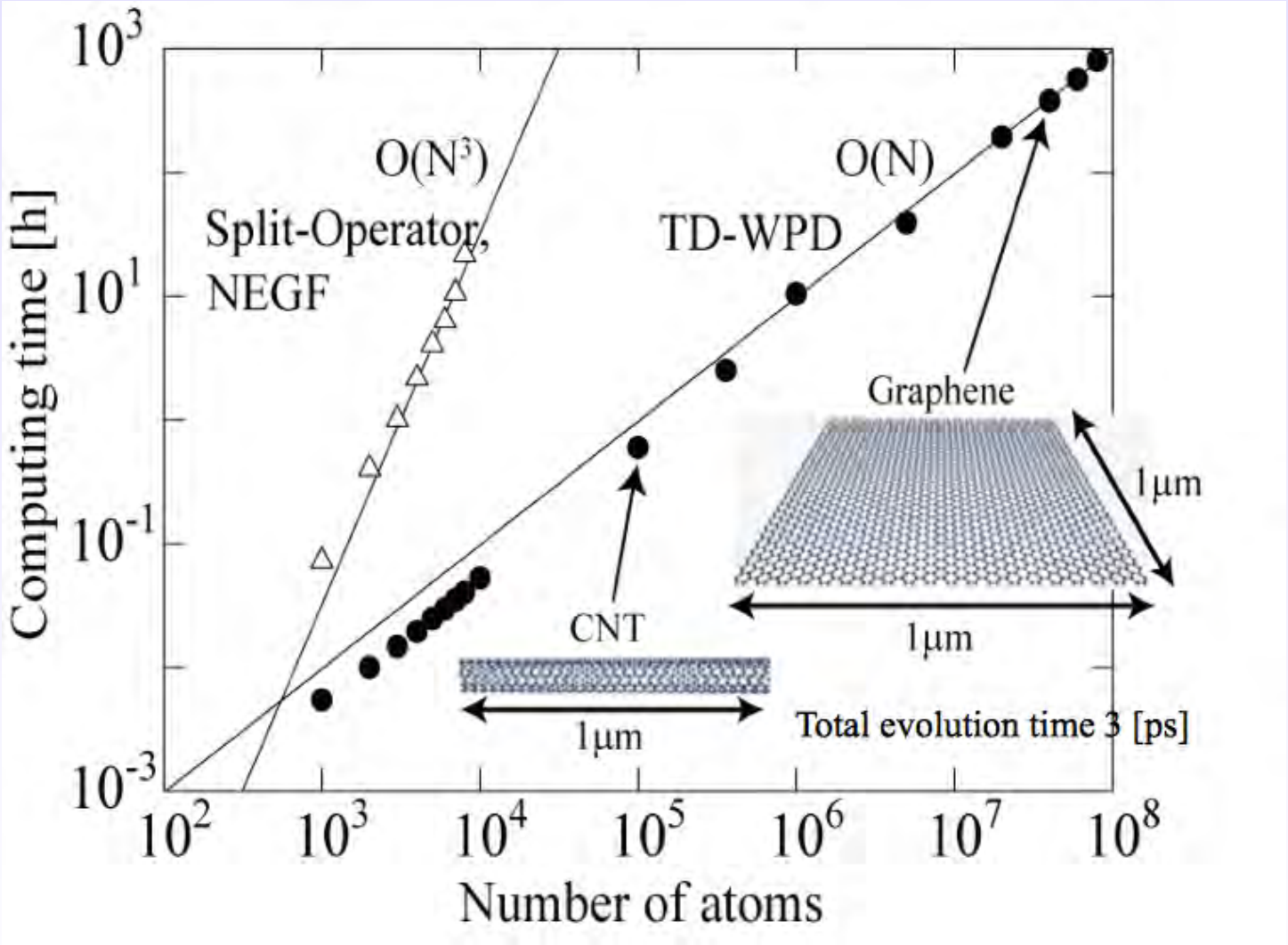
$$\hat{U}(t) = \Pi_{n=0}^{N-1} \exp(i\hat{H}(n\Delta t)\Delta t/\hbar)$$



S. Roche, PRB'99

Lherbier, A.; Biel, B.; Niquet, Y.-M.; Roche, S. *Phys. Rev. Lett.* **2008**, *100*, 036803.

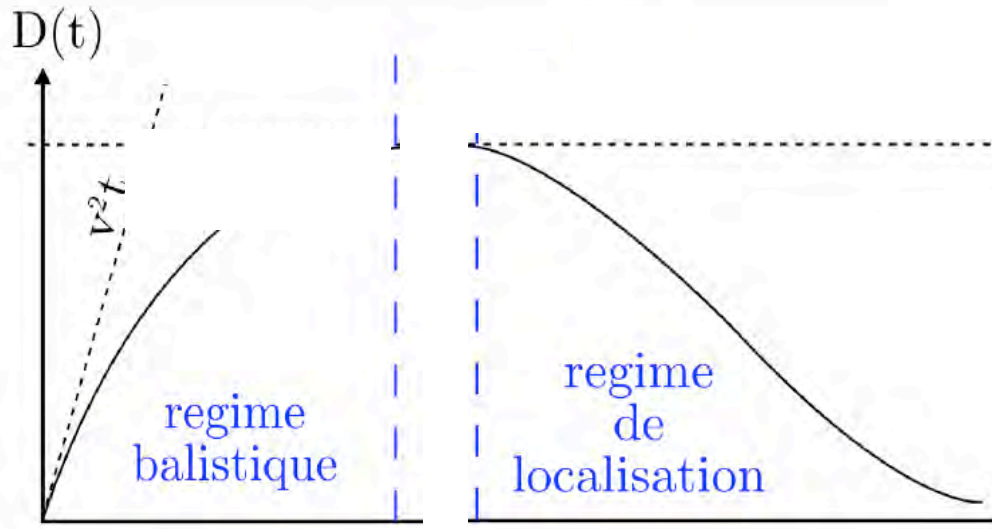
Kubo-Greenwood calculation for transport
(S. Roche, CIN2)



Kubo-Greenwood calculation for transport

Diffusion Coefficient

$$D_x(t) = \frac{\Delta X^2(t)}{t}$$

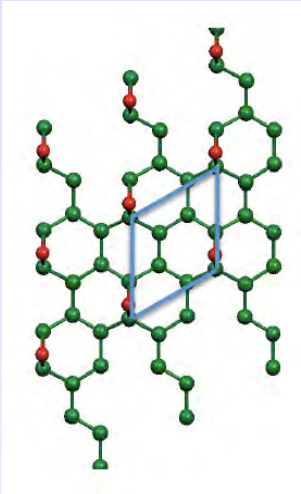


Scattering (defects,...)
& Disorder

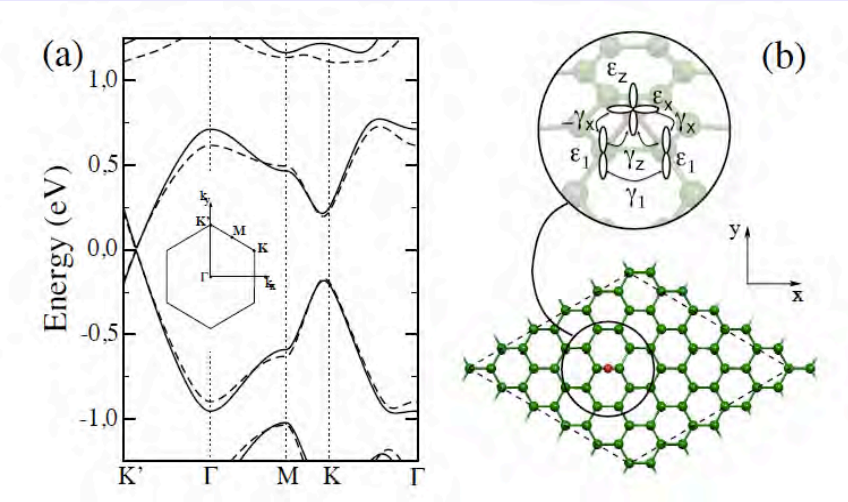
Quantum interference
Anderson Localization

Epoxide - Functionalized graphene -- “Poor-man’s” multiscale approach: Combining approaches to reach relevant sizes and properties

1. **DFT** for small systems



2. **Tight-Biding** model that reproduces the DFT results



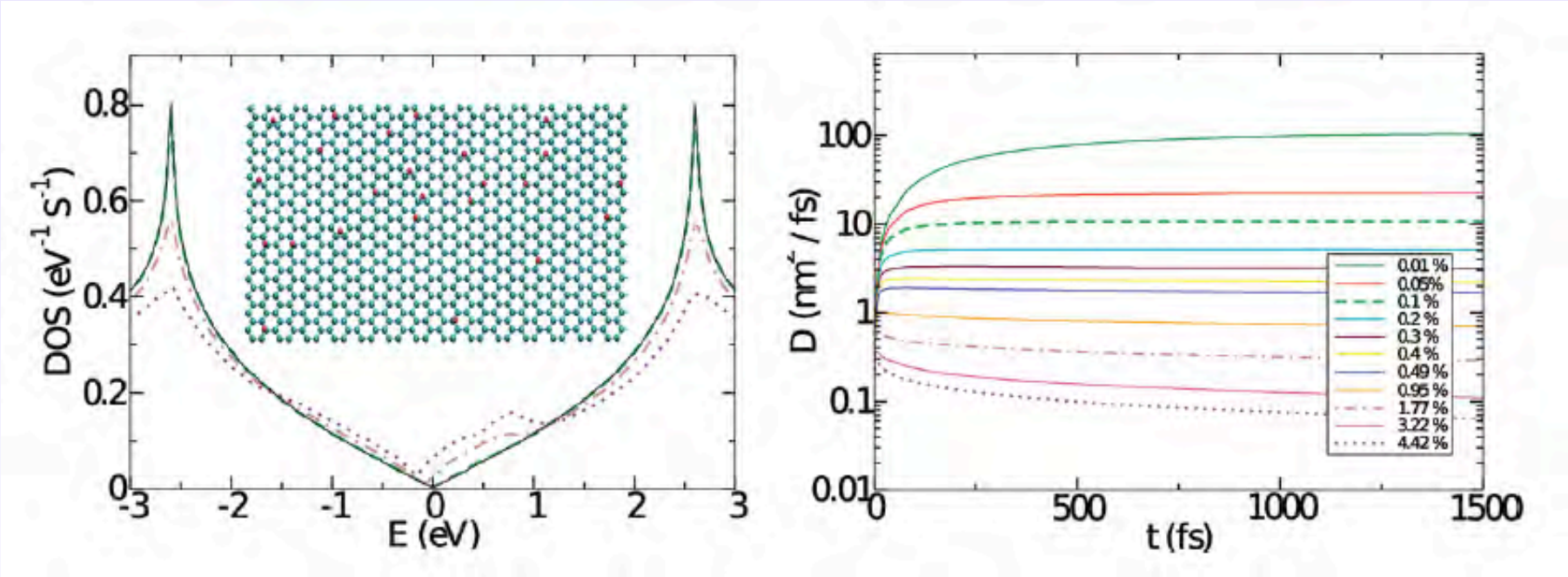
3. **Kubo** approach: conductance for mesoscopic systems (10^6 atoms) (within the TB model)

   Based on wave-packet propagation

Kubo results from TB model derived from ab-initio

N. Leconte, A. Lherbier, J.C. Charlier - U.C. Louvain
S. Roche, CIN2

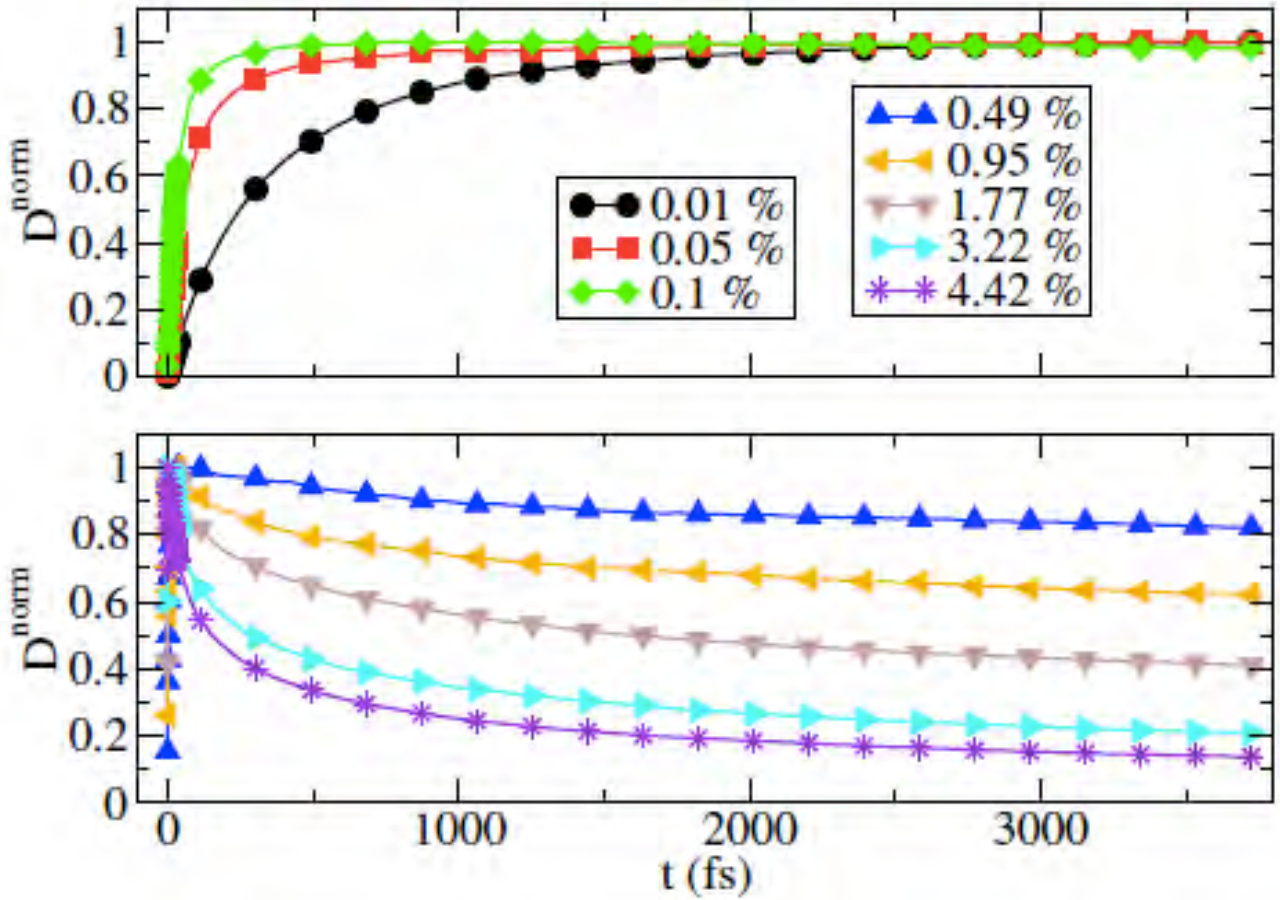
Diffusion coefficient at the Fermi level



Leconte et al., ACS Nano, 4, 4033 (2010)

Evidence for localization, for relatively small concentration

Diffusion coefficient at the Fermi level

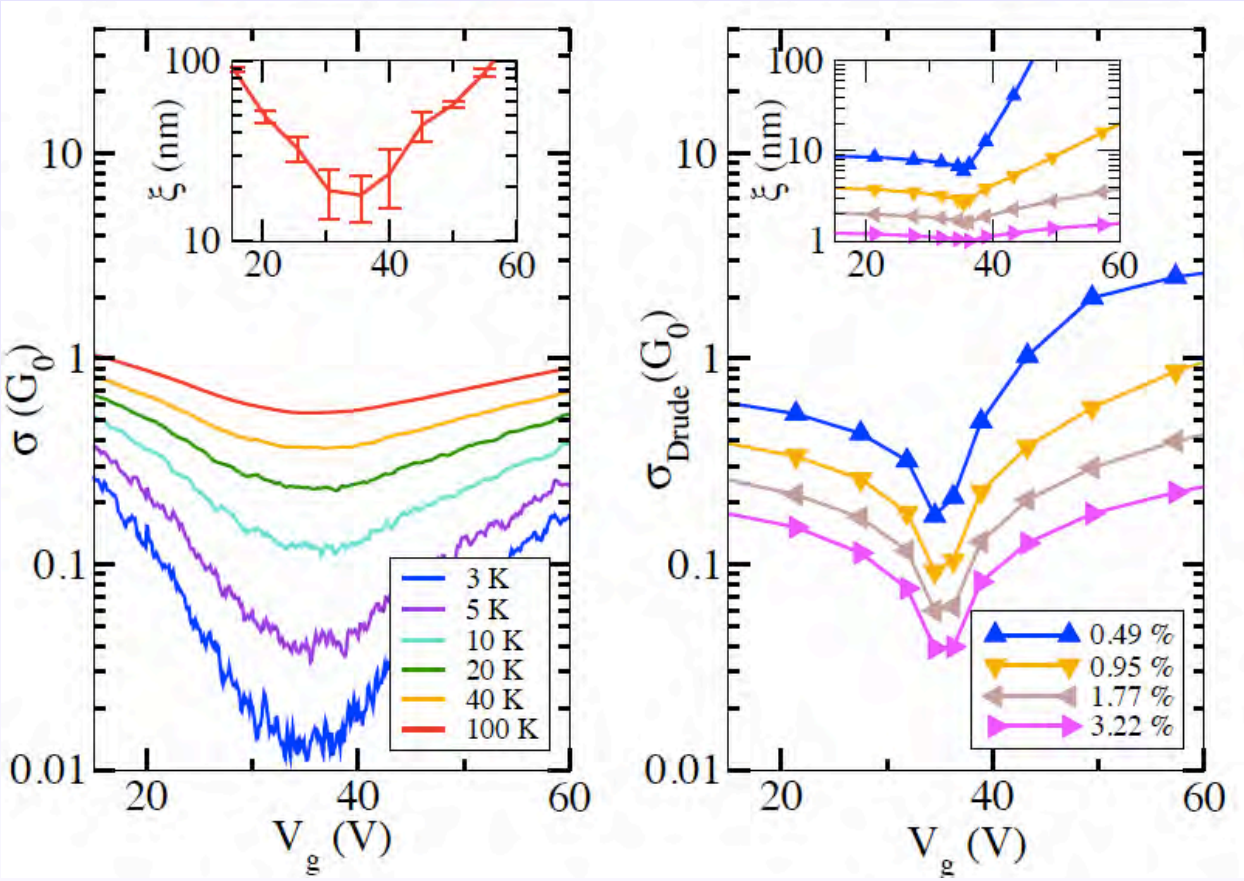


Diffusive
(but Mean Free Path similar to simulation cell size)

Localization

Leconte et al., ACS Nano, 4, 4033 (2010)

Comparison with experiments
(A. Bachtold, C. Sotomayor - CIN2)

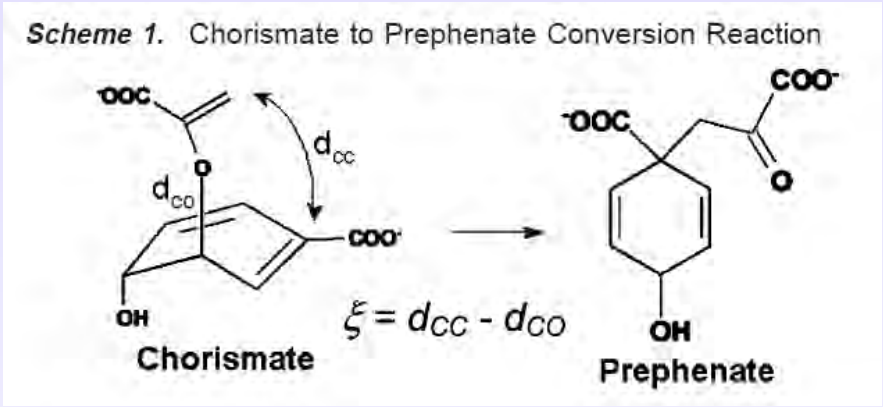


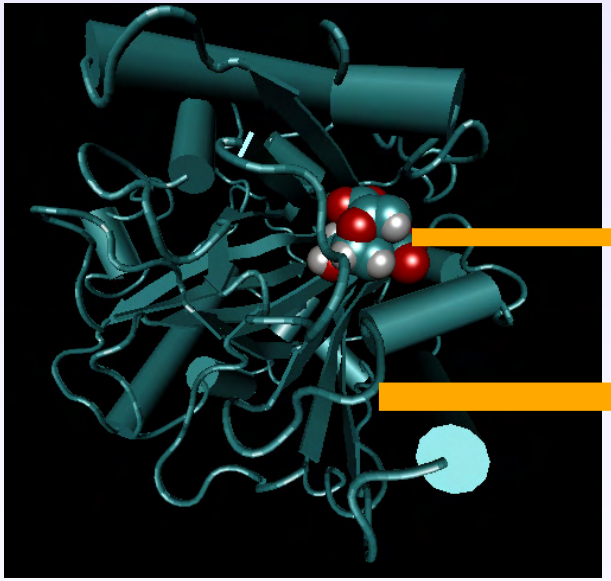
PRB 81, 205445 (2010)

Beyond First-Principles for structure/dynamics: Hybrid QM-MM schemes for local reactivity in complex systems

Issues:

- Reactions in active sites of proteins
- Effects of solvents
- Long dynamics for floppy modes (MM)
- Similar methods for non-bio systems





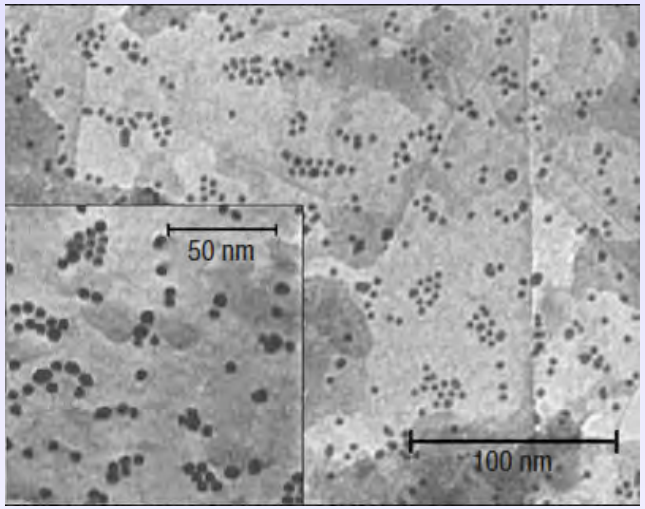
Reactive subsystem: QM

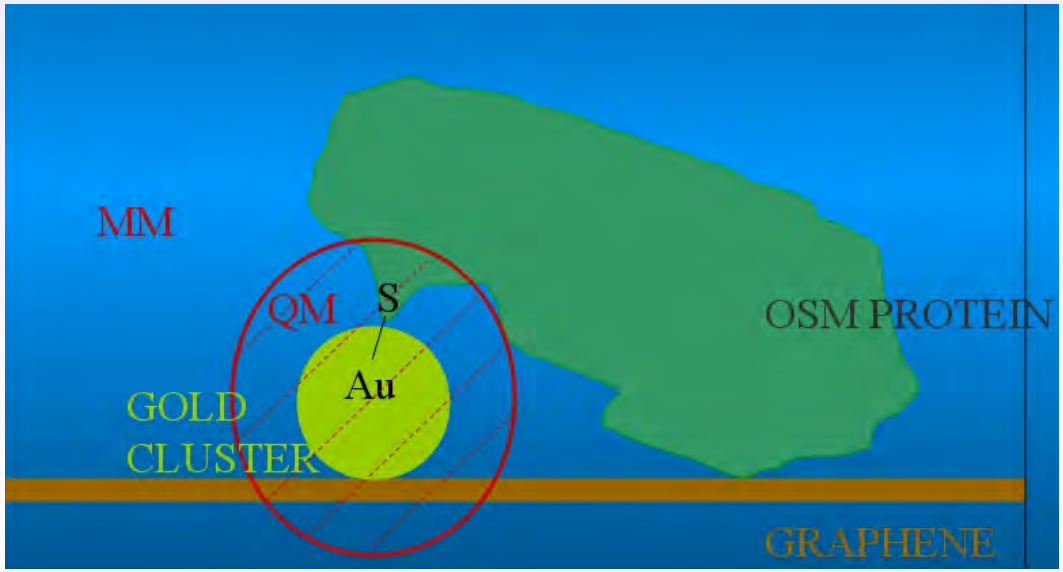
Environment: MM (AMBER)

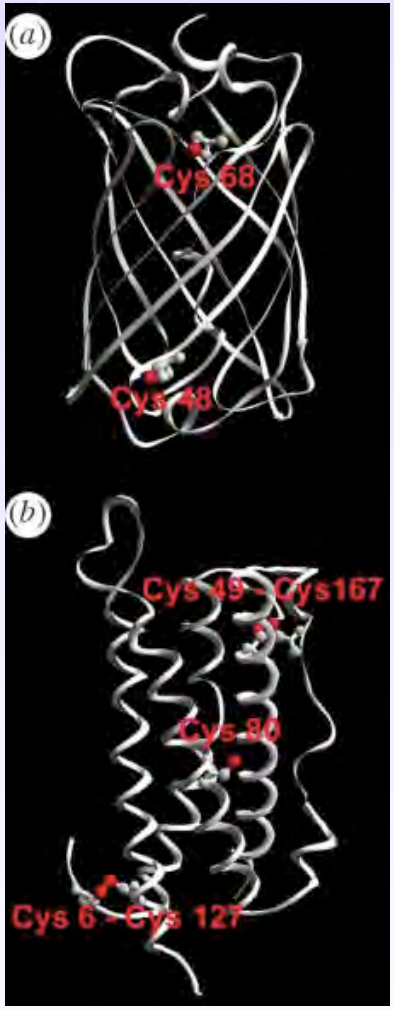
Crespo, Martí, Scherlis, Ordejón Roitberg and Estrín
J. Phys. Chem. B, **107**, 13728 (2003)

Sanz et al., Theor Chem Acc **128**, 825 (2011)

Protein inmovilization on Graphite by Gold Nanoclusters (Carlos Sanz, in collaboration with Richard Palmer, Birmingham)



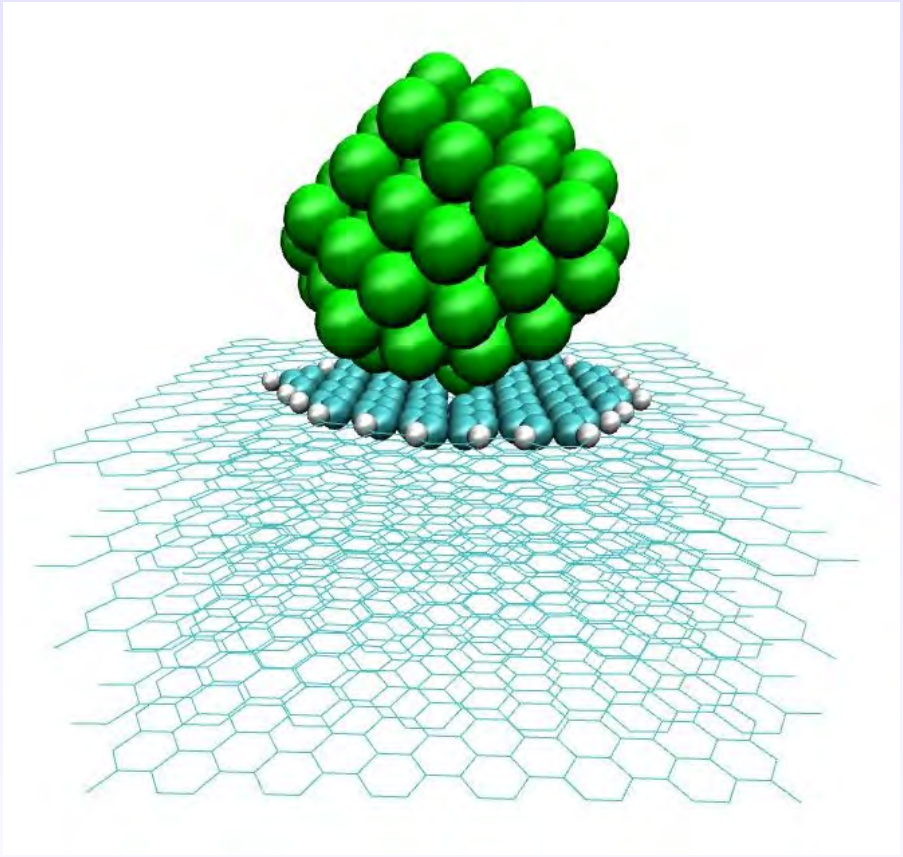


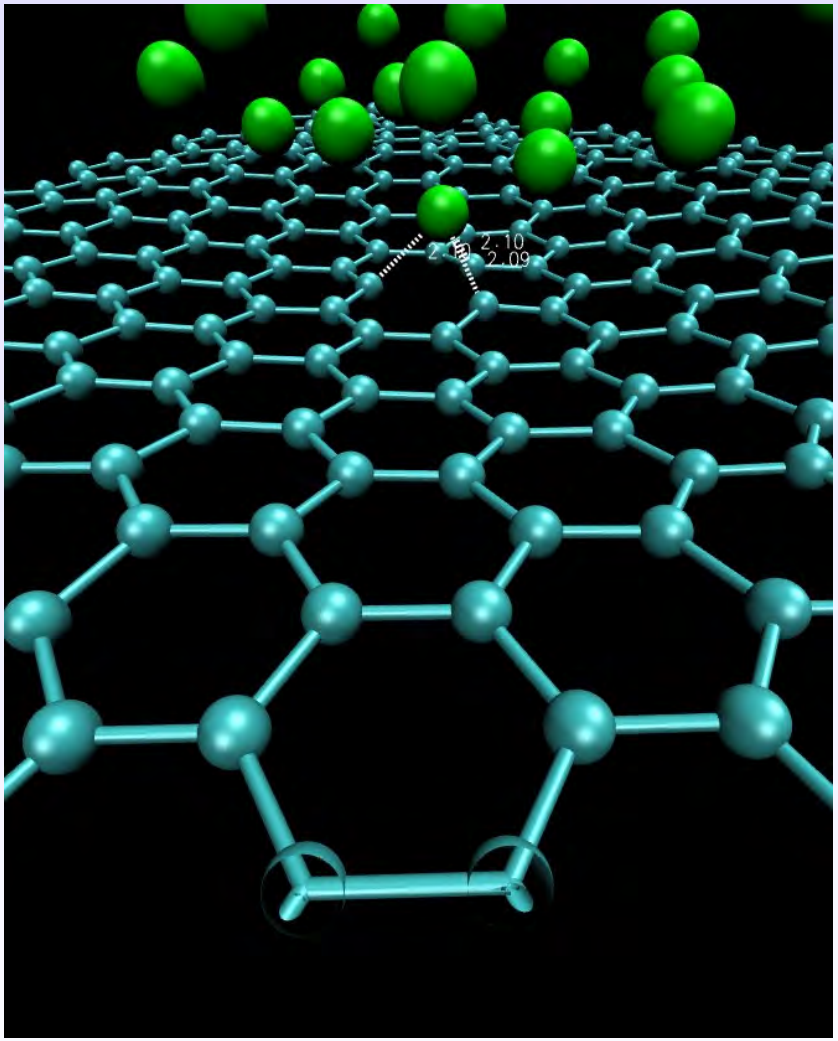


GFP (Green fluorescent protein)

OSM (Human oncostatin M)

Gold nanoclusters on Graphite: QM/MM Simulations (Carlos Sanz)





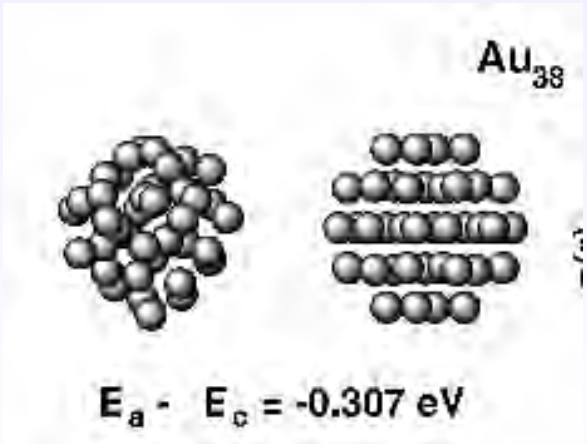
What is the structure of the free clusters?

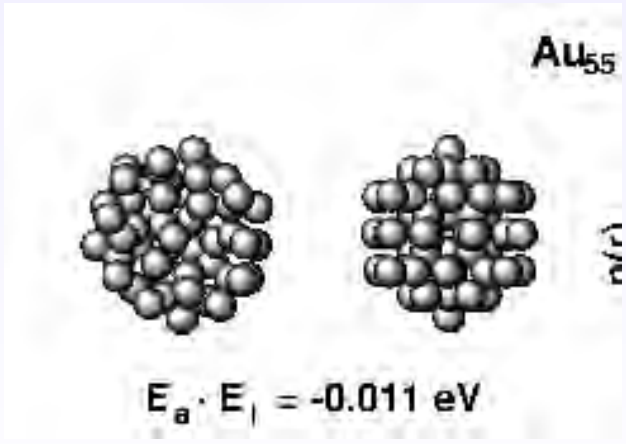
VOLUME 81, NUMBER 8 PHYSICAL REVIEW LETTERS 24 AUGUST 1998

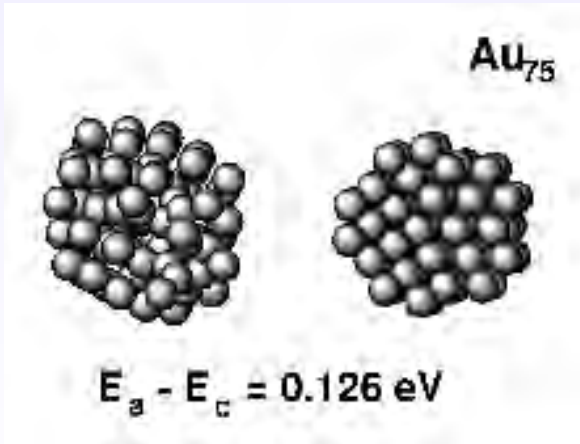
Lowest Energy Structures of Gold Nanoclusters

I.L. Garzón,[1] K. Michaelian,[1] M.R. Beltrán,[2] A. Posada-Amarillas,[3] P. Ordejón,[4] E. Artacho,[5]
D. Sánchez-Portal,[5] and J.M. Soler[5]

The lowest energy structures of Au_n ($n = 38, 55, 75$) nanoclusters are obtained by unconstrained dynamical and genetic-symbiotic optimization methods, using a Gupta n-body potential. A set of amorphous structures, nearly degenerate in energy, are found as the most stable configurations. Some crystalline or quasicrystalline isomers are also minima of the cluster potential energy surface with similar energy. First principles calculations using density functional theory confirm these results and give different electronic properties for the ordered and disordered gold cluster isomers.



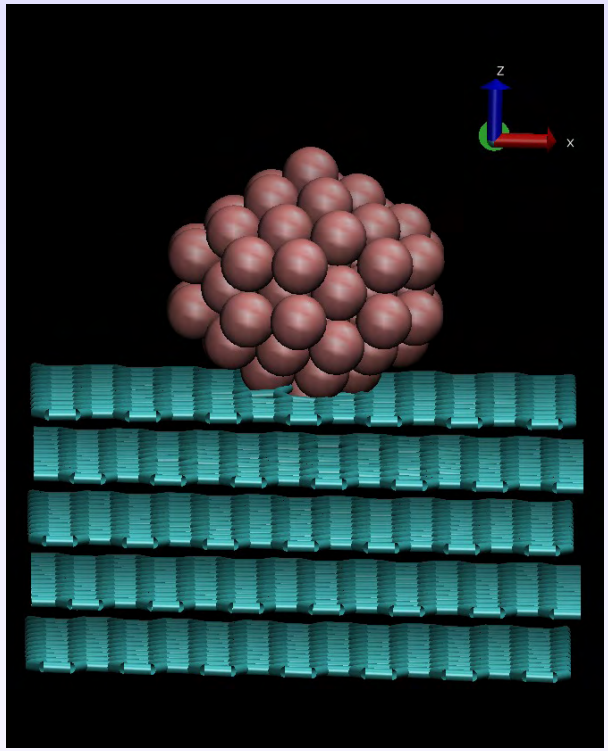




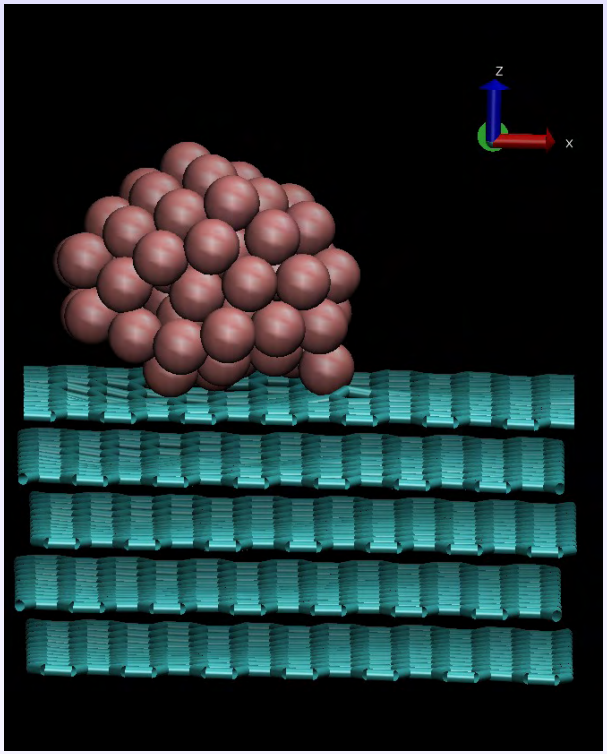
Gold nanoclusters on Graphite: QM/MM Simulations (Carlos Sanz)

Au_{75}

INITIAL

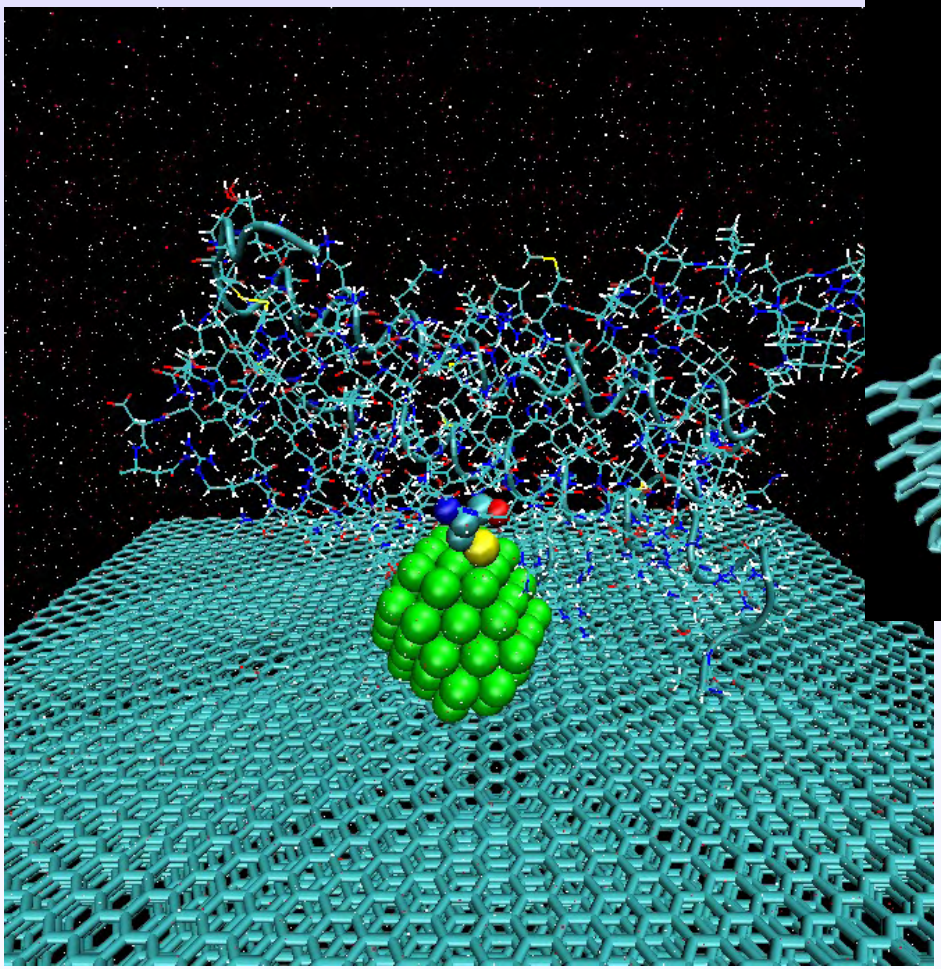


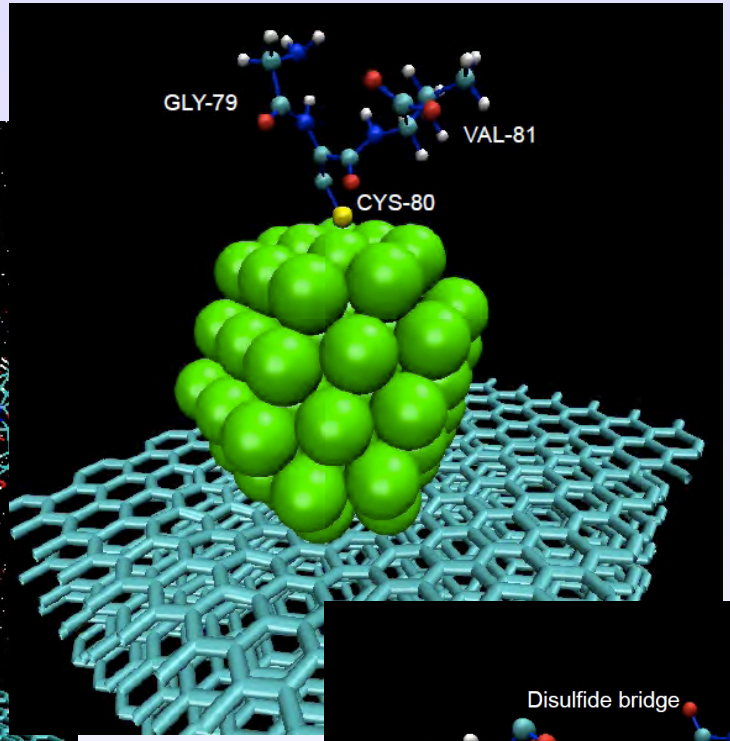
FINAL

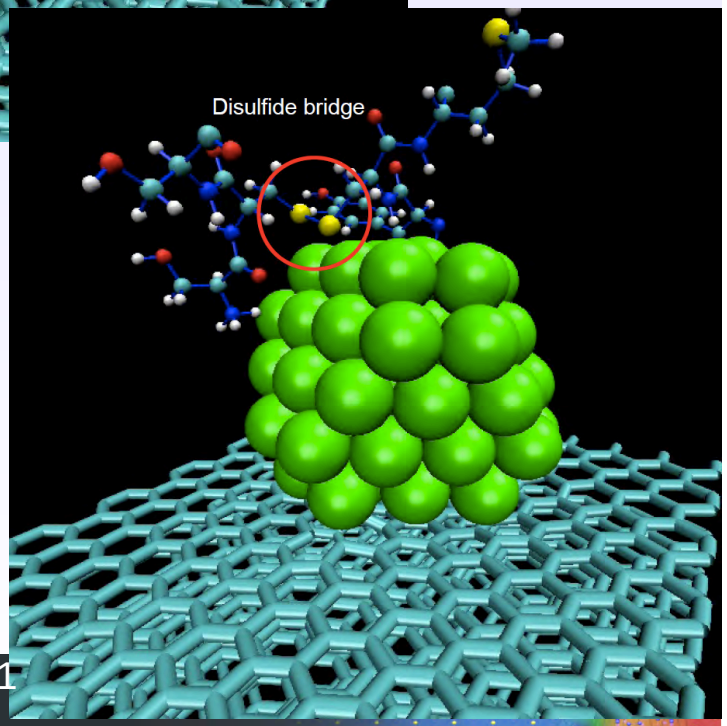


- Strong rearrangement upon adsorption on the graphite surface
- Energetic ordering of the structures changes on the surface with respect to the free cluster
- 'Soft modes' present (rotations, shear, ...) which make the relaxations very time-consuming

Protein - Gold interaction through Cys residues (Carlos Sanz)

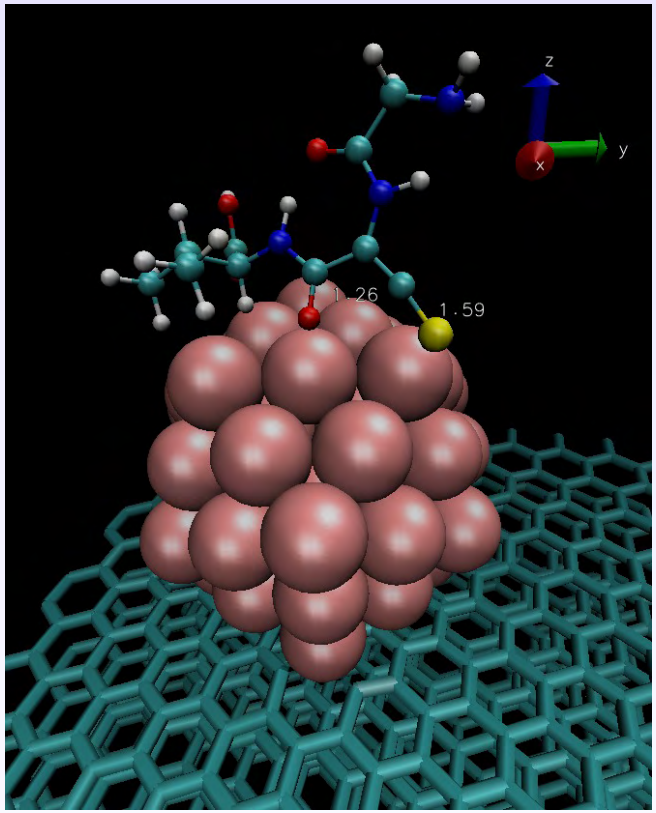




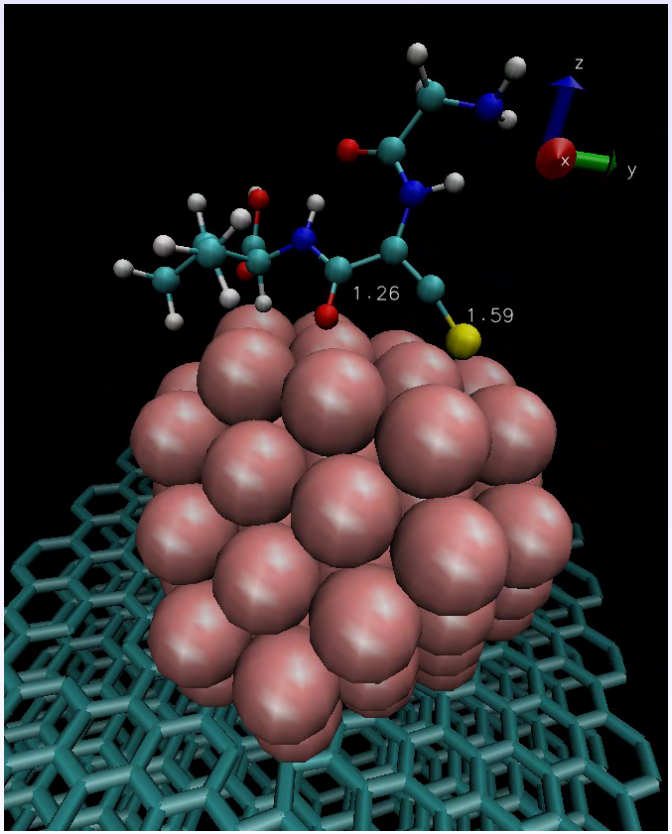


Protein - Gold interaction through Cys residues (Carlos Sanz)

Au_{55}



Au_{75}



CONCLUSIONS

- HPC and atomistic simulations:
  - Large sizes are under our reach, but only for simple methods - Multiscale needed to bridge the size gap.
  - Time scale is still a problem that must be solved (multiscale methods only helps to some extent). New methods (accelerated dynamics, etc) needed.

- A simple ‘multi-scale’ approach, combining DFT, Tight-Binding and Kubo, allows us to study transport in large samples

- Localization due to chemical functionalization of graphene with Epoxide
  - Metal to insulator crossover upon increasing impurity concentration
  - Strong localization for relatively small amounts of adsorbed Oxygen

- Hybrid QM/MM methods to explore structure and dynamical properties of nanostructures - organic-inorganic interfaces.

Work done in collaboration with:

- **The SIESTA Team** - Soler, Artacho, García, Sanchez-Portal, Junquera

- M. Brandbyge, J. Taylor, K. Stokbro - T.U. Denmark
- J.L. Mozos, F.D. Novaes - CSIC-Barcelona

- F.D. Novaes, R. Rurali, J.A. Silva - CSIC-Barcelona

- S. Roche - CIN2 (**ICN**-CSIC) - ICREA Professor
- D. Soriano, J.J. Palacios - Univ. Autónoma Madrid
- N. Leconte, A. Lherbier, J.-C. Charlier - Univ. Cath. Louvain

- C. Sanz - CIN2 (ICN)

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