THE SIMULATION OF MOLECULAR AND ORGANIC DEVICES: A CRITICAL REVIEW AND A LOOK AT FUTURE DEVELOPMENTS

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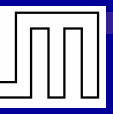
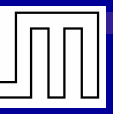
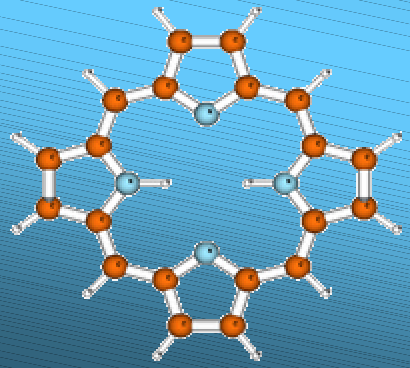


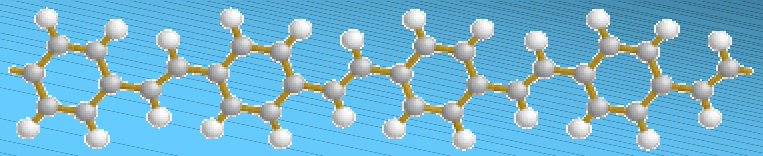
Outline

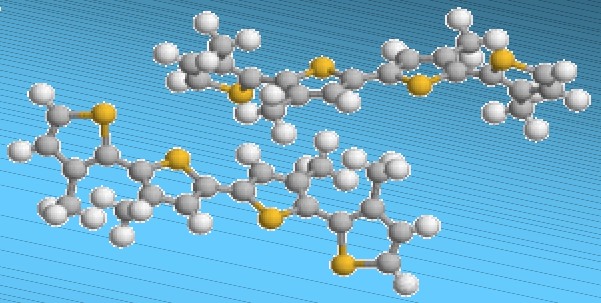
- Overview of molecular electronics
  - Generalities
  - OTFT Simulation
- Single molecule electronics
  - DFTB method
  - Simulation of molecular diodes
- Carbon Nanotubes
  - CNTs as sensors and transistors
- Open questions and closing remarks



Approaches to molecular electronics







Organic Molecules
100-1000 atoms or more

Organic Material for electronics

Conventional simulators

- **Organic Transistors**
- **Organic LED**
- **Organic Solar Cells**

Conventional devices with organic semiconductors

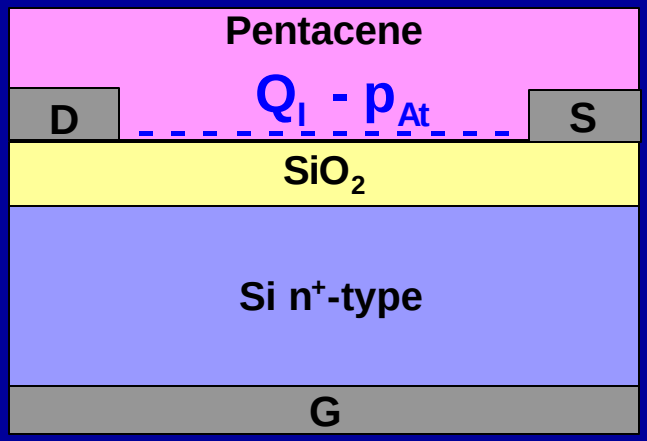
Molecular Electronics

New simulators

- **Diodes**
- **Transistors**
- **Memories**

New devices with nanosize dimension

Simulation Model



The simulation uses a modified drift-diffusion tool (ISETCAD).

Trap model according to Scheinert et al. JAP 92, 330 (2002)

$$m = m_0(T)\exp\left(\sqrt{\frac{E}{E_0}}\right)$$

$$J_n = -qm_n\nabla V + qD_n\nabla n$$

$$J_p = -qm_p\nabla V - qD_p\nabla p$$

$$\nabla\cdot(e_0 e_r\nabla V) = -q(p - n + N_D^+ - N_A^- - p_{At}) - Q_I$$

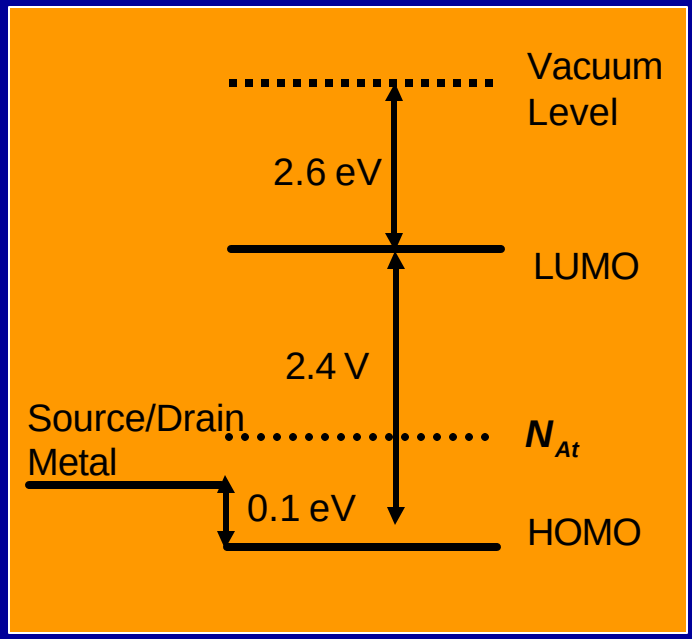
$$\nabla\cdot J_n = q(R - G)$$

$$\nabla\cdot J_p = -q(R - G)$$

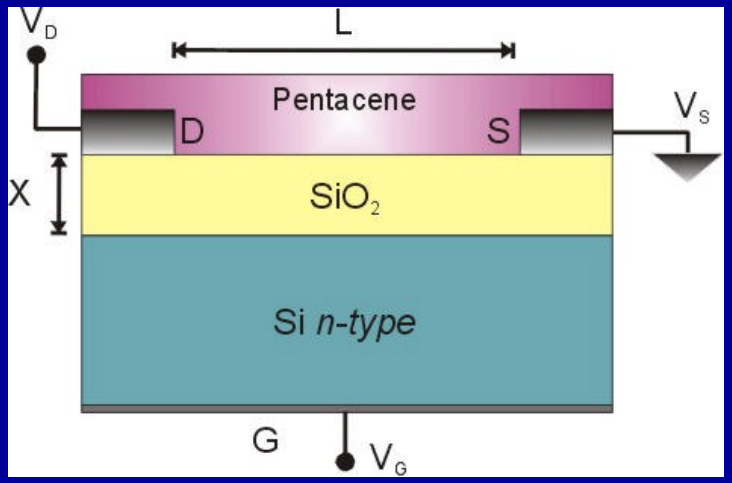
$p_{At} = N_{At} f_n$ Acceptor-like traps

Q_I SiO_2/Pentacene interface charge

Pentacene levels alignment

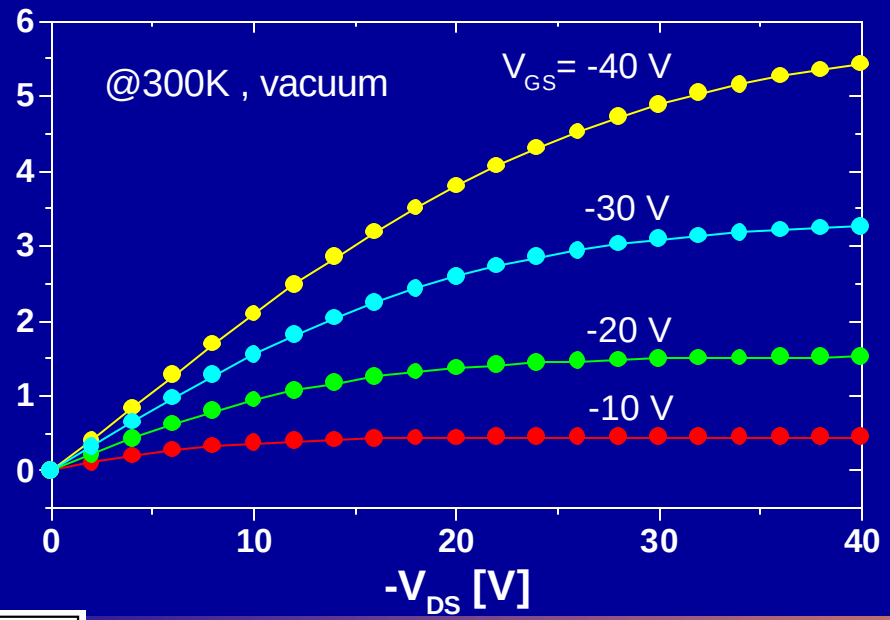


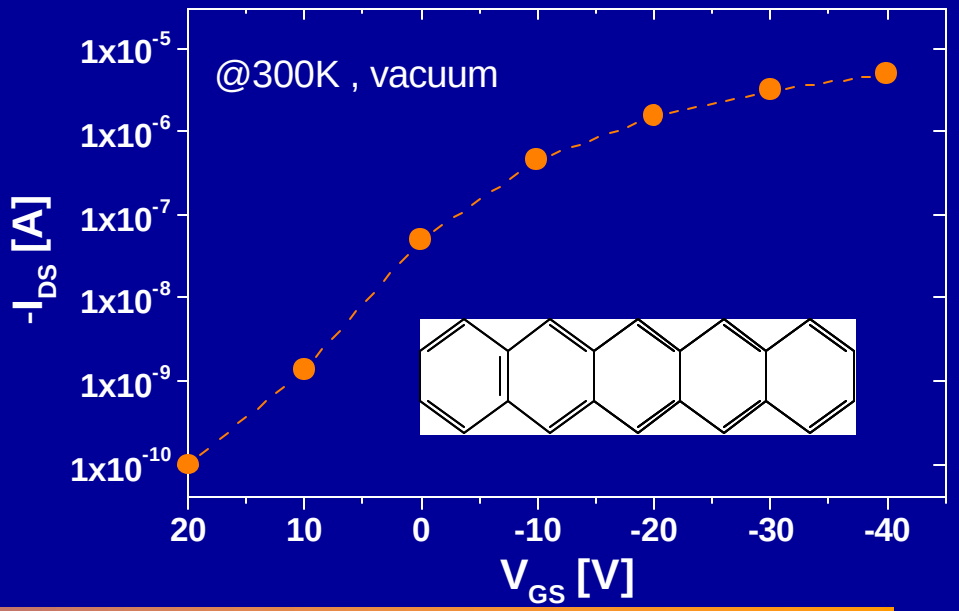
OTFT characteristics



- Thin film transistor were fabricated using bottom contact configuration.
- Cr/Au Source/Drain Contact prepared by vacuum evaporation.
- Pentacene sublimated in vacuum at a rate of 0.2 A/sec.

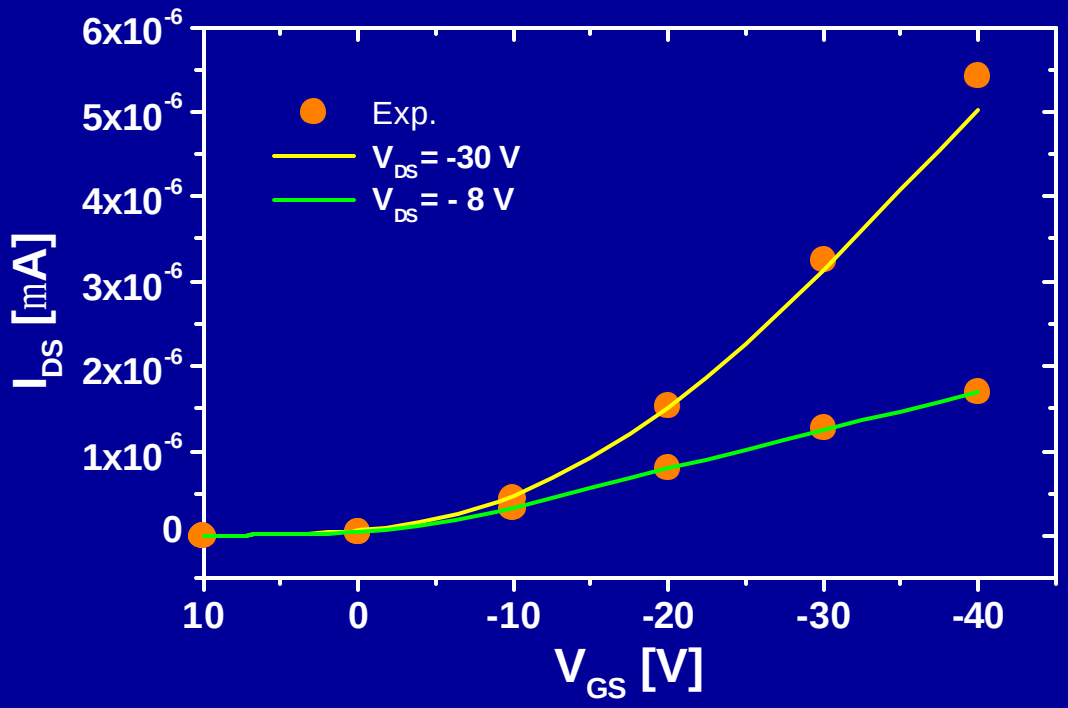
Channel Length L=12µm (L / W = 140)
Oxide Thickness x=250 nm





A. Bolognesi et al., Synthetic Metals 138 (2003) 95–100

Transfer Characteristics



The overall behavior of the device has been simulated and good agreement is found between experiment and simulations.

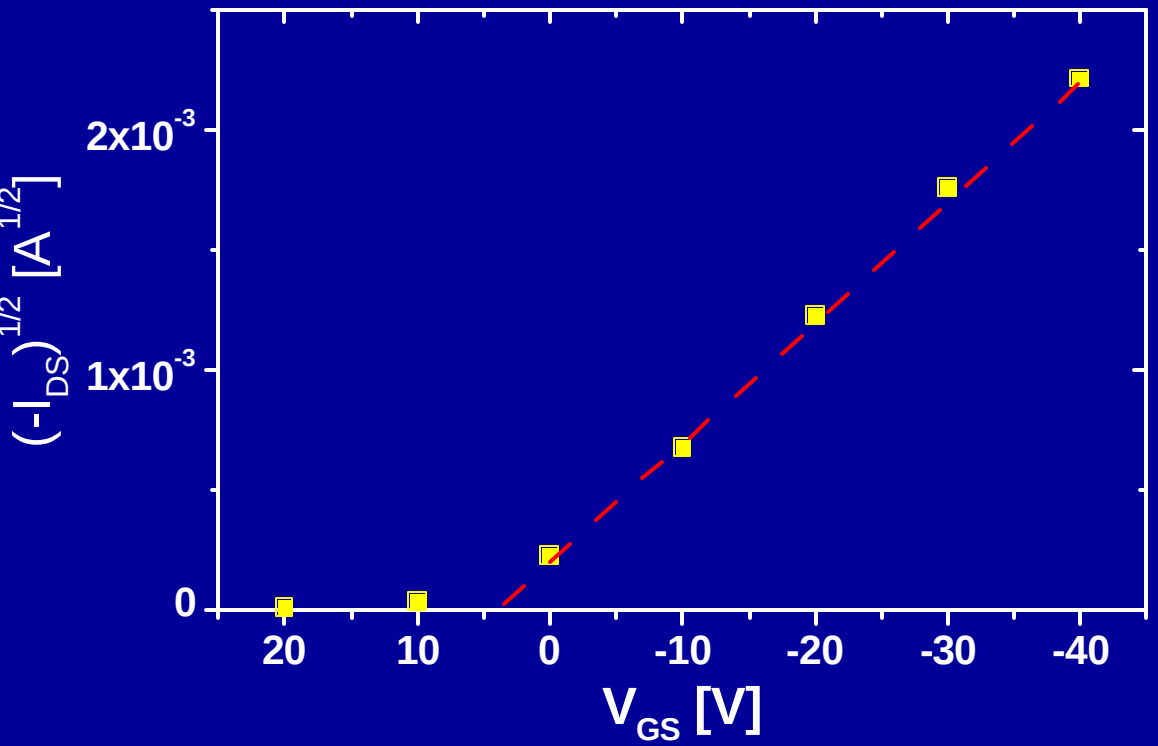
Parameters: μ_0=3.3 cm^2/Vs, N_i=2 10^{11} cm^{-2}, N_{trap} = 10^{12} cm^{-2}, E_{trap}=0.15eV

Is this parameterization transferable to other devices ?

ES, if growth conditions remain the same **NO**, if growth conditions are changed

Experimental determination of mobility

Usually standard MOSFET theory is used to extract the mobility from experimental data via the quadratic relation between V_G and I_{Dsat}

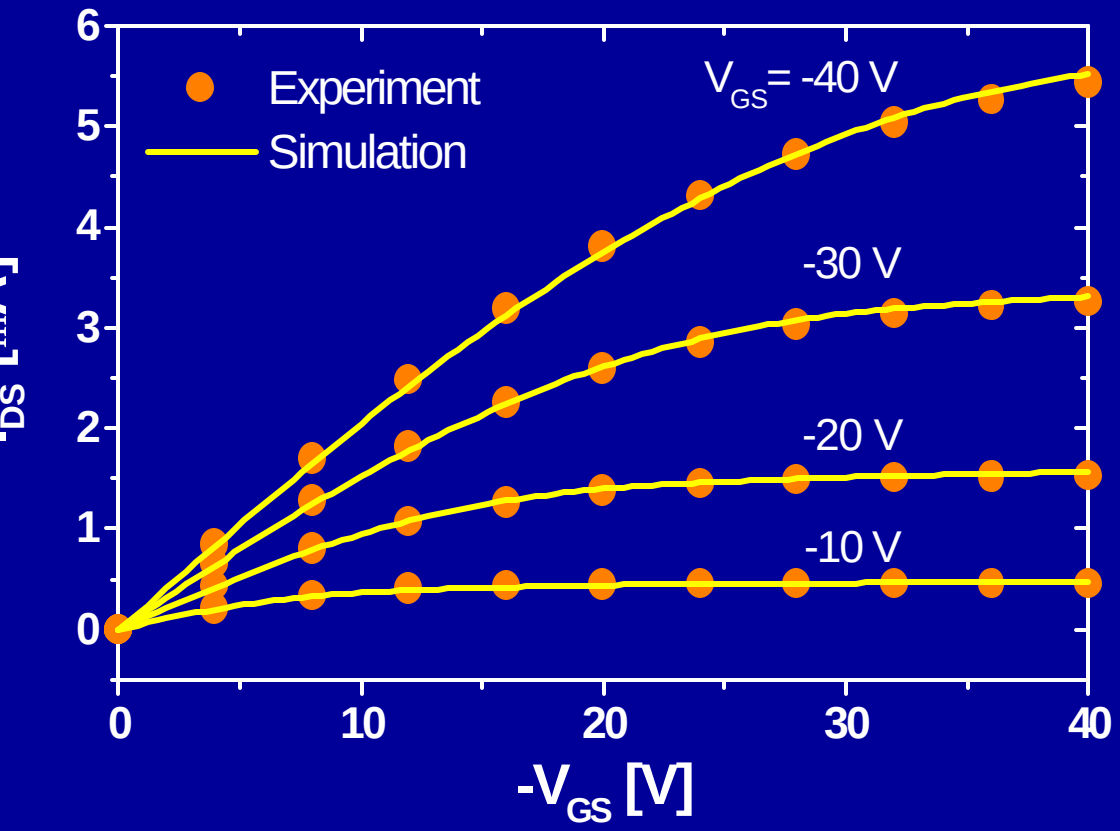


$$I_{Dsat} = m\frac{W}{2L}C_{ox}(V_G - V_T)^2$$

$$m_{\exp} = 4.23\cdot 10^{-3}\ \frac{\mathrm{cm}^2}{\mathrm{Vs}}$$

w does this mobility compare with the field activated mobility $m = m_0 \exp(\sqrt{\frac{E}{E_0}})$?

Output characteristics: Simulation *vs.* experiment



Optimal fitting of the experimental data is found for a

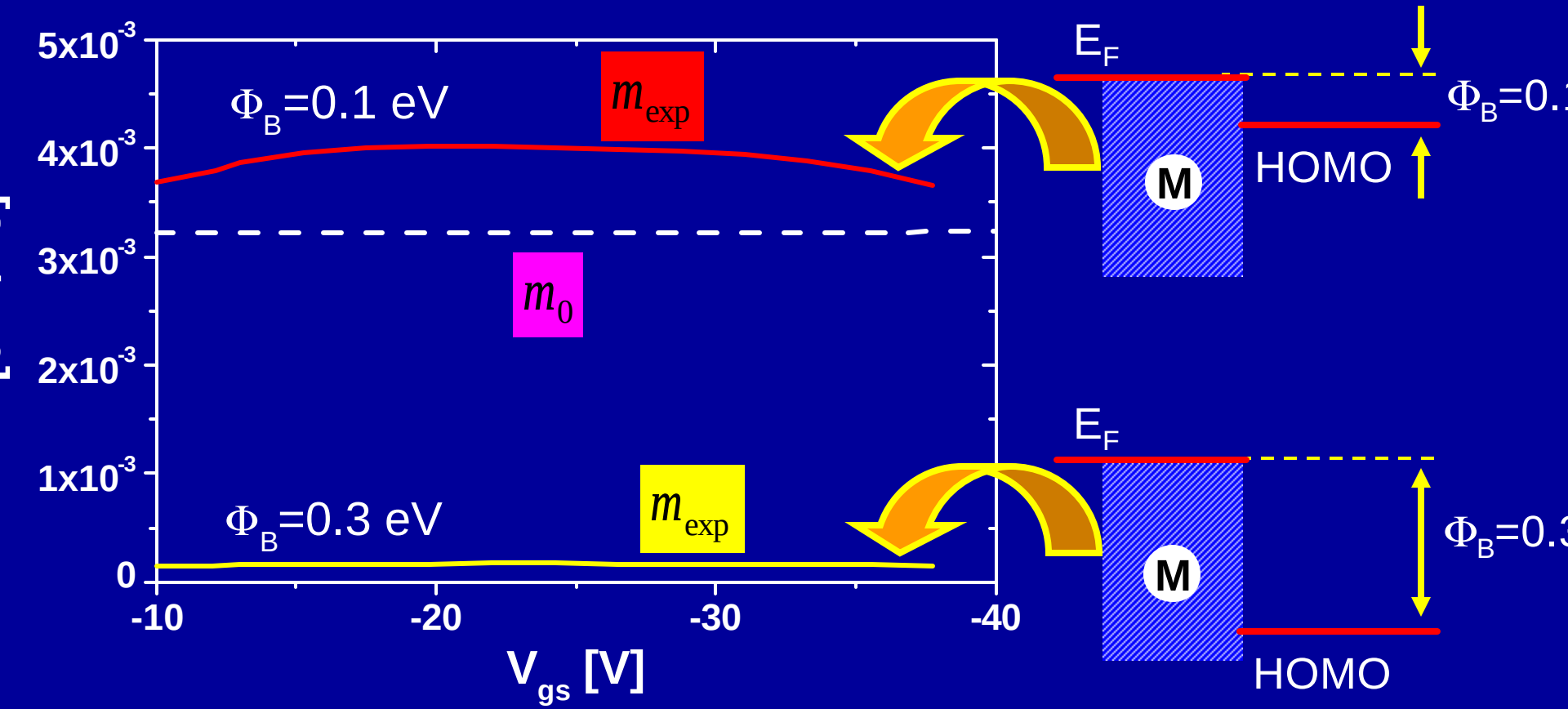
$$m = m_0 \exp\left(\sqrt{\frac{E}{E_0}}\right)$$

with

$$m_0 = 3.3 \cdot 10^{-3} \frac{\text{cm}^2}{\text{Vs}}$$

$$m_{\text{exp}} \neq m_0$$

Influence of contact barrier height

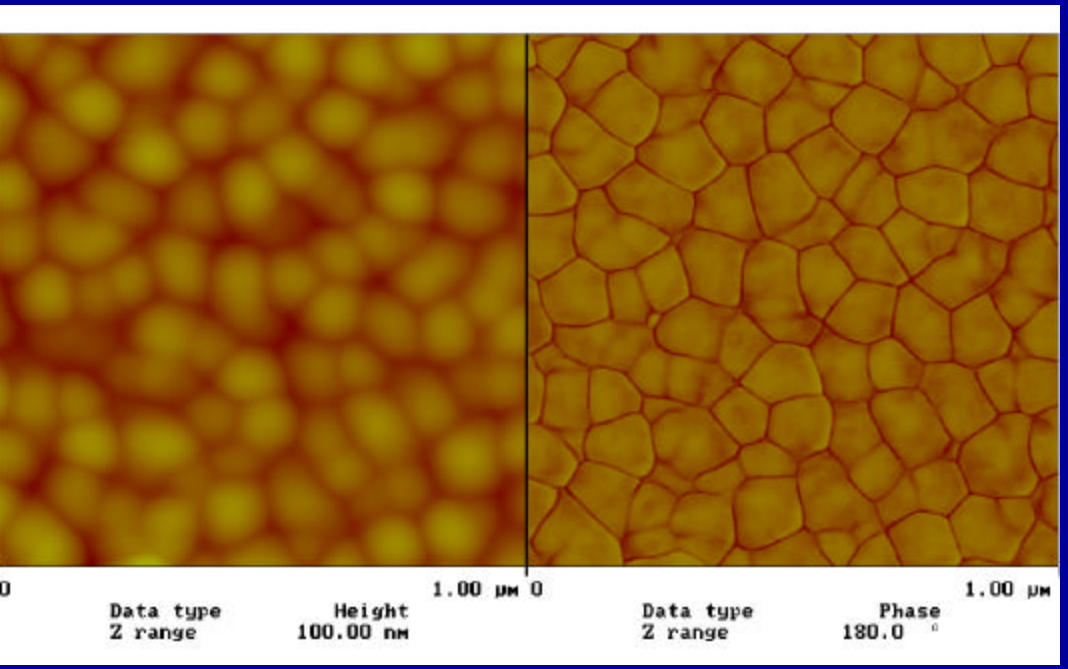


The results are obtained by extracting the mobility from simulation results performe
with the field dependent mobility model using different barrier height for the contact

Mobility extraction is strongly influenced by the barrier height.

A. Bolognesi et al, APL 81, 4646 (2002)

Grain Boundaries

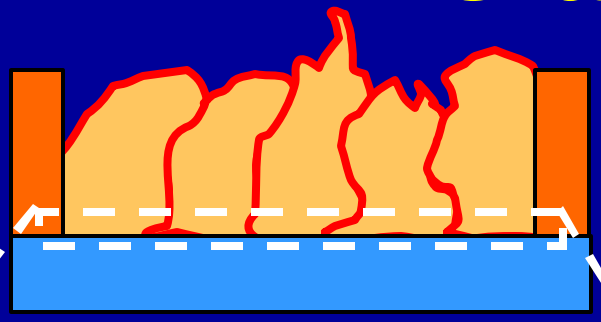


AFM picture of pentacene sample. The size of the grain is about 0.1 µm.

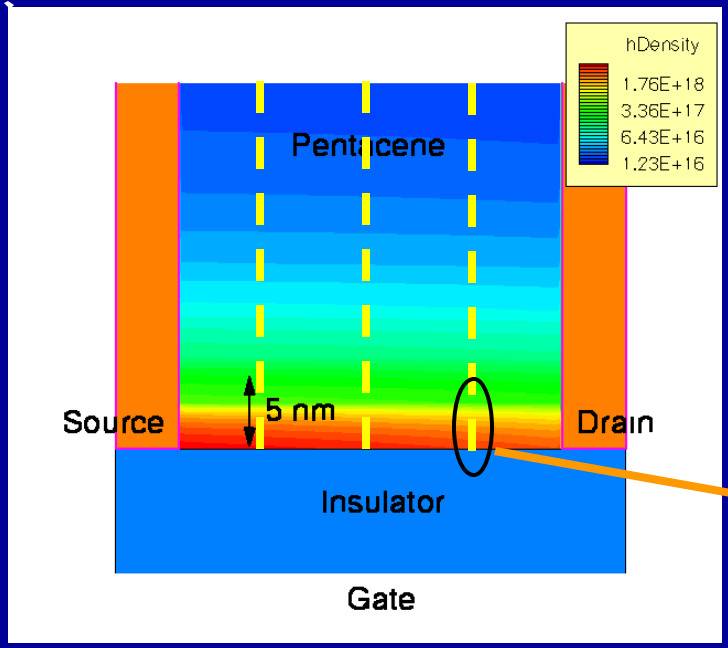
The concentration of charges trapped at grain boundaries depends on the density of the traps and the position of the Fermi level.

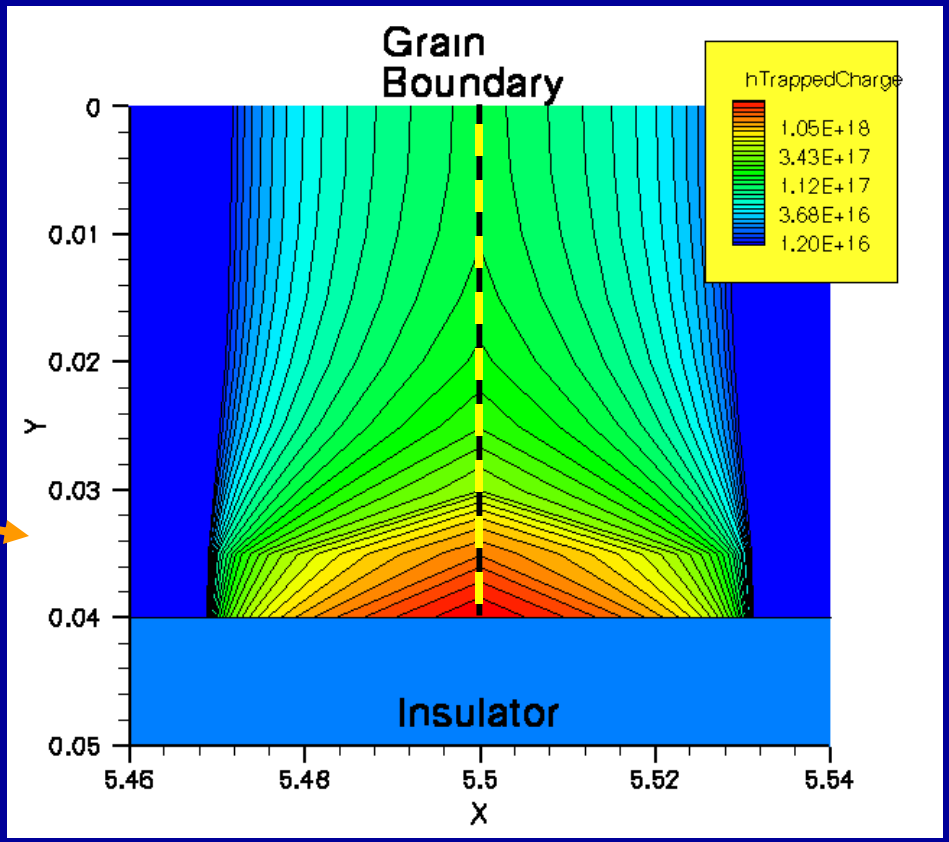
We use single trap level of surface density N_t=1x10^{13} cm^{-2} and energy E_t=0.3 eV

Grain Boundaries



Trapped charge density for Vgs=-20 V and Vds=-20 V



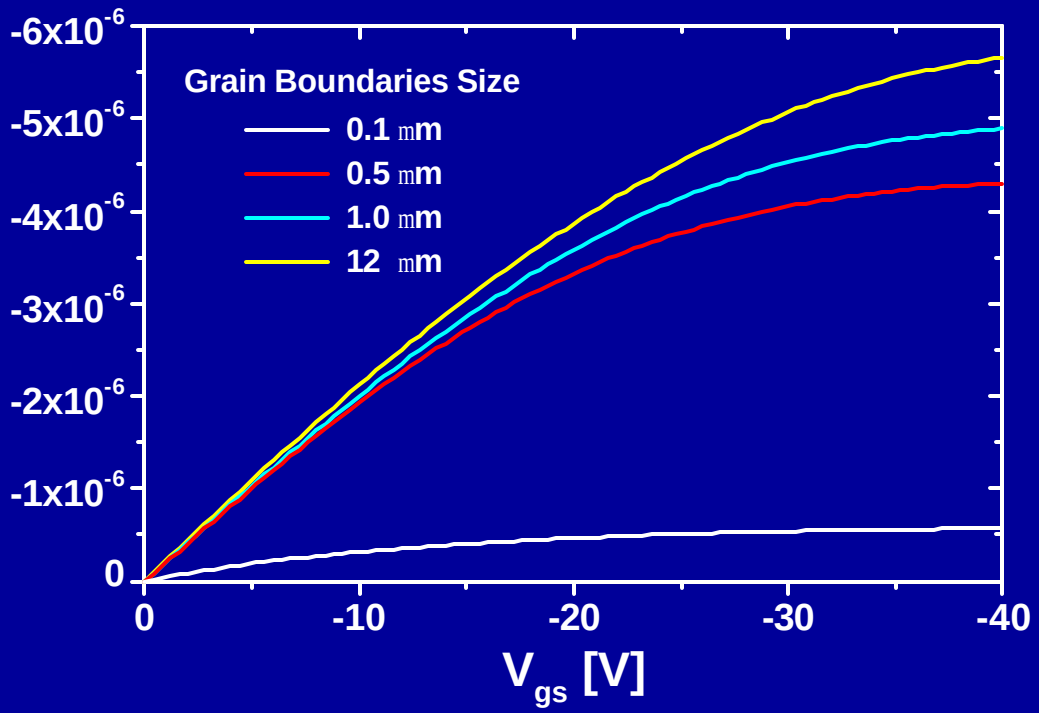


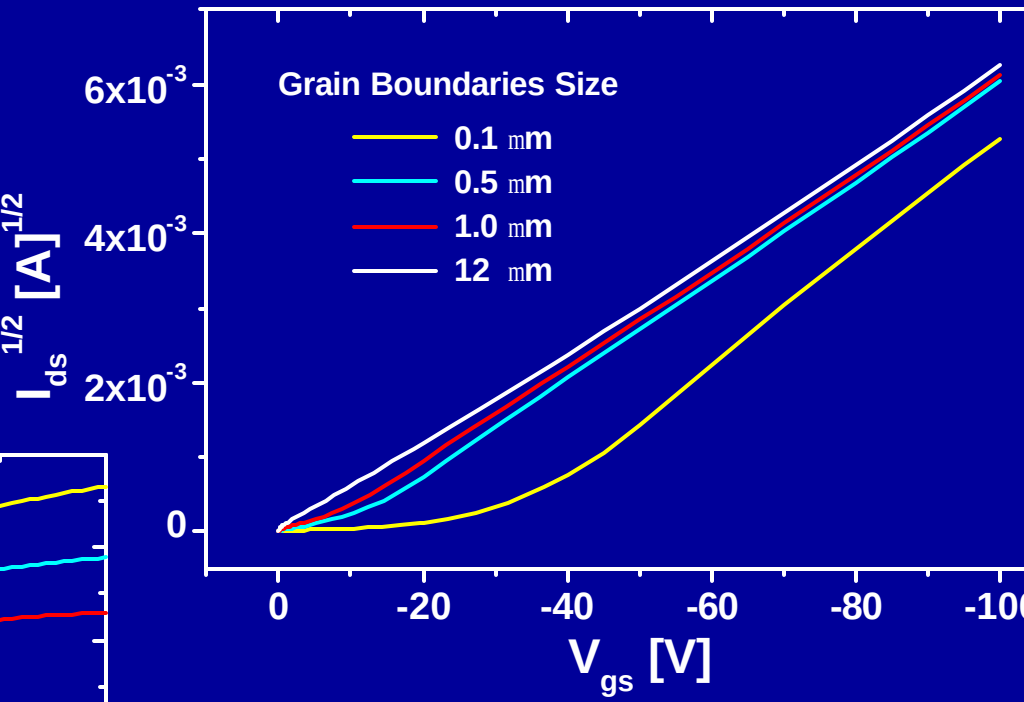
The thickness of conducting channel is lower than 5nm, Thus, it is possible to model the grain with regular shape.

A. Bolognesi et al., IEEE Trans. El. Dev, Dec. 2004 (in press)

Electrical characteristics

Output characteristics

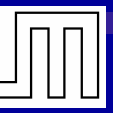




Trans-characteristics

Open problems and perspectives

- Find a reliable model for carrier mobility and contact injection mechanism
- Enhance the predictibility of the simulation tools
- Move to physically based circuit simulations



Mobility Model

Field-dependent mobility calculated from MC simulation

- cubic lattice of 170x170x20 hopping sites
- Energies of the sites chosen randomly from a Gaussian DOS
- Under the influence of external field the mean energy is given as

$$E(x) = E_0(x) - qFx$$

- Rate of hopping described by Miller-Abrahams expression

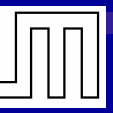
$$\Gamma_{i,j} = \nu_0 \exp(-2\gamma R_{ij}) \exp\left(-\frac{E_j - E_i + |E_j - E_i|}{2kT}\right)$$

- MC estimator for the mobility:

$$\mu = \left\langle \frac{L}{(\sum t_i) F} \right\rangle$$

from carrier lifetime t_i

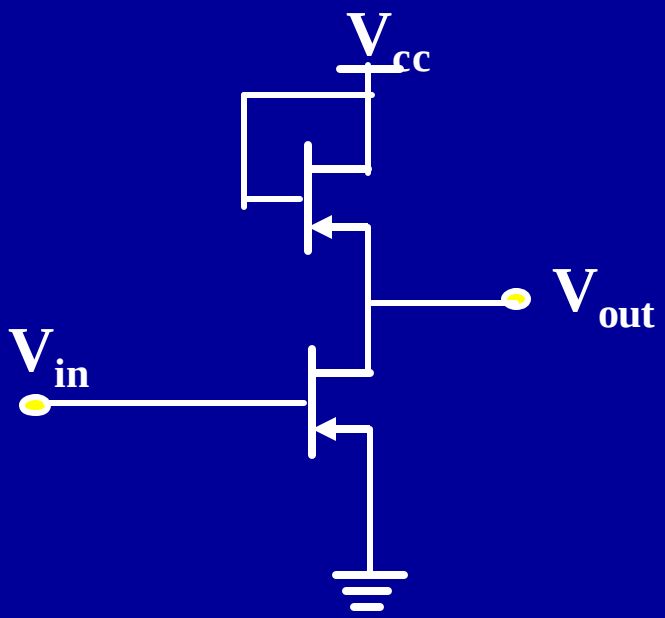
$$t_i = -\frac{\ln(u)}{\sum_j \Gamma_{ij}}$$

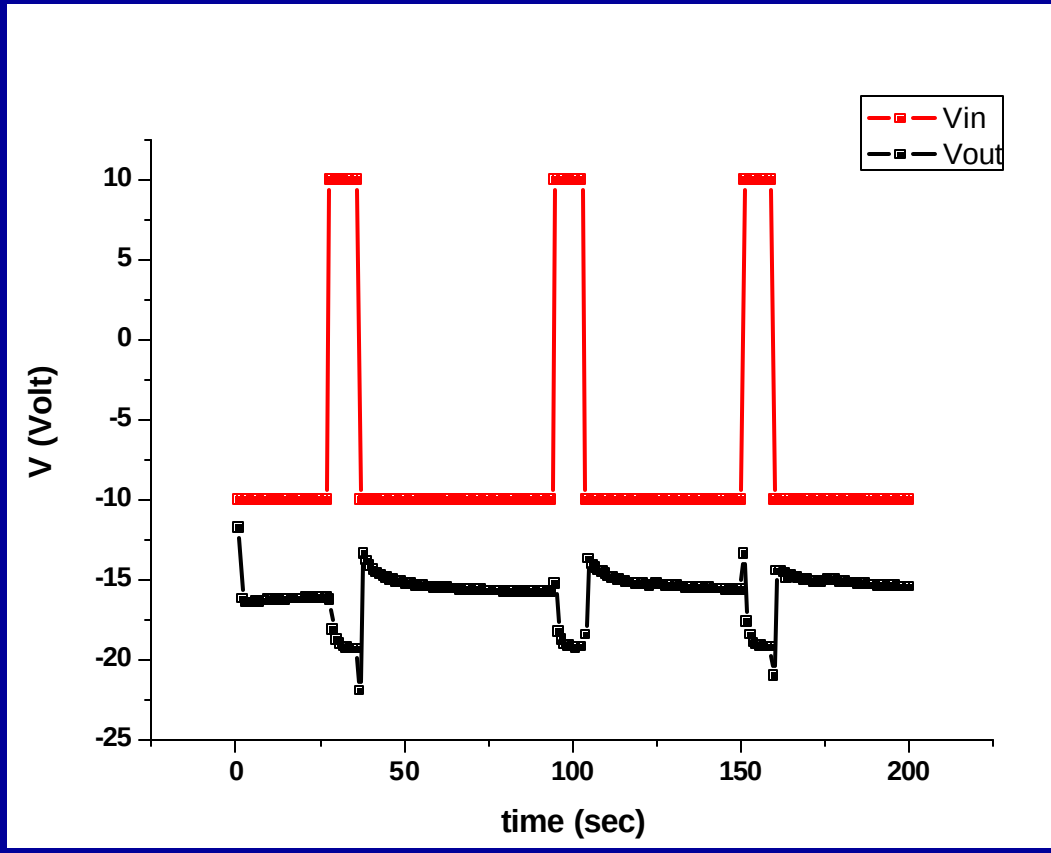


A. Bolognesi et al., Synthetic Metals 138, 95-100 (2003)

OTFT-based circuits

Inveters and ring oscillators can be simulated directly using the ISETCAD tool





Vin_{pp}: 20 V

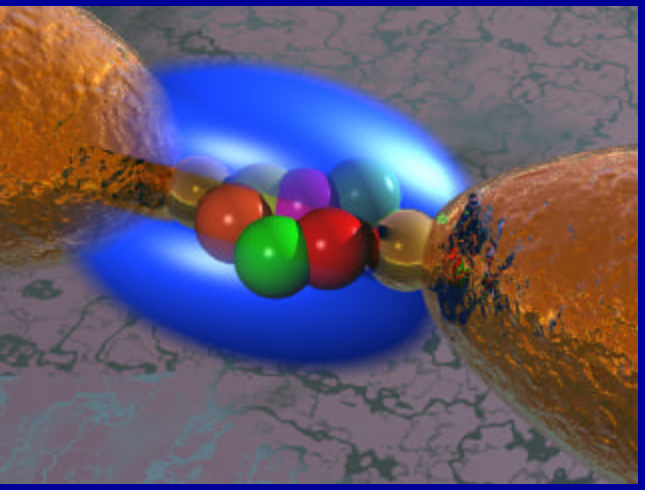
Vcc: -20V

Channel lenght: 20 μm

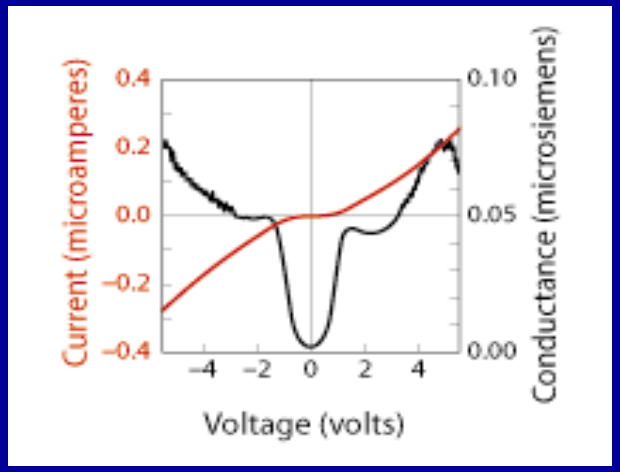
Pentacene

M. Berliocchi et al., Sem. Sci. Techn. 19, 354 (2004)

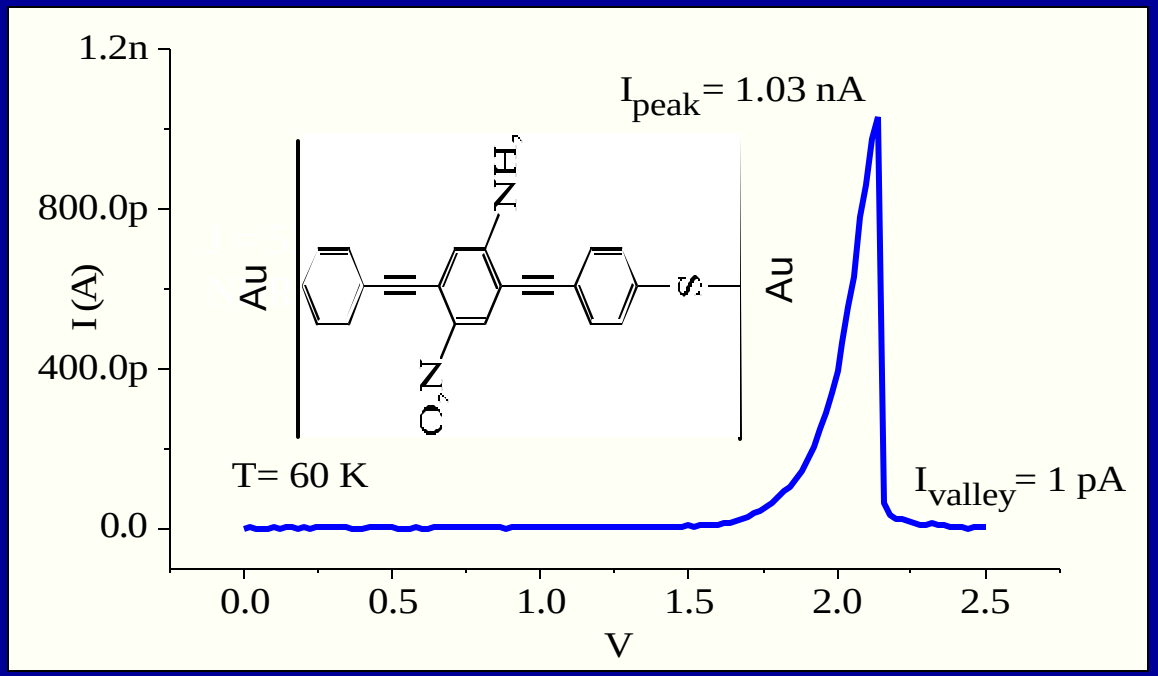
Molecular electronics



Single molecule can be conductive and display an electrical nonlinear response

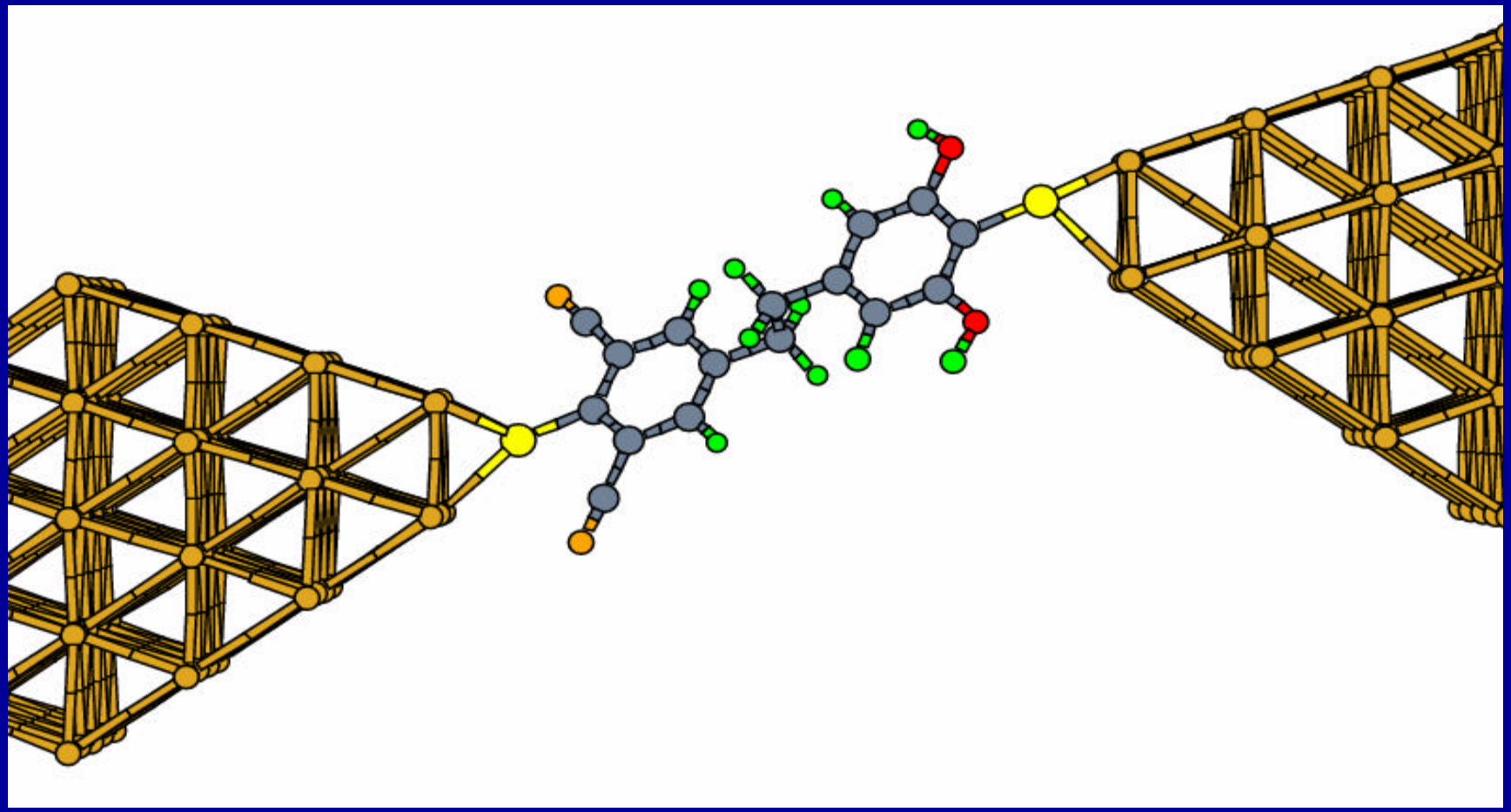


M. Reed et al, Scientific American 2002



J. Chen *et. al*, *Science* 286, 1550-1552 (1999)

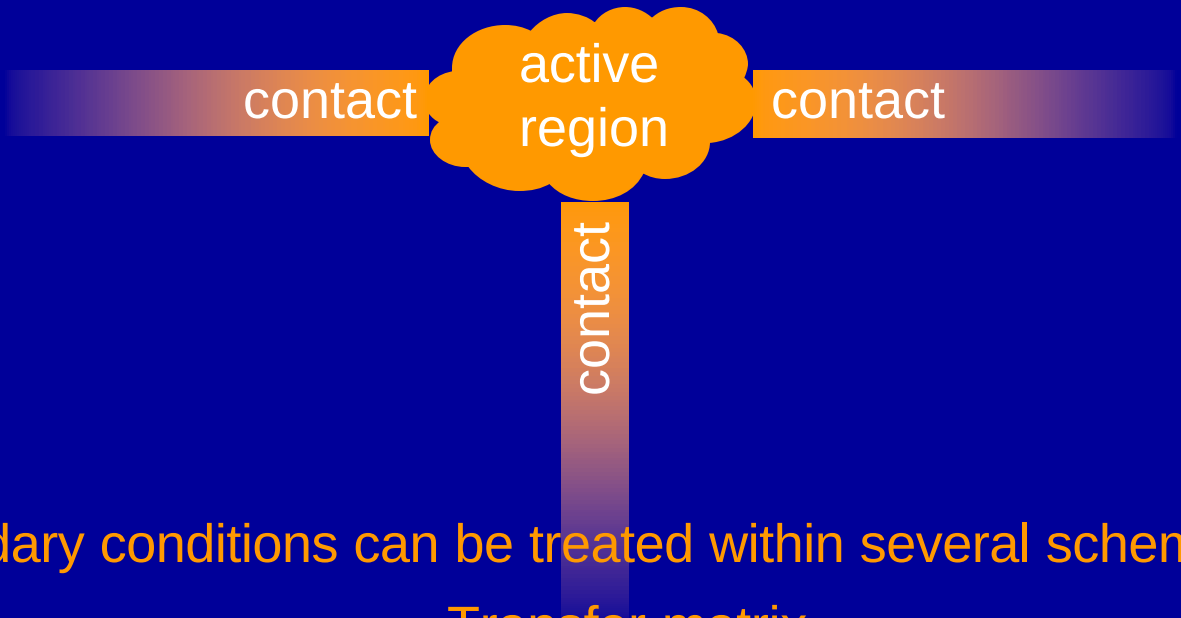
Molecular device



A physically-based method is needed that determines the electronic structure of the molecule and solves the transport problem

Transport problem

active region where symmetry is lost
+
contact regions (semi-infinite bulk)



Open-boundary conditions can be treated within several schemes:

- Transfer matrix
- LS scattering theory
- Green Functions ….

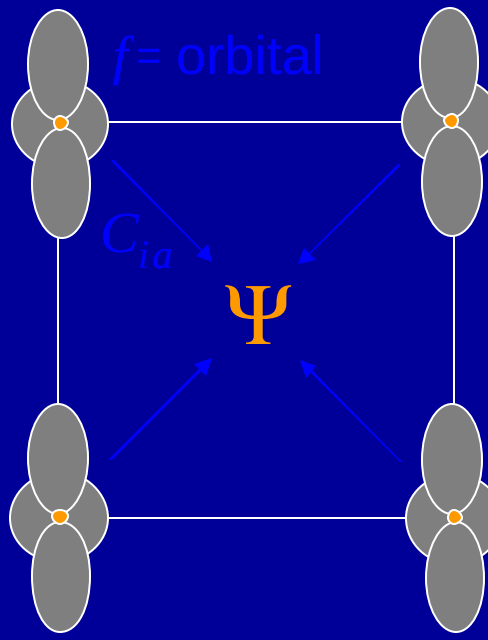
These schemes are well suited for localized orbital approach like TB

Atomistic approaches

We attempt to solve the one electron Hamiltonian in terms of a Linear Combination of Atomic Orbitals (LCAO)

$$\Psi_n(\mathbf{r}) = \sum_{\substack{\text{atomic} \\ \text{site, } i}} \sum_{\text{orbitals}, a} C_{ia}\, f_{ia}(\mathbf{r} + \mathbf{R}_i)$$

$$\sum_{\substack{\text{atomic} \\ \text{site, j}}} \sum_{\text{orbitals}, b} \left[H_{ia,jb} - ES_{ia,jb} \right] C_{jb} = 0$$



$$H_{ia,jb} = \langle f_{ia} | H | f_{jb} \rangle \qquad S_{ia,jb} = \langle f_{ia} | f_{jb} \rangle$$

The approach can be implemented “ab-initio” where the orbitals are the basis functions and $H_{ia,jb}$ is evaluated numerically

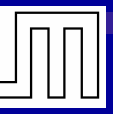
Toward ”ab-initio” approaches: Density Functional Tight-Binding

Many DFT codes exist based on localized basis sets:
SIESTA (Soler etc.), FIREBALL (Sankey), DMOL (Delley)

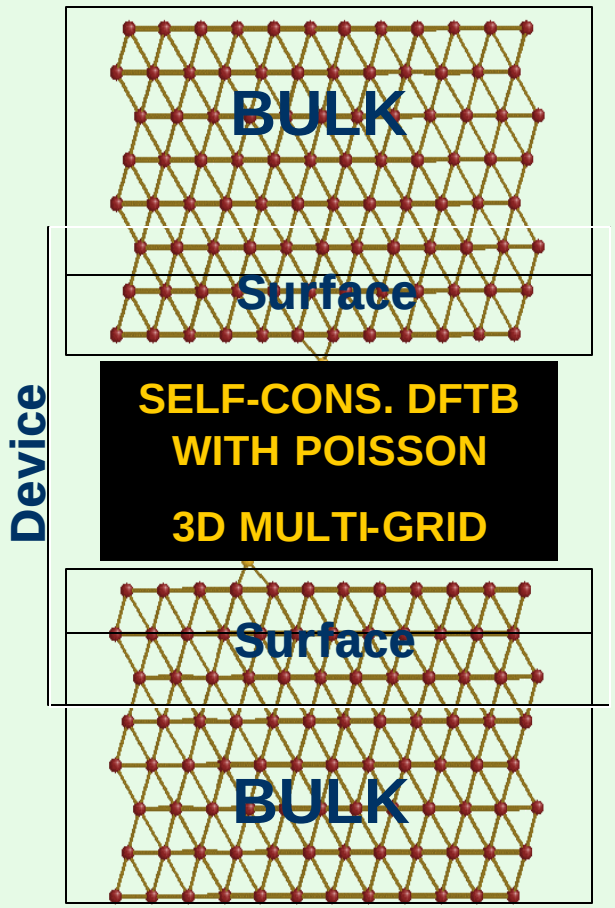
The DFTB approach [Elstner, et al. Phys. Rev. B 58 (1998) 7260] provides transferable and accurate interaction potentials. The numerical efficiency of the method allows for molecular dynamics simulations in large super cells, containing several thousand of atoms.

- DFTB is fully scalable (from empirical to DFT)
- DFTB allows also for TD-DFT simulations

We have extended the DFTB to account for transport in organic/inorganic nanostructures by using **Non Equilibrium Green Function approach** self-consistently coupled with Poisson equation



Self-consistent quantum transport



Self-consistent loop:

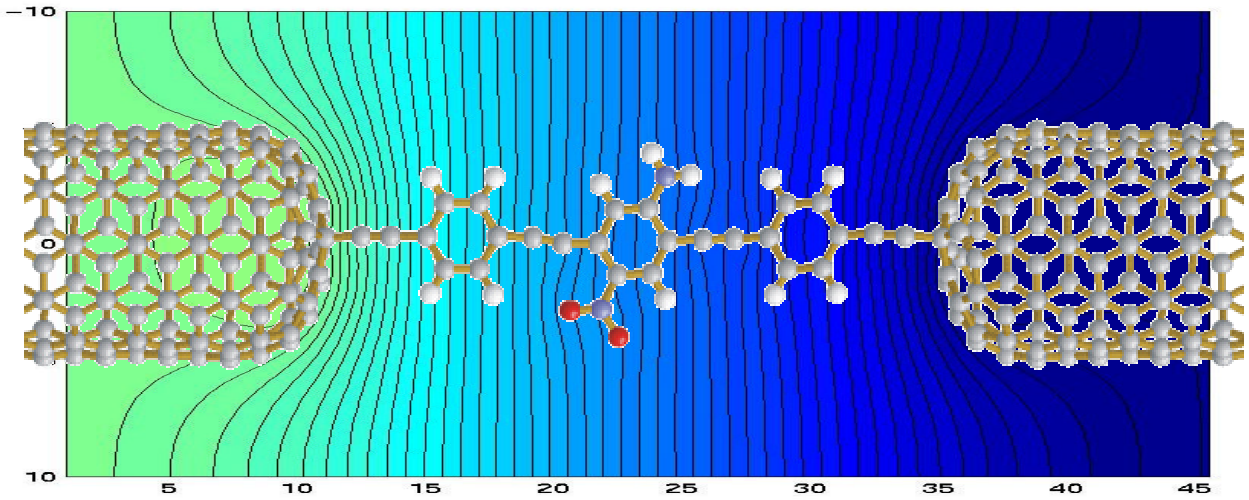
$$dn \rightarrow \nabla^2 dV_H = -4\pi dn$$
$$\rightarrow dH \rightarrow dG^n \rightarrow dn'$$

Current computation:

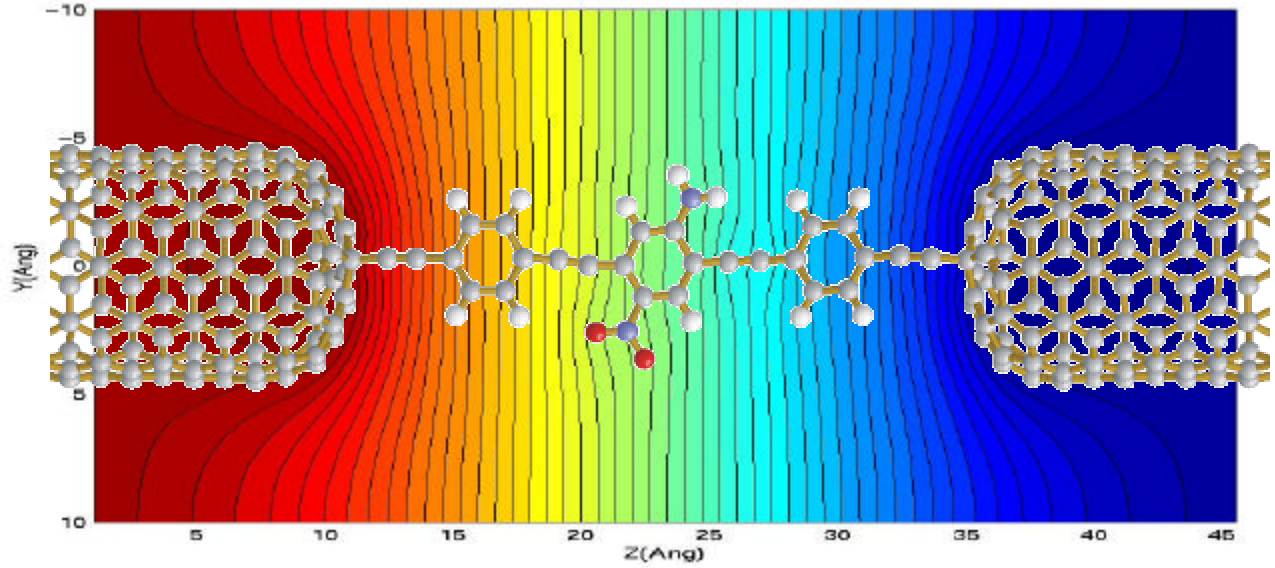
$$T = tr\left(\Gamma_L G_D^r \Gamma_R G_D^a\right)$$

$$i(E) = \frac{2e}{h}\int T(E)[f_L(E) - f_R(E)]dE$$

Self-consistent charge in a molecular wire



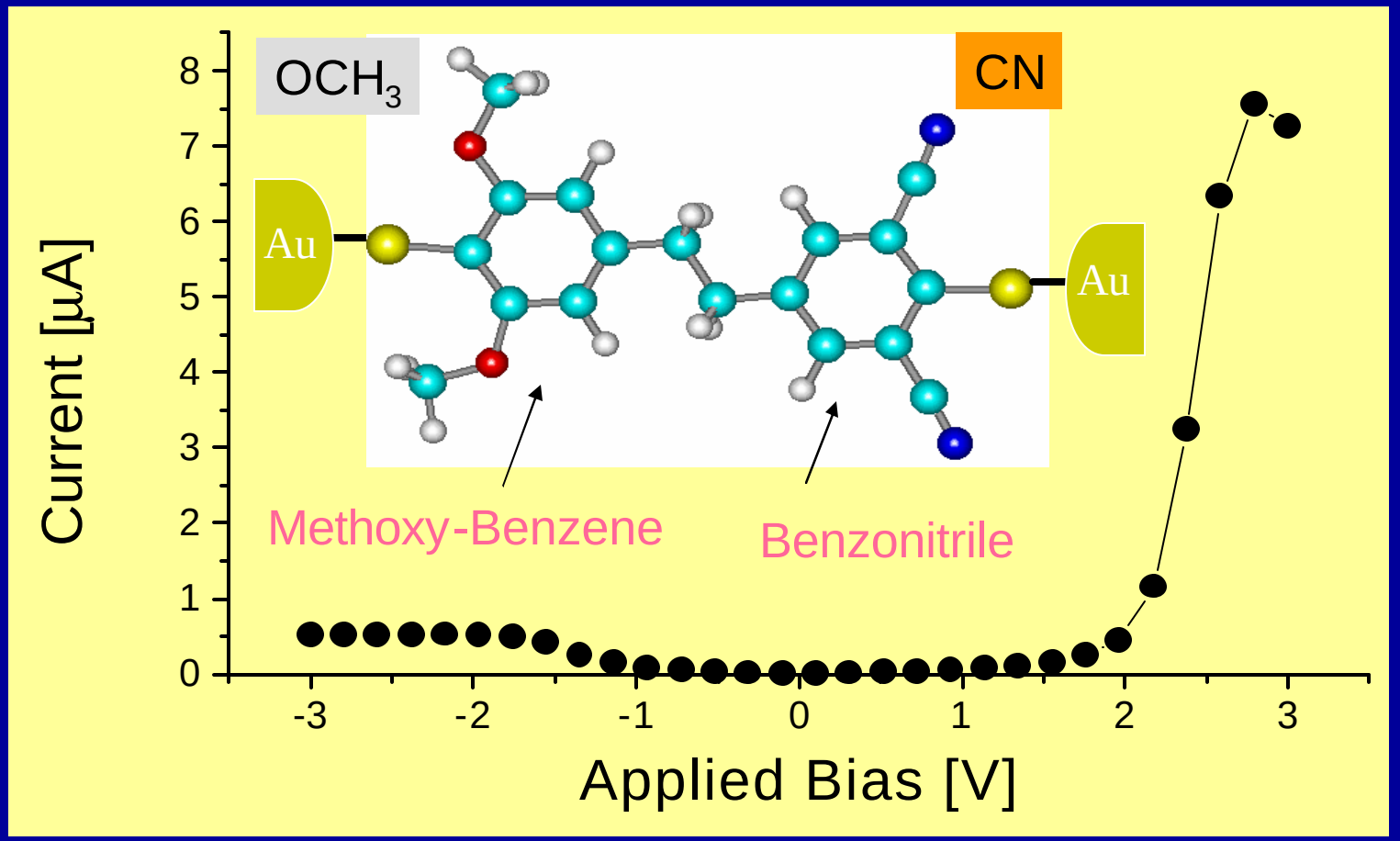
0.5 V



1.0 V

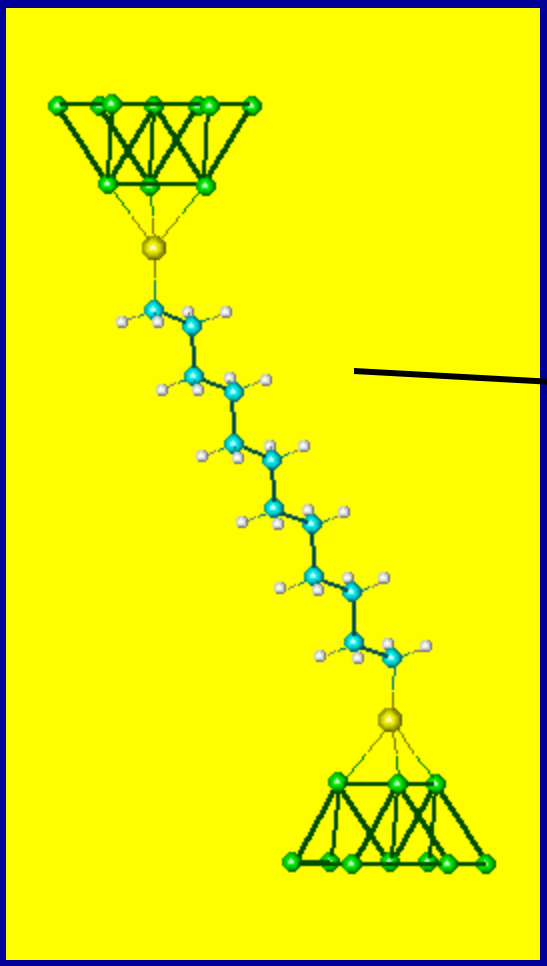
Simulation of molecular devices

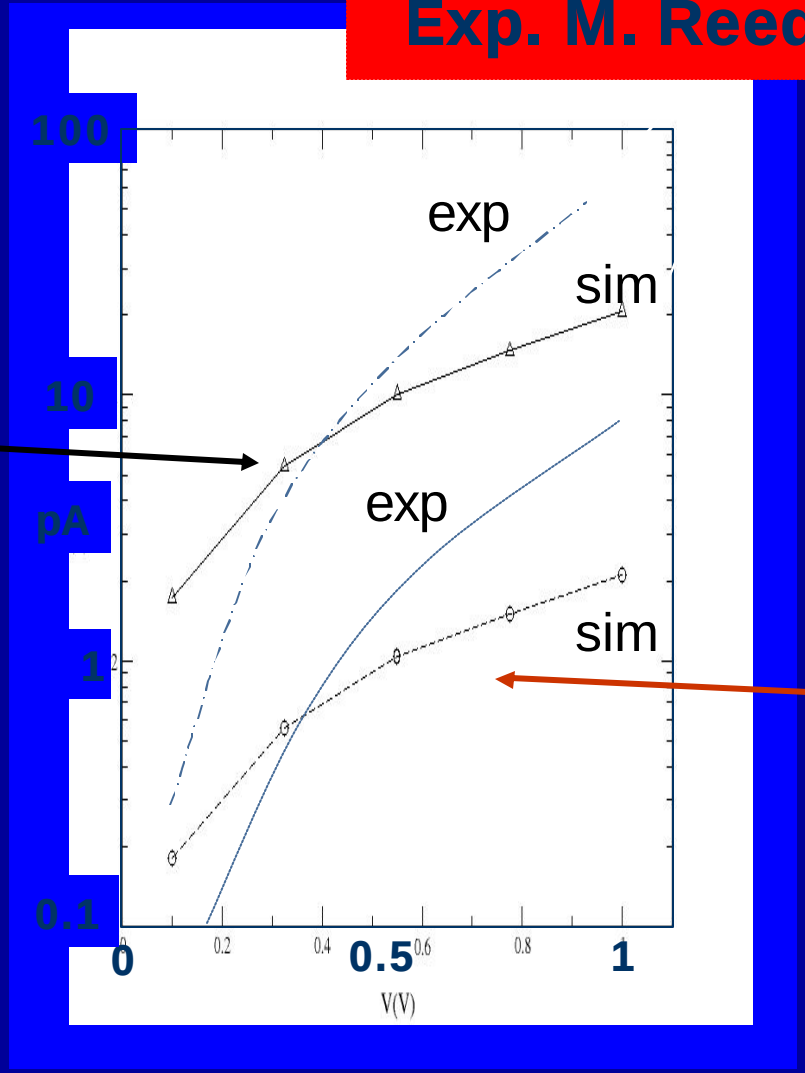
New physically-based simulations are needed that accounts for the electronic structure of the molecule => Approach: Non equilibrium Green Function (based on a Density Functional Tight Binding method) calculation selfconsistently coupled to a 3D Poisson solver

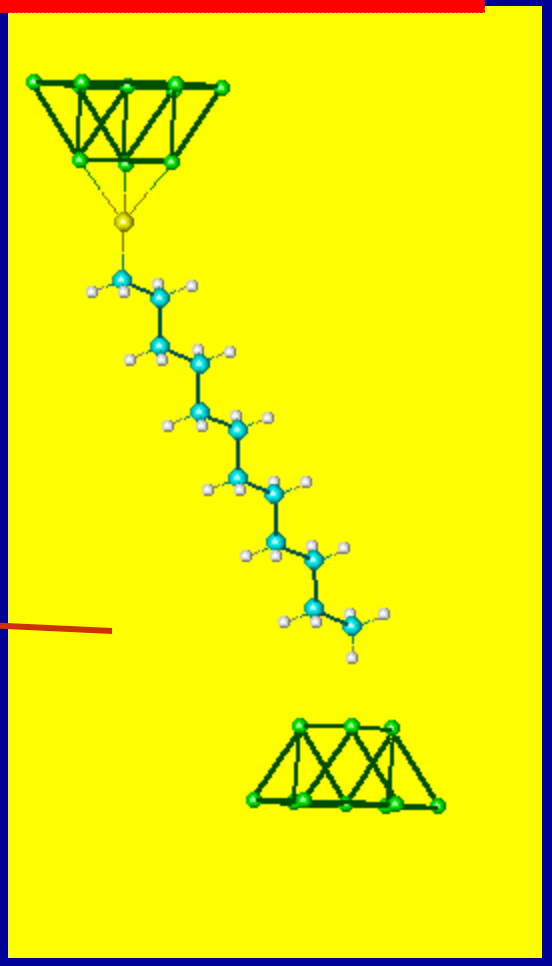


Tunneling currents in alkeno-thiols

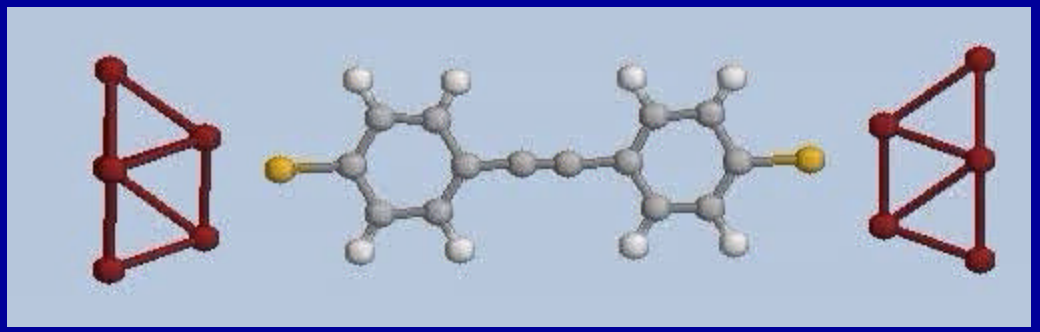
Exp. M. Reed et al. (2003)







The role of molecular vibrations



T= 300 K

An organic molecule is a rather “floppy” entity

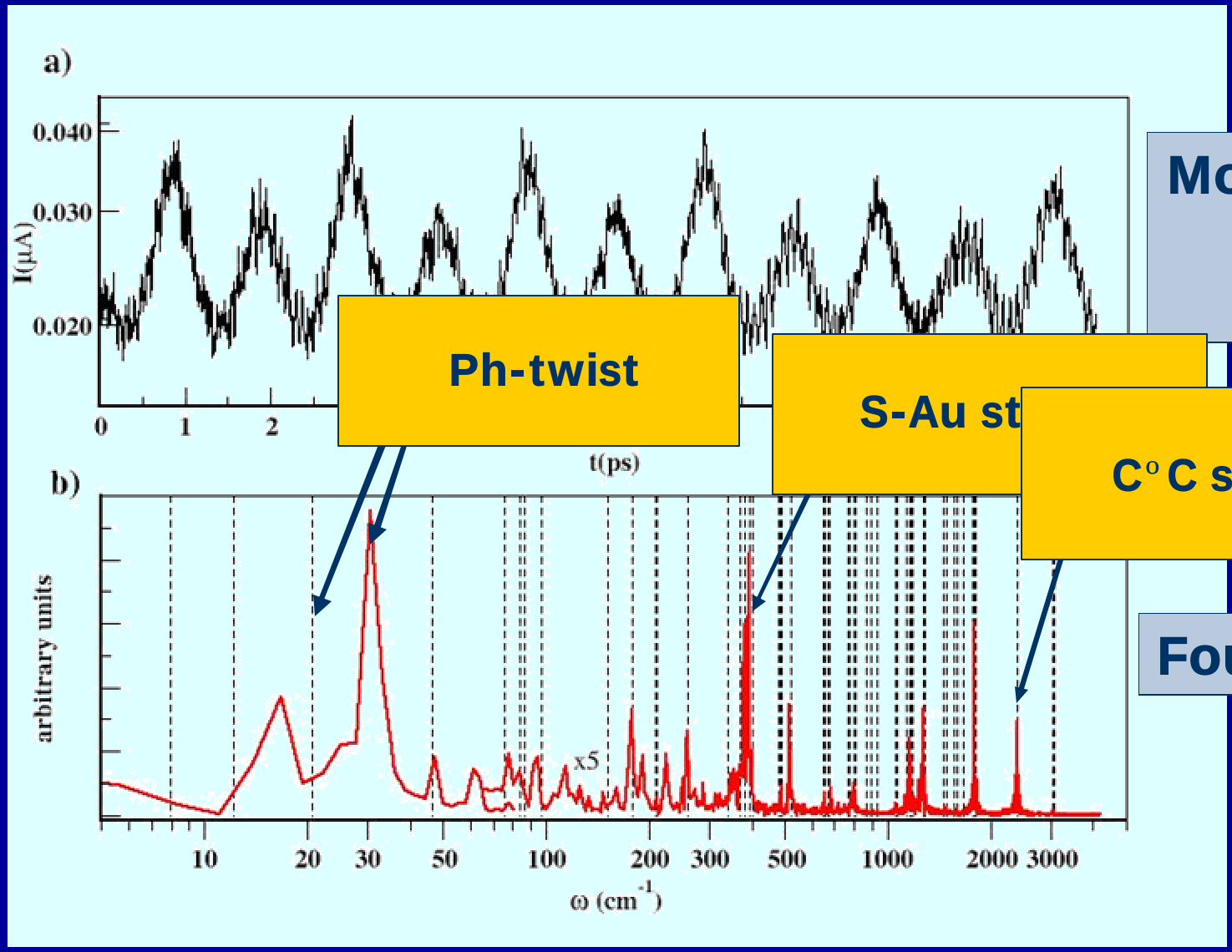
Electron-phonon interactions are a difficult issue

Can we still use the phonon approximation ?

Two approaches:

- **Time-average of the current computed at every step of a MD simulation**
- **Ensemble average of over the lattice fluctuations.**

Frequency analysis



Ph-twist

S-Au st

C° C stretch

Mol. Dynamic

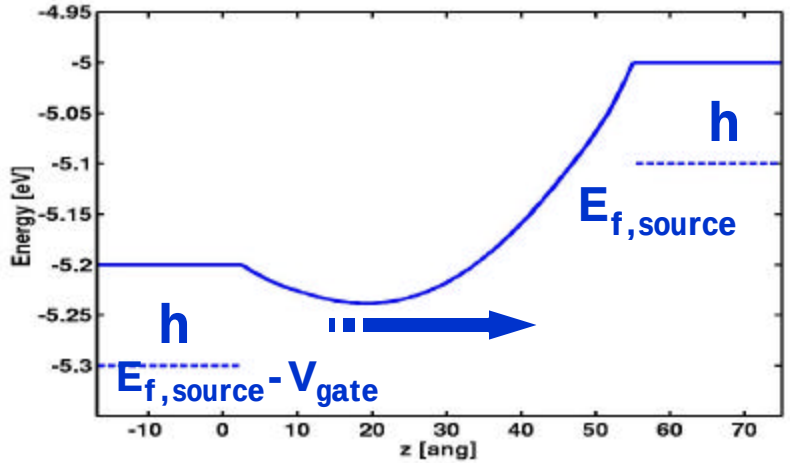
T=10 K

Fourier Trans

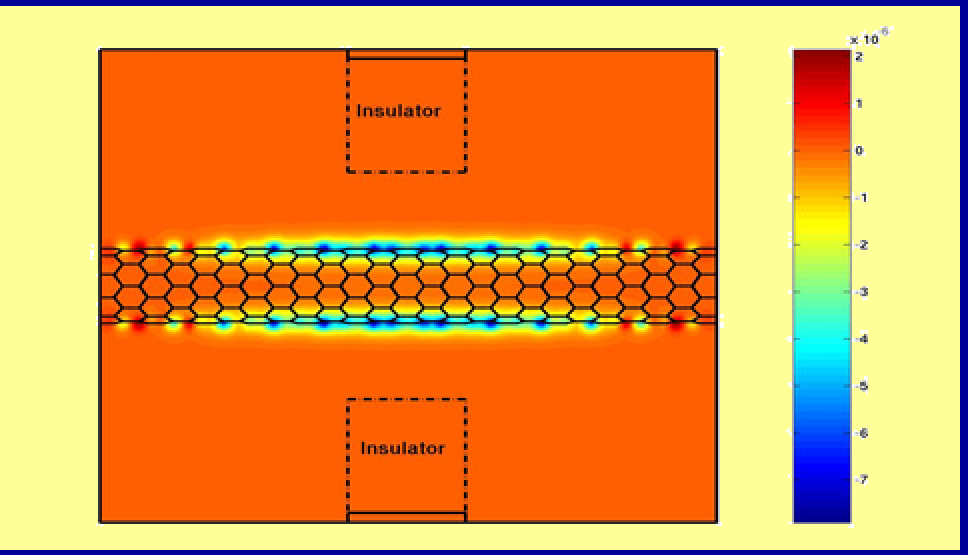
A. Pecchia et al. Phys. Rev. B. 68, 235321 (2003)

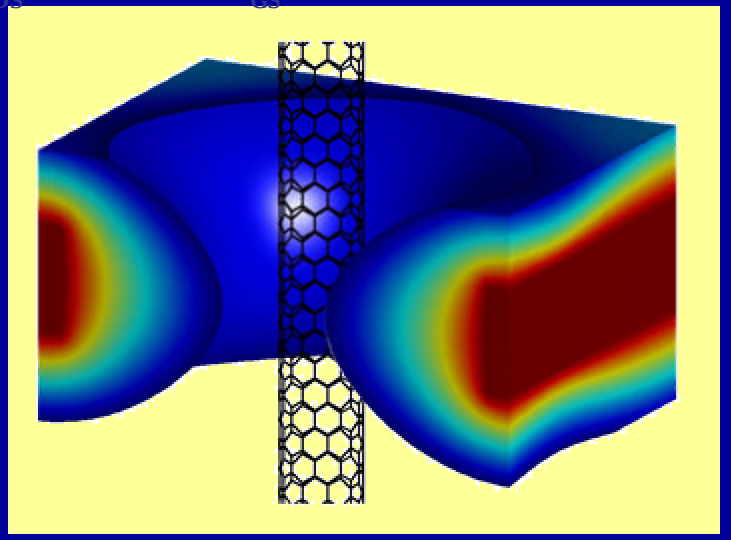
Simulation of CNT-Transistors

The CNTs behave like ideal p-type nanowires. The gate voltage modulates the transmission of the holes which are injected from the source contact.



Das Energie-Profil des Valenz-Subbandes einer (10,0) C
für V_{DS} = 0.2 V und V_{GS} = 0.6 V.

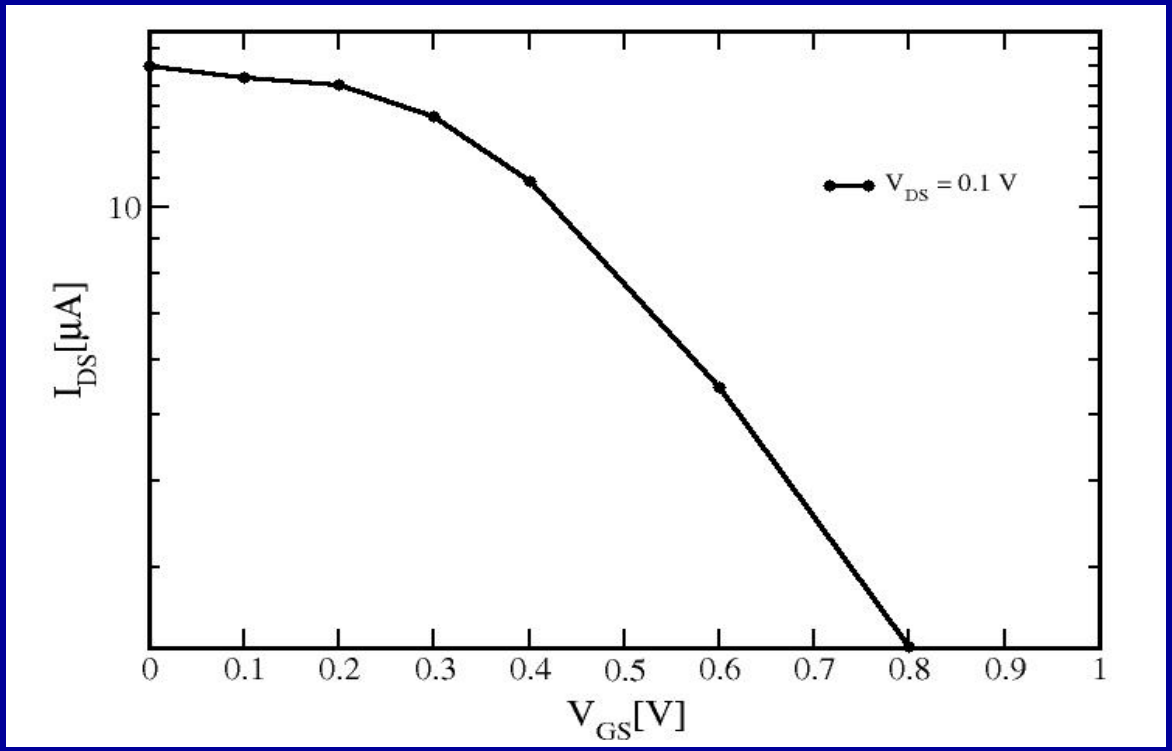




Current in CNT-Transistors

Landauer Formalism is used to calculate the current between souce and drain

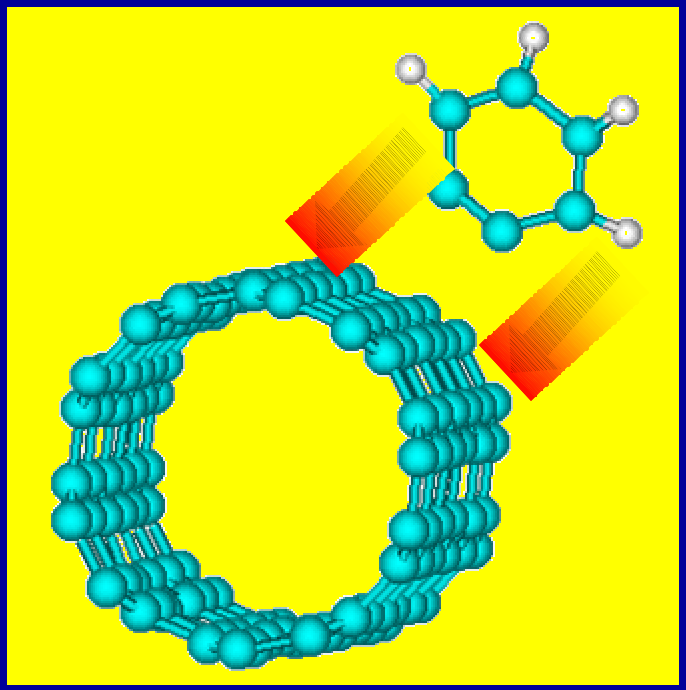
$$I = \frac{2e}{h}\int \overline{T}(E)\left[f_1^{+}(E) - f_2^{-}(E)\right]dE$$

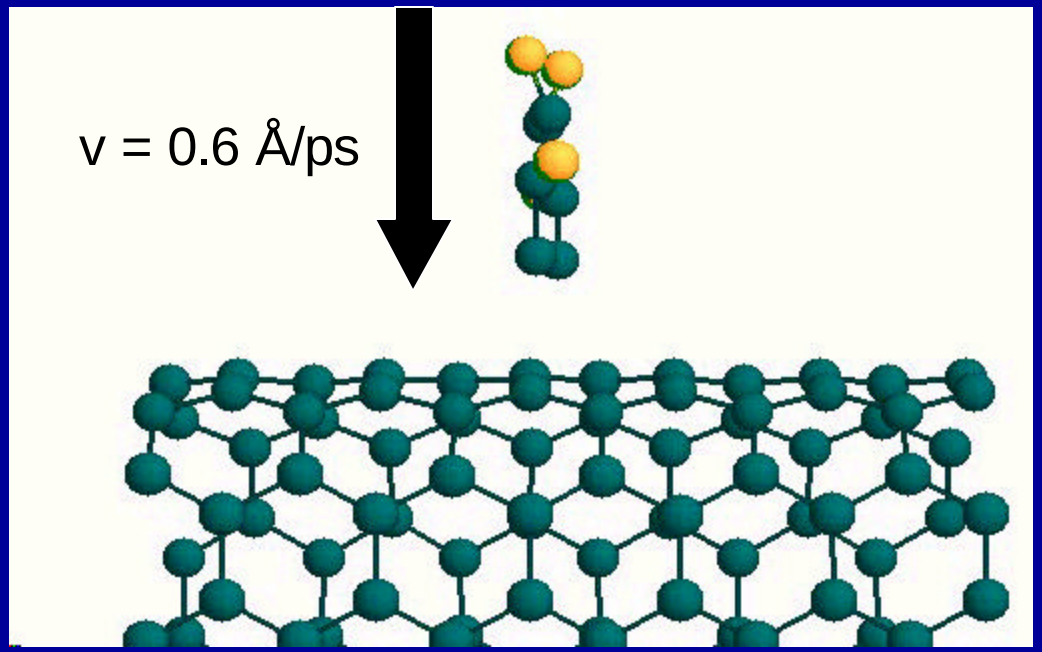


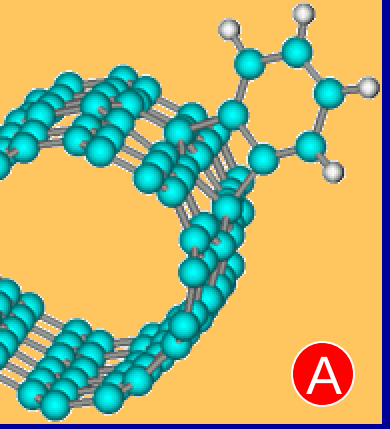
Transport in Carbon Nanotube Green + MD

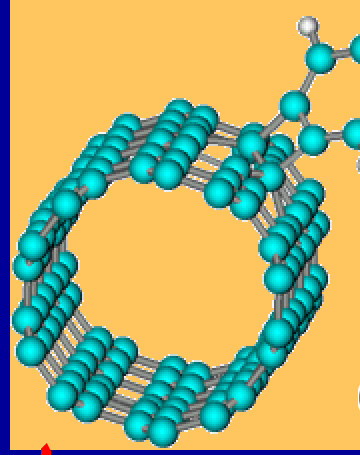
We have performed Molecular Dynamics simulations of a reactive collision of a biased nanotube (V=100mV) and benzyne and we have calculated the current flowing in the nanotube at each MD step

[Following the NASA MD simulations (J. Han, A. Globus, R. Jaffe, G. Deardorff)]









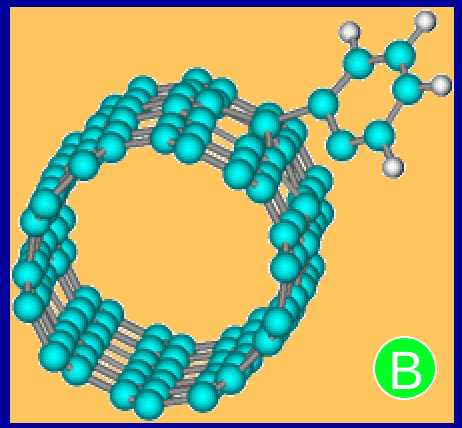
CNT without C_6H_4

$\Delta I = 20\%$

Current [m A]

12
11
10
9
8
7
6
5

A
B
C



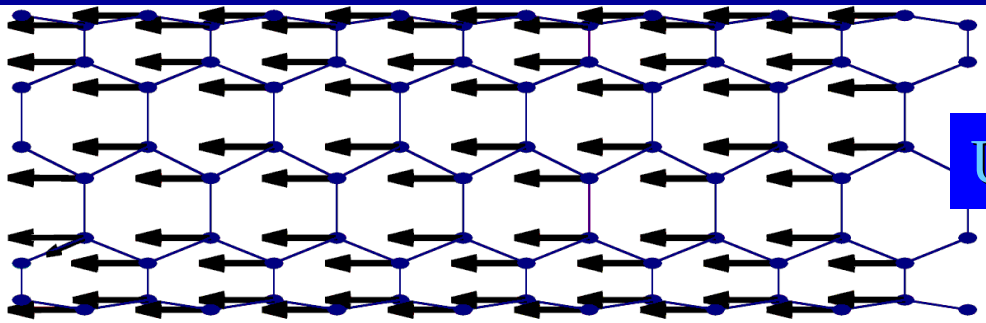
0.0 0.2 0.4 0.6 0.8 1.

Time [ps]

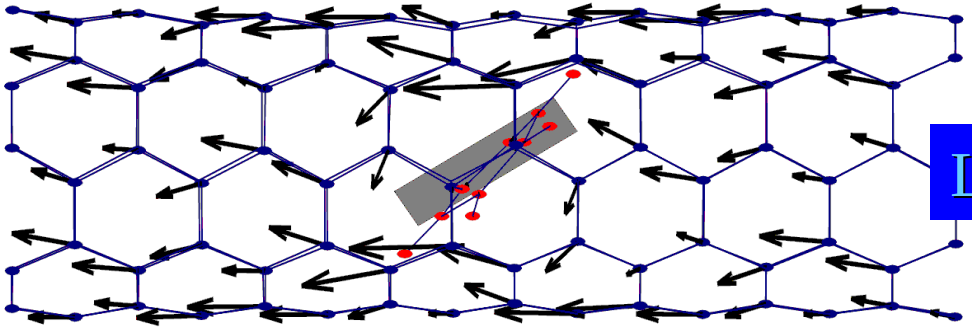
$R_{CN-C6H4}$ = 10KΩ

R_{CN} = 8 KΩ

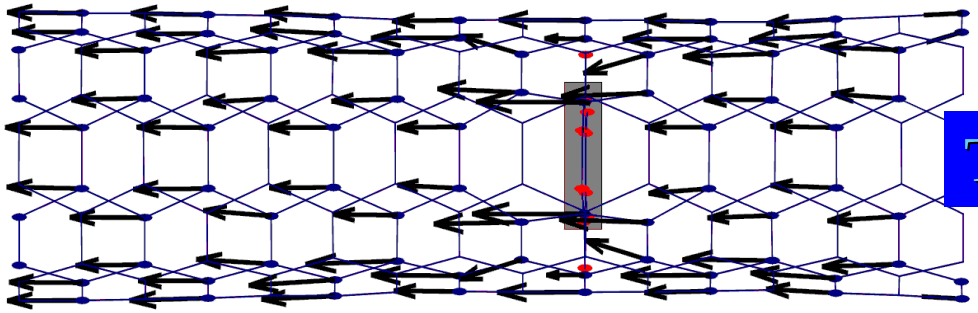
Current Flux in CNT (5,5)



Unperturbed Nanotube



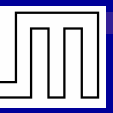
Longitudinal Molecule



Transverse Molecule

Open problems

- the theoretical treatment of excited states in molecular system;
- the interaction with phonons and in general the dissipative part of transport;
- the description of the contact and the molecule-contact interface;
- the integration of models properly accounting for excited states, dissipation and contacts in a simulator
- the identification of optimal circuits and architectures for molecular devices
- the availability and reliability of experimental results

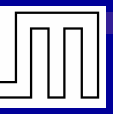


Architectures

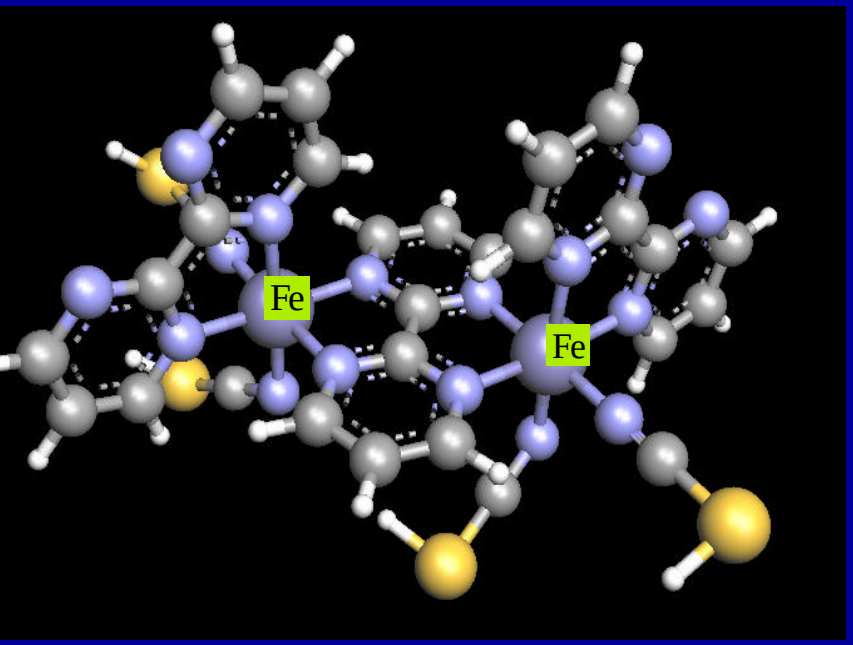
Single molecule devices require not only novel simulation tools, but also novel architectures that can exploit the interaction between molecules and the high parallelism intrinsic in the molecular systems

Some suggestions:

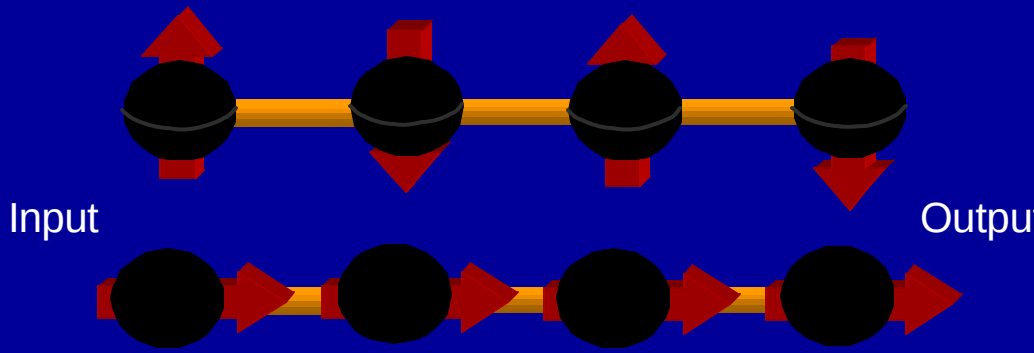
- Molecular Logic gates (J. Tour, MITRE Corp.)
- Crossbar memory (HP, STMicroelectronics)
- Quantum Cellular Automata (Notre Dame)



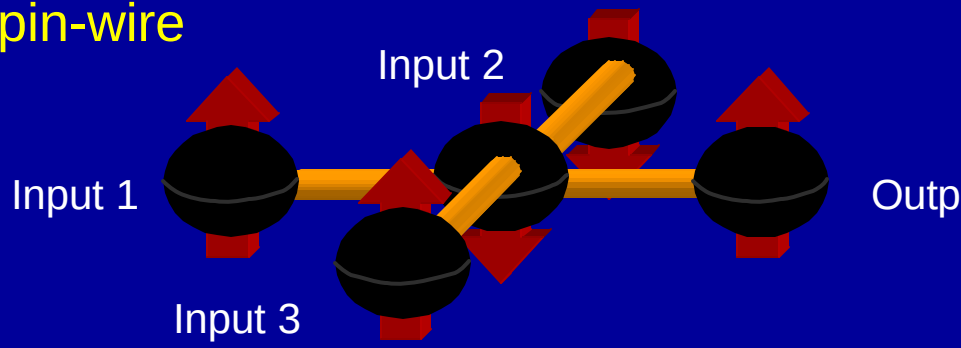
Field-Coupling by Molecular Magnets



$[Fe(bpym)(NCS)]_2bpym$



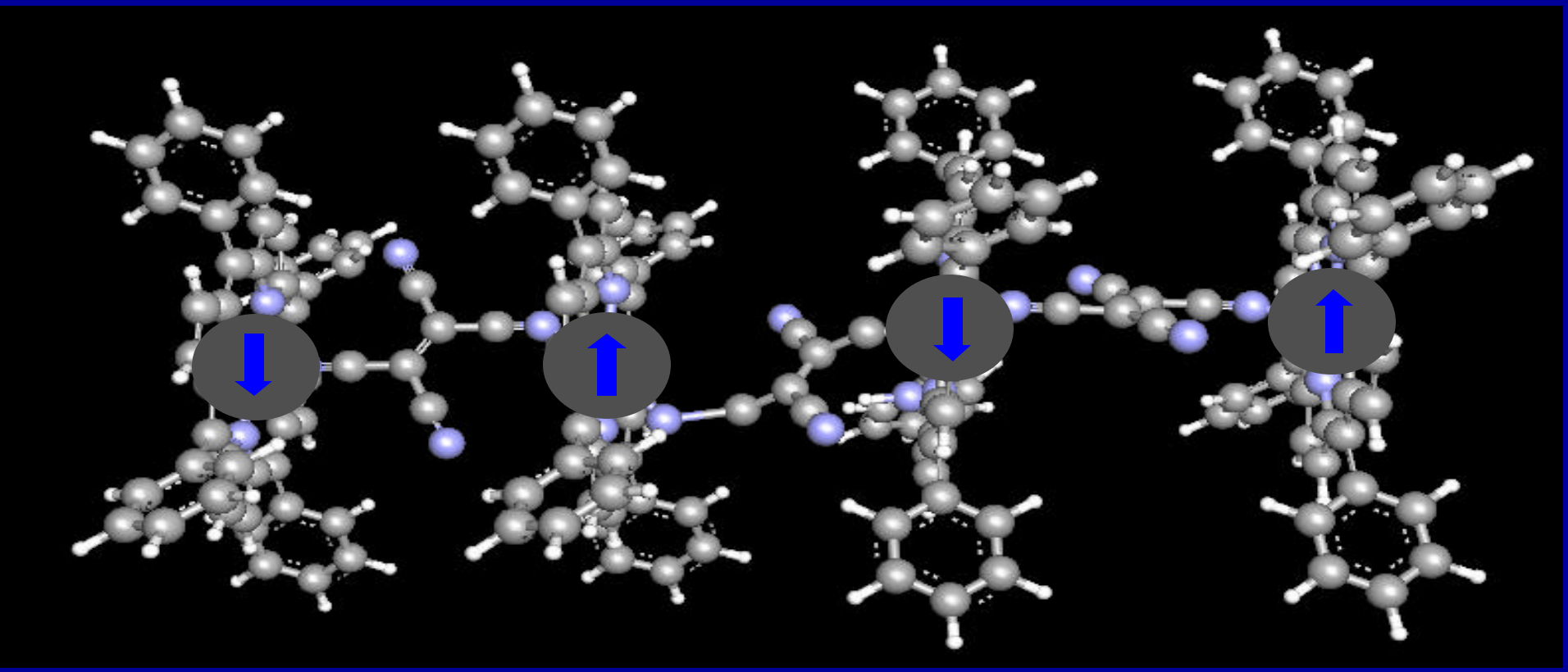
Spin-wire



Spin-majority gate

In molecular magnets, exchange interaction between metal ions is mediated by organic ligands. Certain arrangements could make QCA-like logic gates.

A 1D Molecular Magnet Chain



Manganese ions in a [MnIII(Porphyrin)][TCNE] chain might play the role of lithographycally fabricated nanoscale magnets. This would yield to a molecular-scale computing device.

Conclusions

- The simulation of molecular structures has progressed greatly in the last few years
- Future advances require an even stronger integration of quantum chemistry and transport codes
- As reliable experiments will become available, validation of the models will be possible;
- Circuit design will be performed with the same codes used to analyzed molecular nanostructures