Atomistic simulations of electronic transport in organic nanostructures

(Role of incoherent transport in molecular wires)

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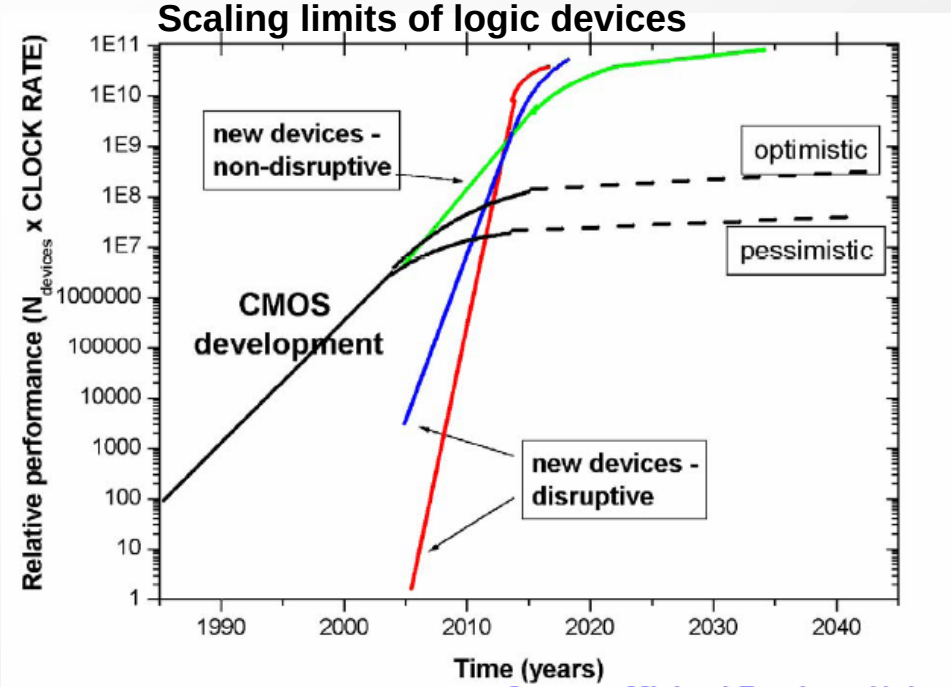
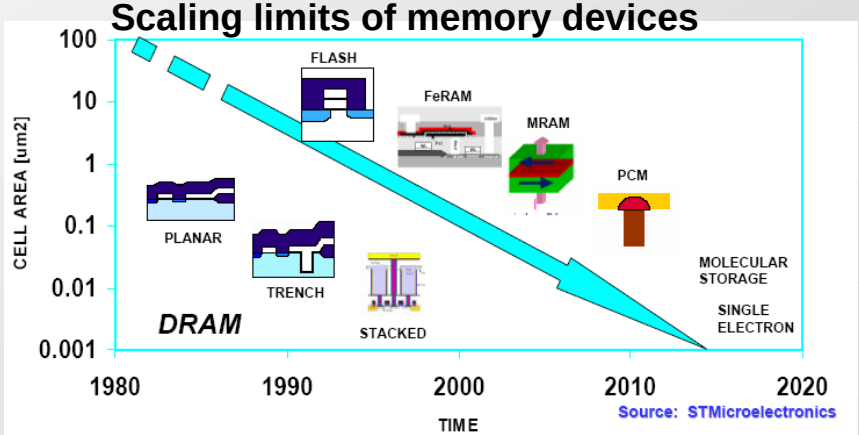
Why Organics ?





Versatile

Easy to produce

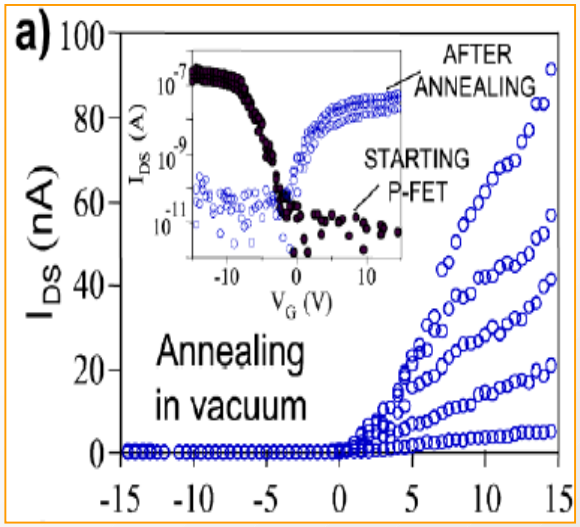
Easy to interface with the bio-world

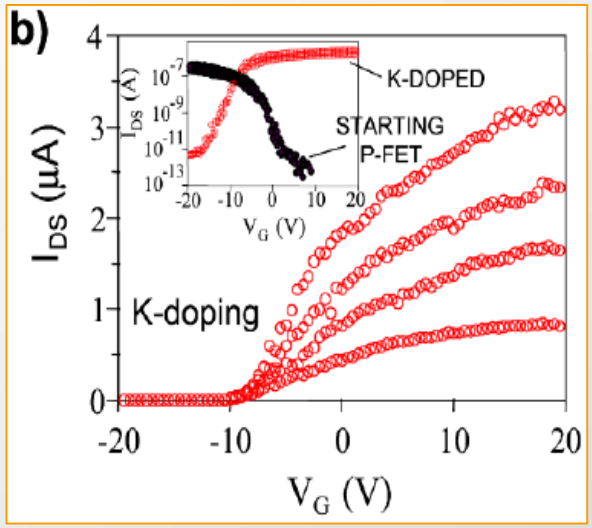
Building blocks for complex structures

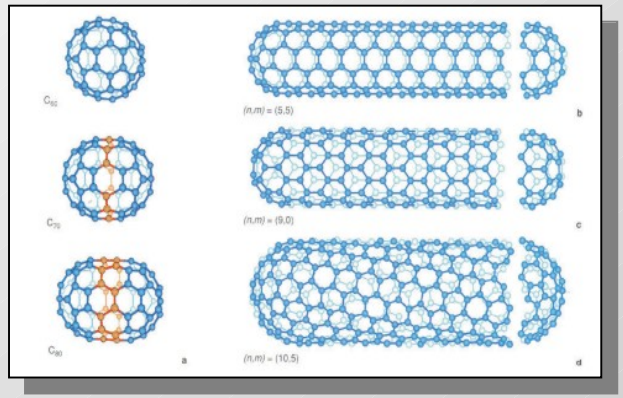
Organics for:

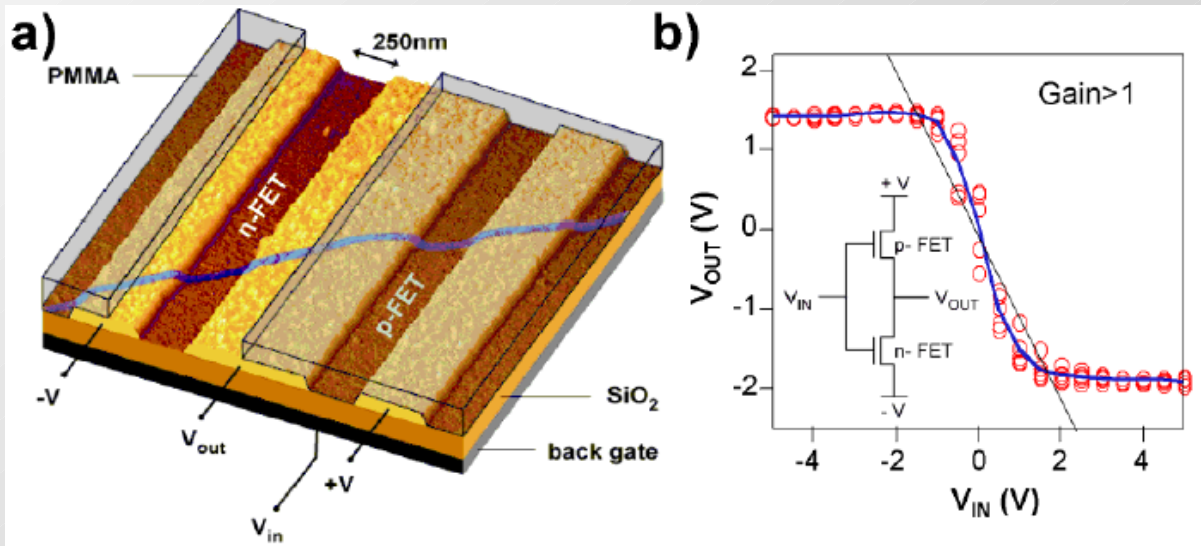
- Transistors
- Sensor
- Memories
- Field emission devices
- Mechanical components

Carbon Nanotubes

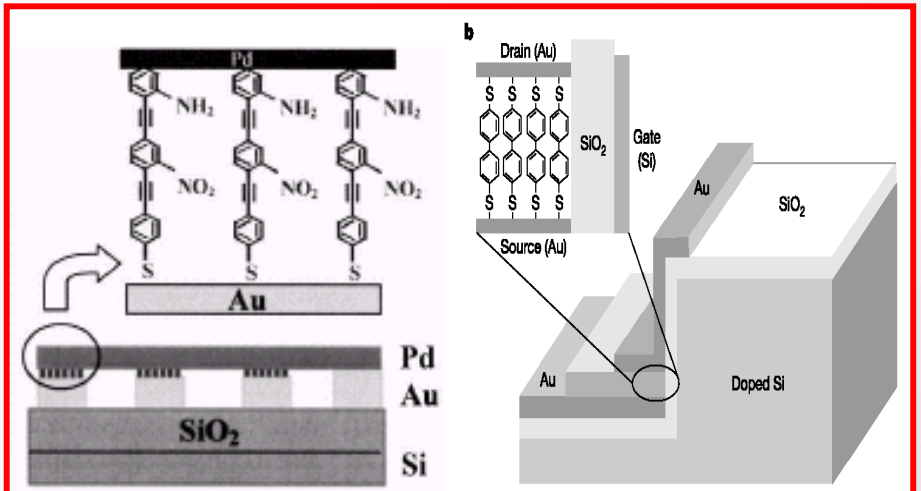


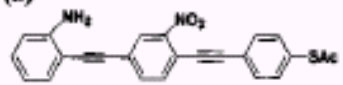
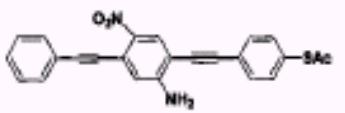


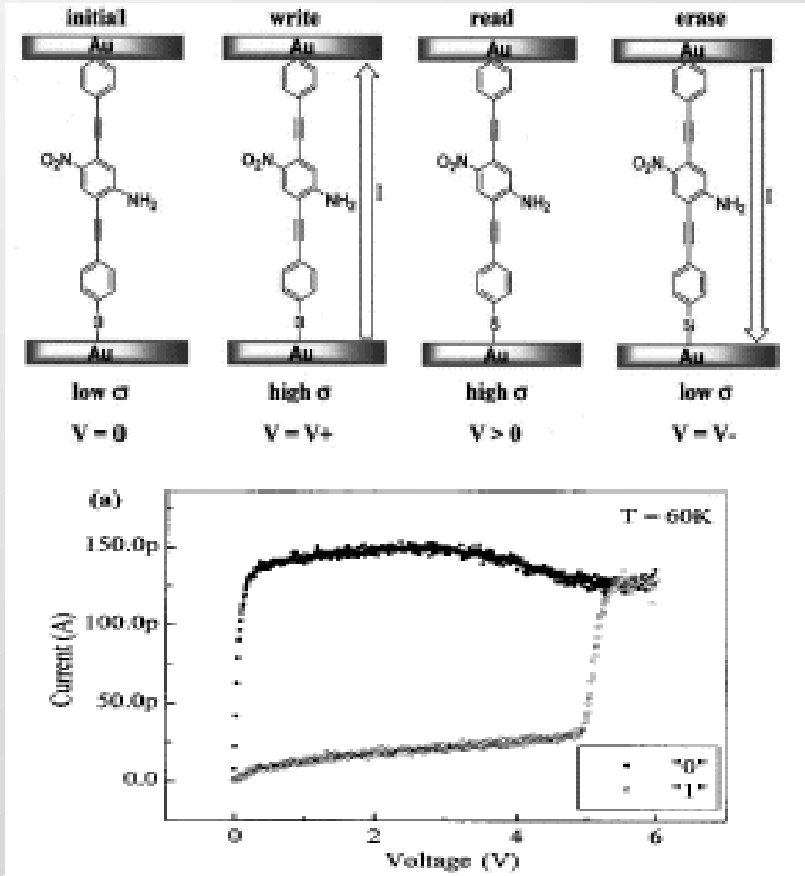




Molecular Devices

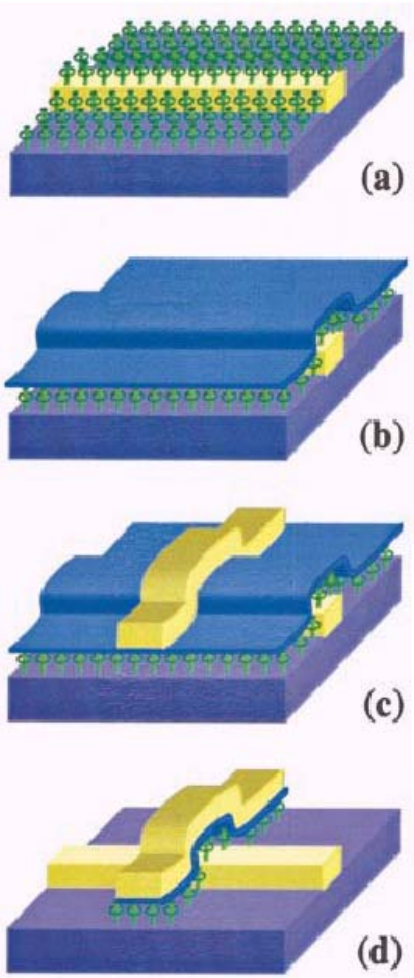


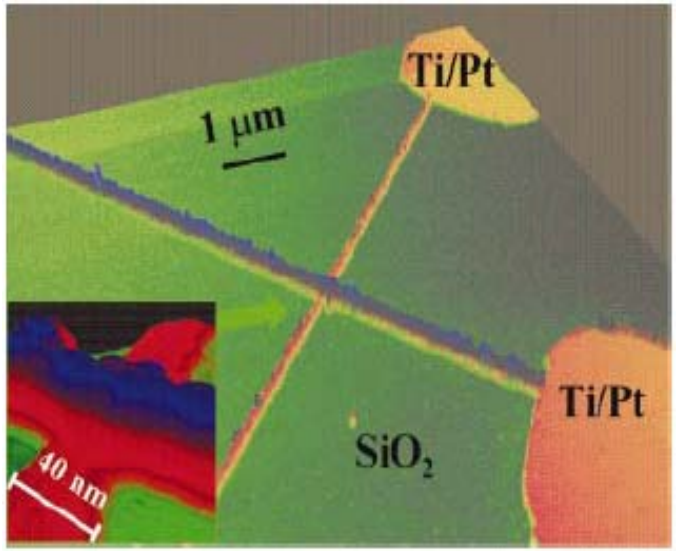
Molecular wires	Hysteresis	Retention time	On/Off ratio
(a) 	Yes	69 s	370 (-1 V)
 (b)	Yes	440 s	30 (-0.5 V)
 (c)	Yes		260 (-1.2 V)
 (d)	No		



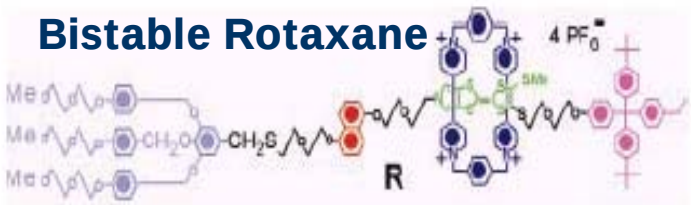
M. Reed *et al*, APL 78, 3735 (2001)
J.M. Tour *et al*, APL 82, 645 (2003)

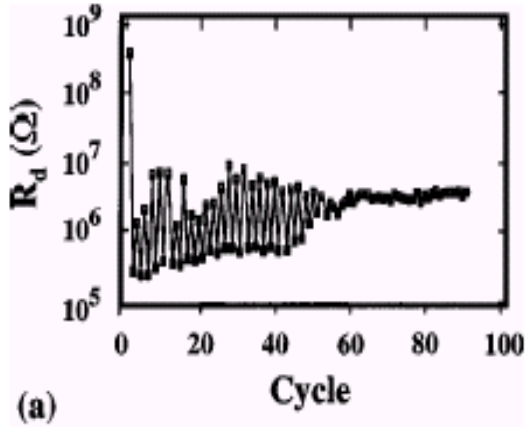
HP - Cross-bar Memories

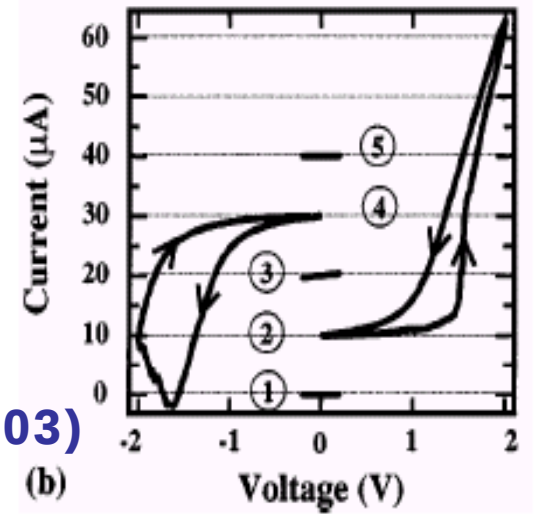




Bistable Rotaxane







S. Williams, APL 82, 1610 (2003)

The DFTB approach I

[Porezag et al. Phys. Rev. B 51, 12947 (1995)]

LCAO expansion of the wave-function

$$\psi_i(\vec{r}) = \sum_\nu C_{\nu i}\phi_\nu(\vec{r} - \vec{R}_k) \qquad \sum_\nu C_{\nu i}(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0 \quad \forall \mu, i$$

The Hamiltonian matrix elements are obtained as following:

1) Creation of (pseudo)atomic orbitals fn by self-consistent solution of the atomic Kohn-Sham eq.

2) Calculation of the matrix elements

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$$

$$H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$$

$$= \begin{cases} \langle \phi_\mu^A | \hat{T} + V_0^A + V_0^B | \phi_\nu^B \rangle & A \neq B \\ \varepsilon_\mu^{free\ atom} & \mu = \nu \\ 0 & \text{otherwise} \end{cases}$$

$$V_0 = V^{LDA}[\eta_{compressed}(r)]$$

3) Determination of the short-range core

$$V_{core}(R) = E_{tot}^{scf-LDA}(R) - E_{bs}^{DFTB}(R)$$

$$V_{core}(R) = \begin{cases} \sum_{n=2}^{N_p} d_n (R_c - R)^n & R < R_c \\ 0 & R \geq R_c \end{cases}$$

The DFTB approach II

[Elstner, et al. Phys. Rev. B 58 (1998) 7260]

Atomistic simulations with an approximate DFT method:

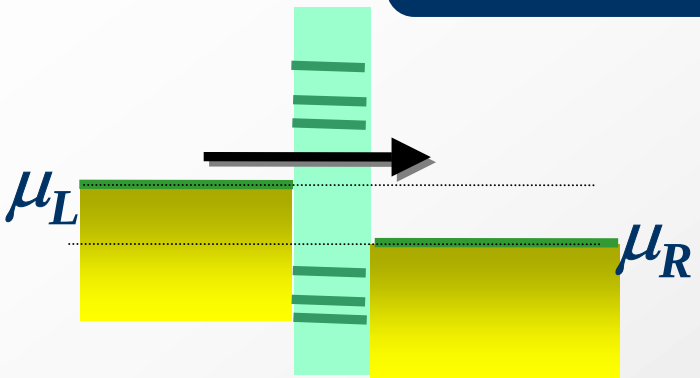
$$\hat{H}\psi_k(\vec{r}) = E_k\psi_k(\vec{r})$$

$$E[n(\vec{r})] = T_0[n(\vec{r})] + E_{Hartree}[n(\vec{r})] + E_{XC}[n(\vec{r})]$$

2nd order expansion of LDA functional

$$E^{(2)} = \sum_i n_i \langle \psi_i | H_0 | \psi_i \rangle + \frac{1}{2}\sum_{\mu,\nu}\gamma_{\mu\nu}\Delta q_\mu \Delta q_\nu + E^{rep}$$

Non-equilibrium transport



Open Boundary conditions

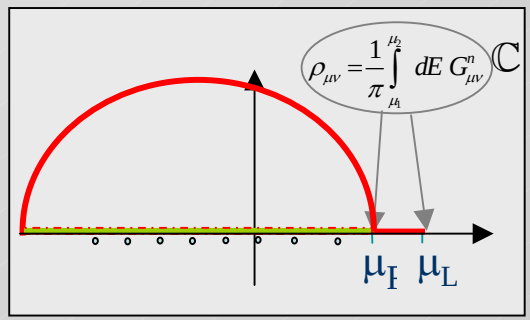
Carriers do not equilibrate

How do we fill up the states ?

In the absence of scattering:

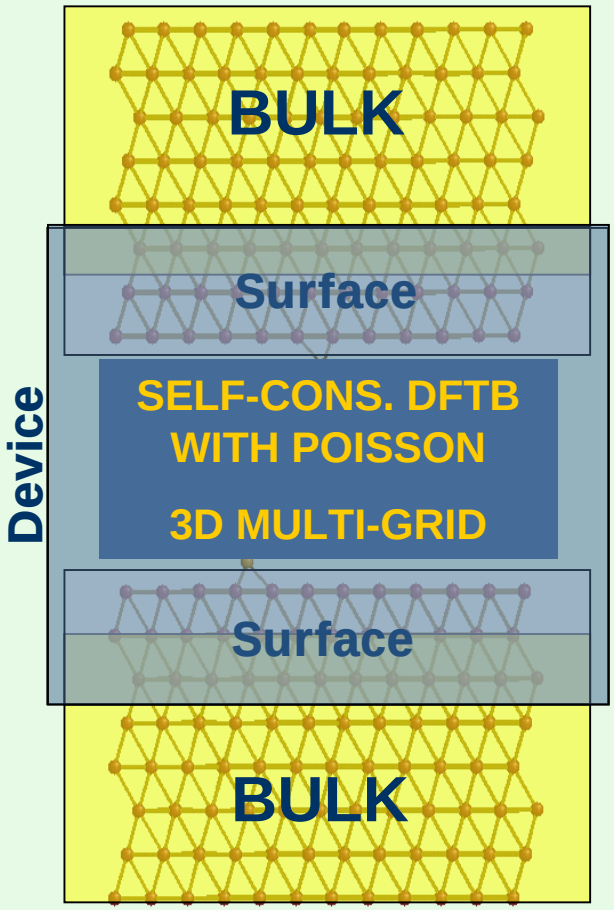
$$iG^{<}_{\mu\nu} = \rho^{L}_{\mu\nu} f_L(E) + \rho^{R}_{\mu\nu} f_R(E)$$

$$\rho_{\mu\nu} = \frac{1}{2\pi i}\int dE\ G^{<}_{\mu\nu}(E) \qquad \text{Density Matrix}$$



- **Green's function approaches are numerically stable**
- **Inclusion of scattering (e-ph, e-e, etc) by self-energy functions.**

NEGF + DFTB = gDFTB



$$\rho_{\mu\nu} = \frac{1}{2\pi i}\int dE\; G^{<}_{\mu\nu}$$

Density Matrix

$$\Delta q_{\mu} = q^{0}_{\mu} - \sum_{\nu} \rho_{\mu\nu} S_{\mu\nu}$$

Mullikan Charges

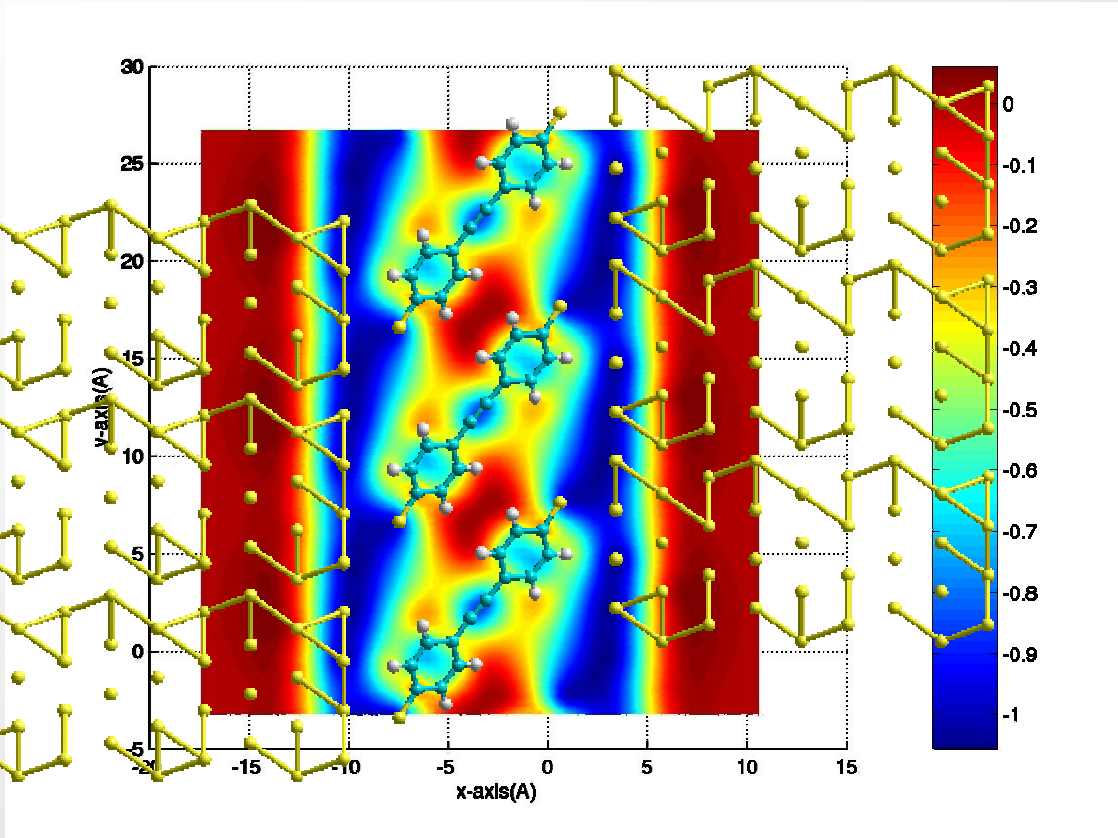
$$\nabla^2 \delta V_H = -4\pi\delta n$$
$$\rightarrow \delta H \rightarrow \delta G^{<} \rightarrow \delta n$$

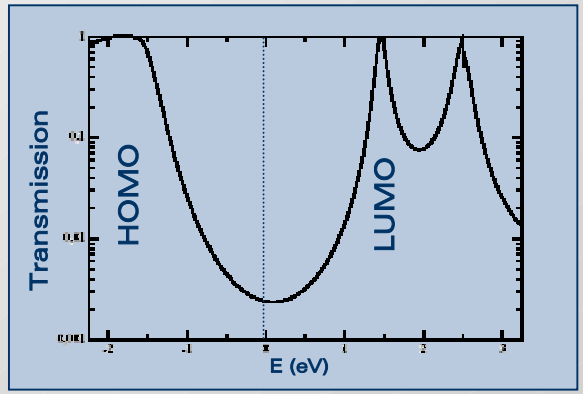
SCC loop

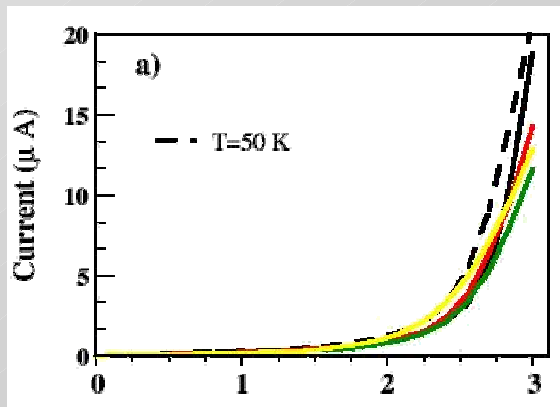
A. Pecchia, A. Di Carlo, **Rep Prog Phys 67**, (2004)

A. Pecchia *et al.*, *Introd. Mol. Elect.*, Springer, NY (2005)

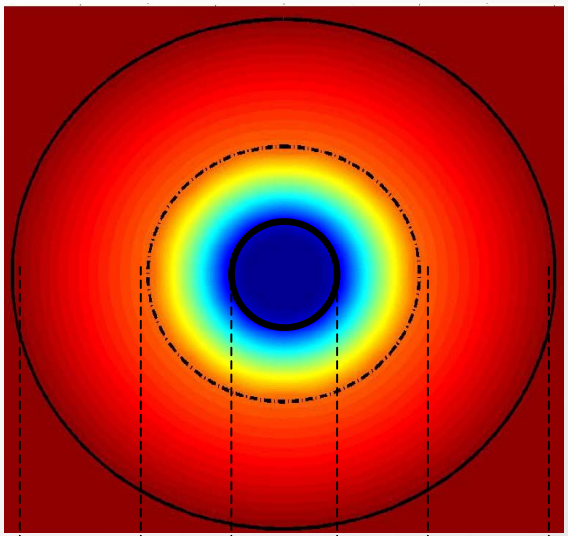
SAMs of dithio-phenylene

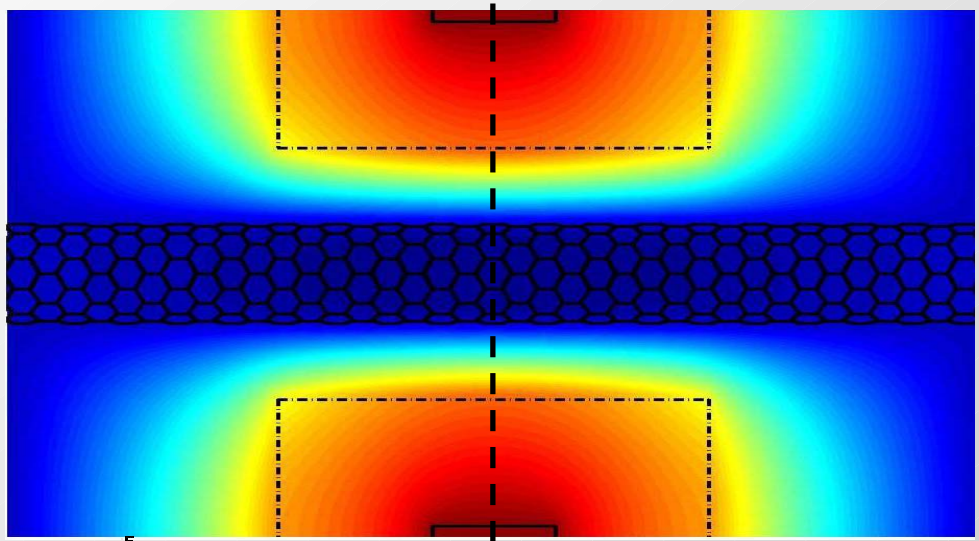


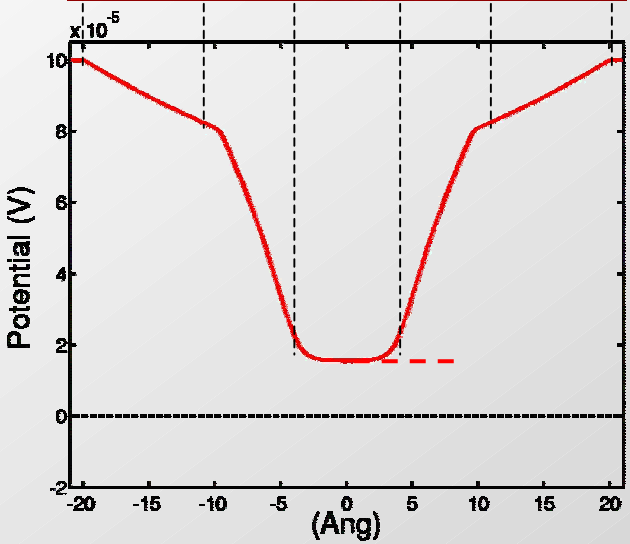


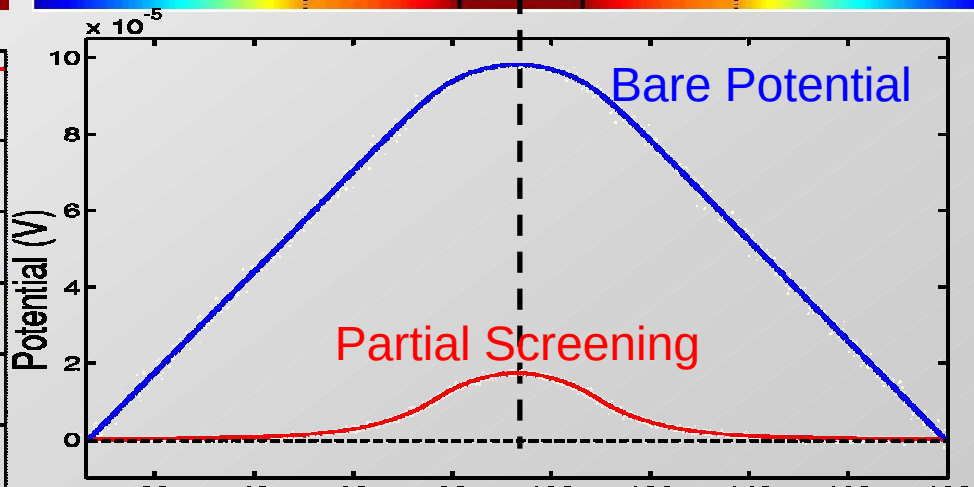


C_Q of CNTs



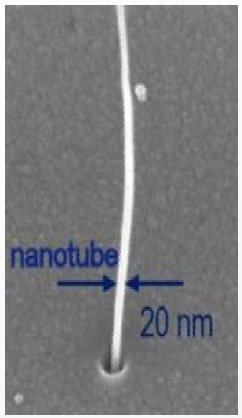


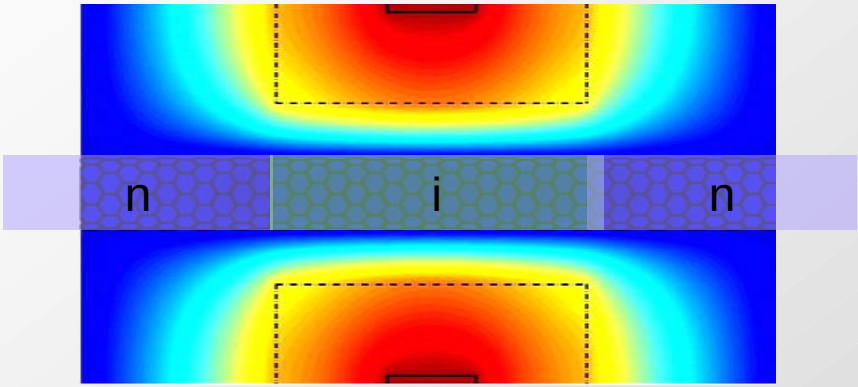


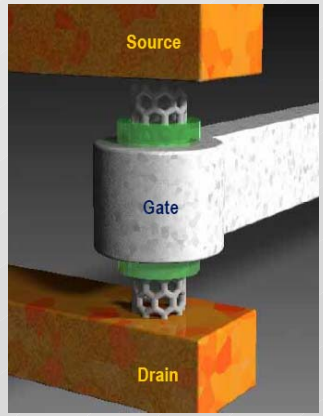


L. Latessa et al., In preparation

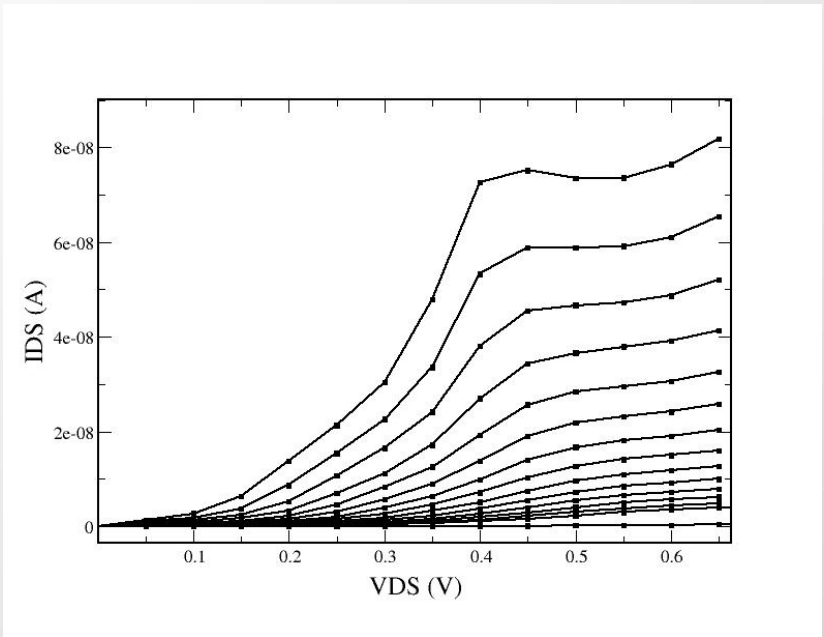
IV Characteristics

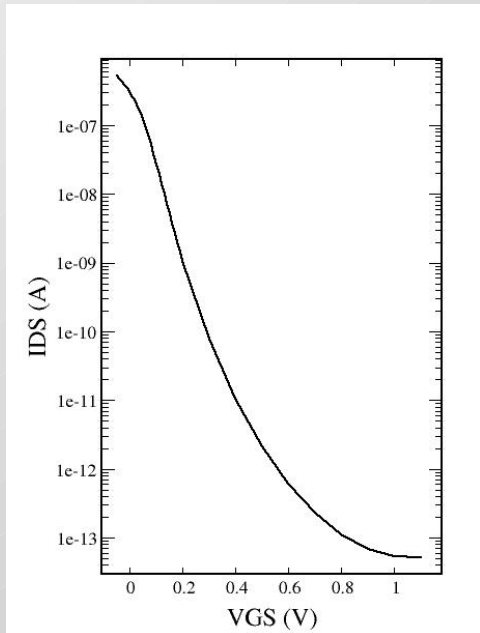


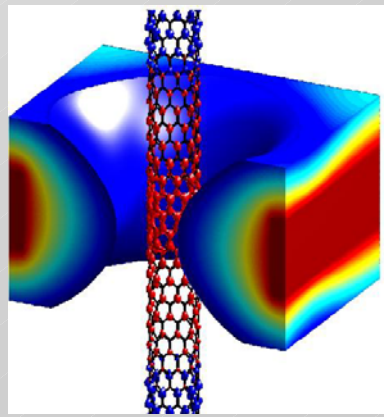




(Infineon)

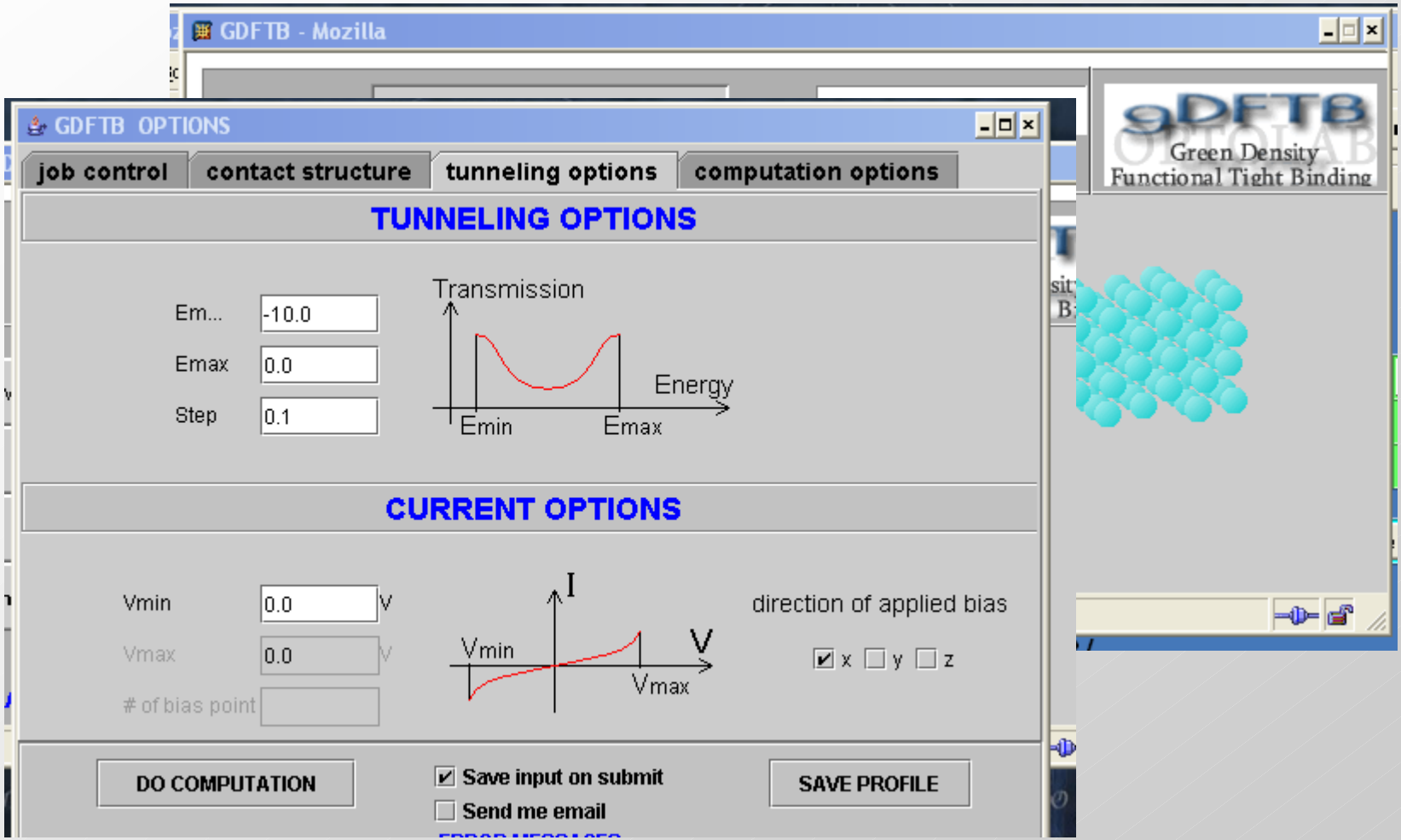






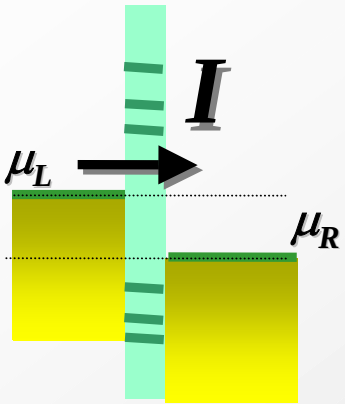
The ICODE HUB

INTERNET COMPUTING ON DEMAND



http://icode.eln.uniroma2.it

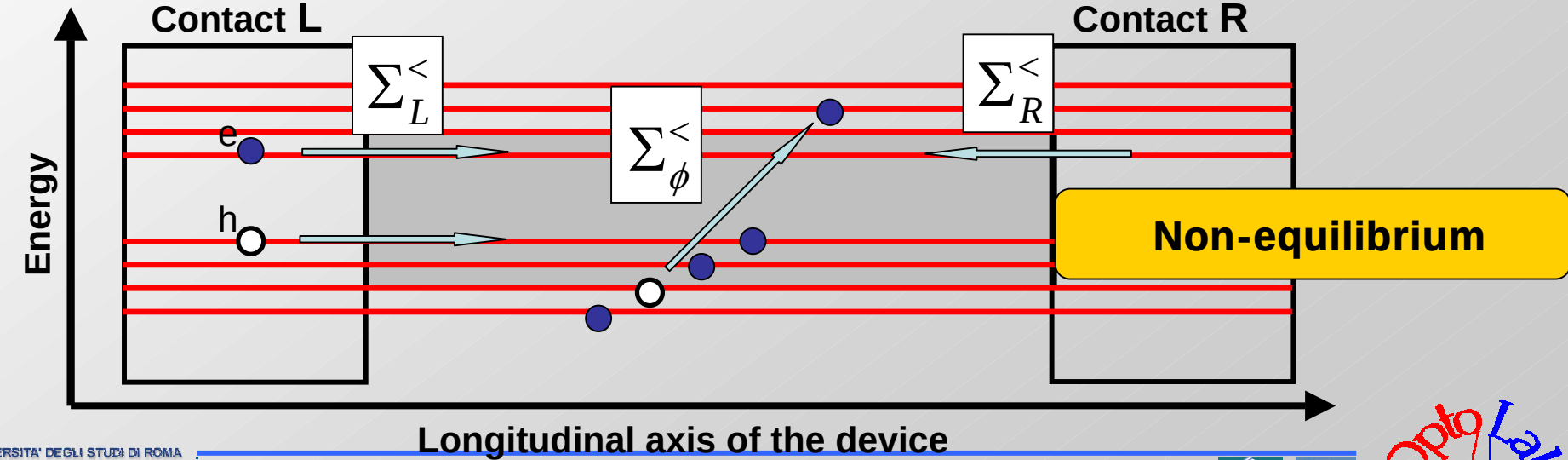
Non-equilibrium scattering



$$I = \frac{2e}{h}\int Tr\left[\Sigma^{<}G^{>} - \Sigma^{>}G^{<}\right]dE$$ **The current**

$$\Sigma^{<} = \Sigma_L^{<} + \Sigma_R^{<} + \Sigma_\phi^{<} \qquad G^{<} = G^{r}\Sigma^{<}G^{a}$$

$$\Sigma_\phi^{<} = D \otimes G^{<}$$ **Scattering flux of particles induced by the interaction**



Electron- phonon

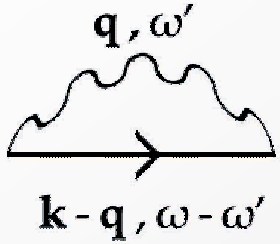
$$\delta\mathcal{H}=\sum_{\mu,\nu}\sum_{q}\gamma_{\mu\nu}^{q}c_{\mu}^{\dagger}c_{\nu}(a_{q}^{+}+a_{q})$$

The electron-phonon coupling Hamiltonian is derived by expanding to first order the TB-Hamiltonian with respect to the atomic positions.

$$\gamma_{\mu\nu}^{q}=\frac{\partial H_{\mu\nu}}{\partial\xi_{q}}-\sum_{\lambda,\sigma}H_{\mu\lambda}S_{\lambda\sigma}^{-1}\frac{\partial S_{\sigma\nu}}{\partial\xi_{q}}-\frac{\partial S_{\mu\sigma}}{\partial\xi_{q}}S_{\sigma\lambda}^{-1}H_{\lambda\mu}$$

ξ_q is the collective displacement of the atoms along a vibrational mode. This quantity is quantized as a position operator

Self-energies



:

$$\Sigma_\phi^<(E) = \frac{i}{2\pi}\sum_q \gamma_q^2 \int dE'\, G^<(E-E')D_q^<(E')$$

Approximation for the phonon self-energy:

$$\mathrm{Im}\{\Sigma_\phi^r\} = \frac{1}{2}\left(\Sigma_\phi^< - \Sigma_\phi^>\right) \qquad \mathrm{Re}\{\Sigma_\phi^r\} = 0$$

Dyson's equation:

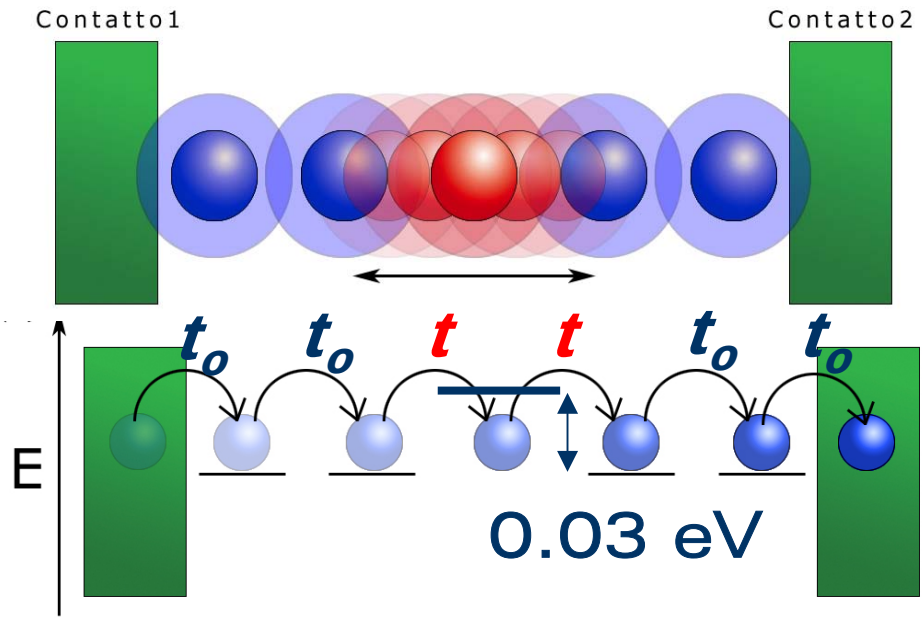
$$G^r(E) = \frac{1}{E - H_0 - \Sigma_c^r(E) - \Sigma_\phi^r(E)}$$

Kinetic equation:

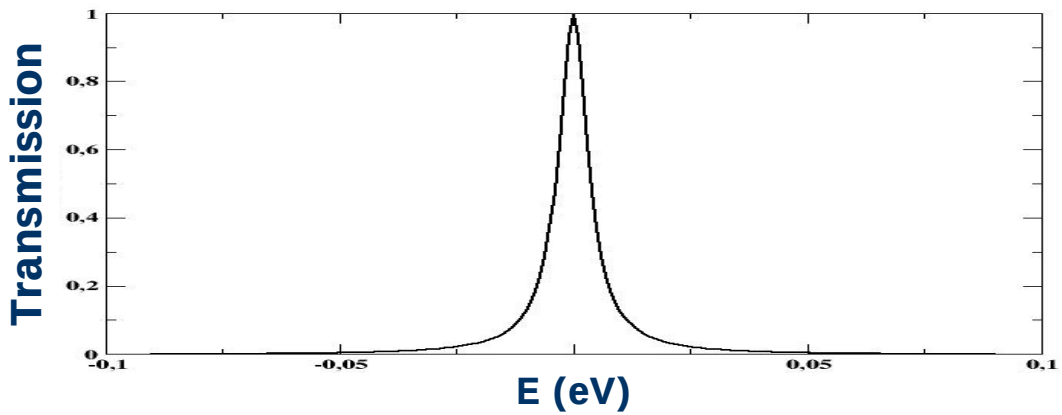
$$G^<(E) = G^r(E)[\Sigma_c^<(E) + \Sigma_\phi^<(E)]G^a(E)$$

Self-consistent Born approx.

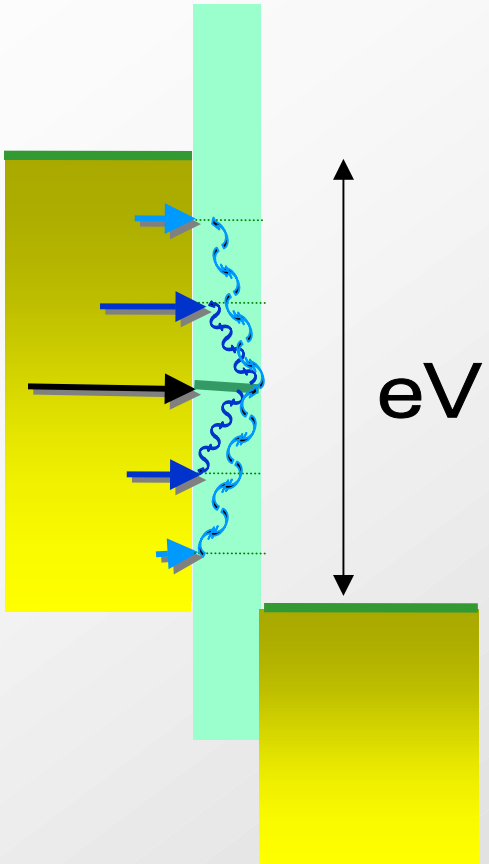
A simple model

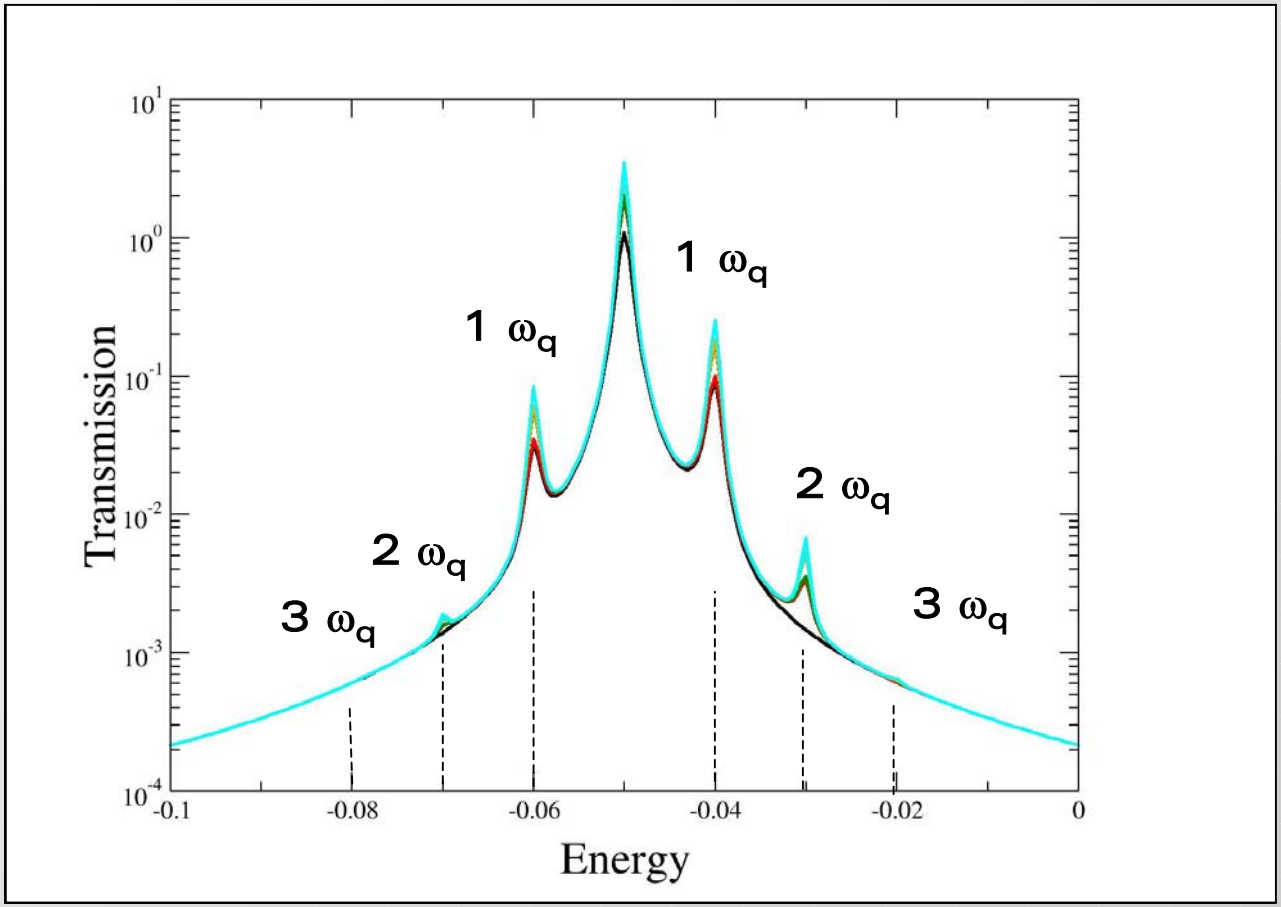


$$\frac{t}{t_o} = 0.01$$

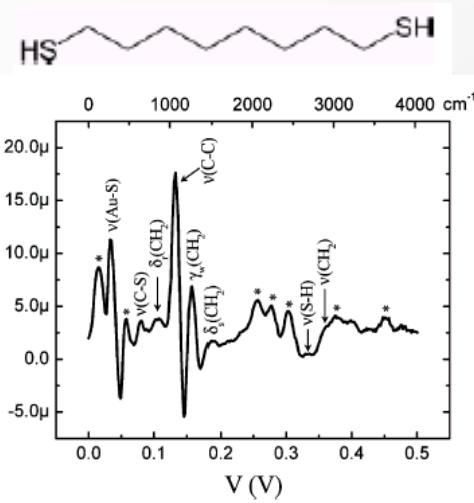


Self-consistent solution

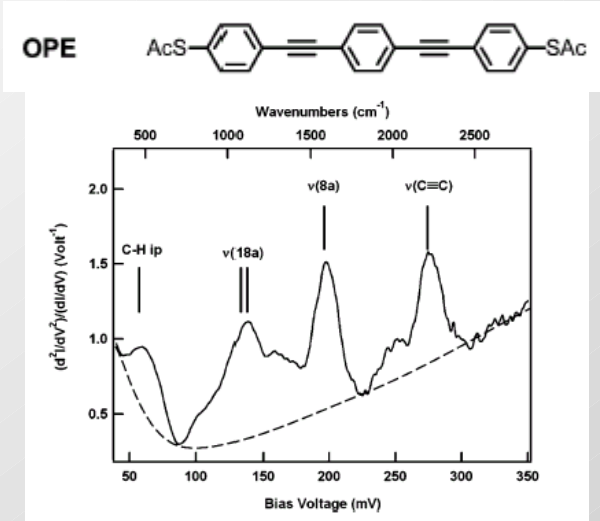




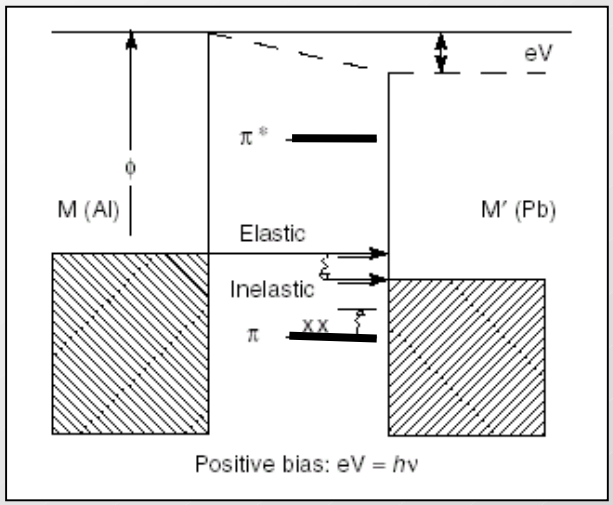
Inelastic spectroscopy

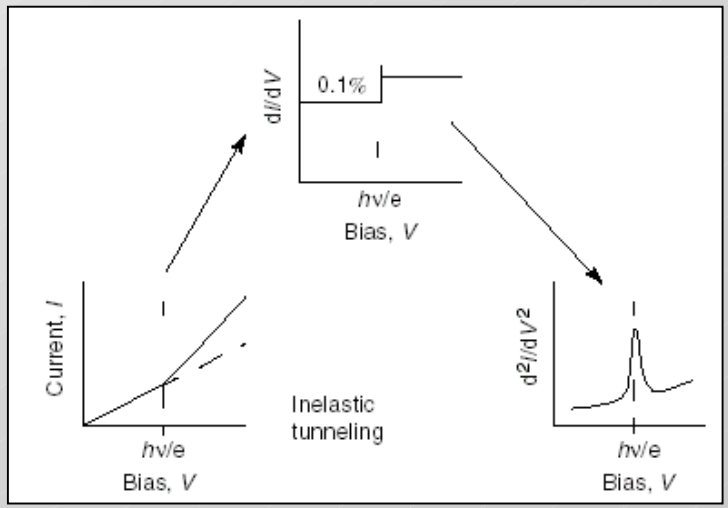


Wang, Nano Letters, 5, 450 (2004)

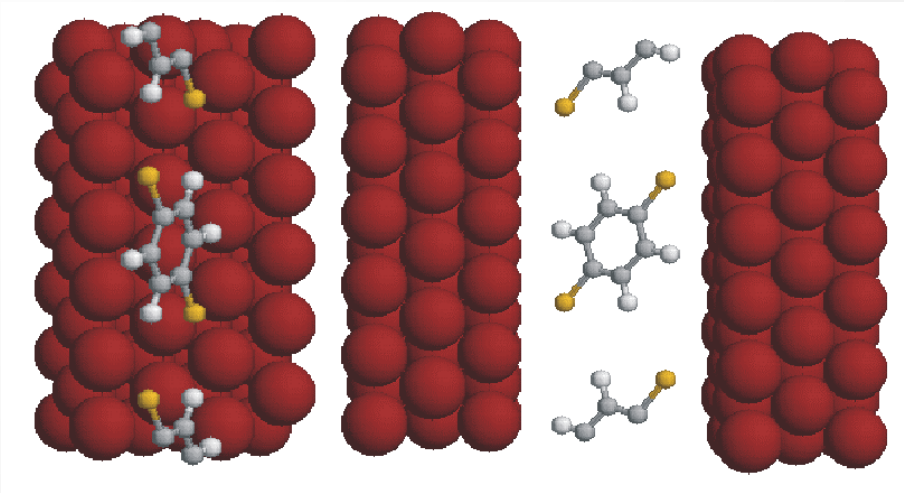


Kushmerick, Nano Letters, 4, 639 (2004)

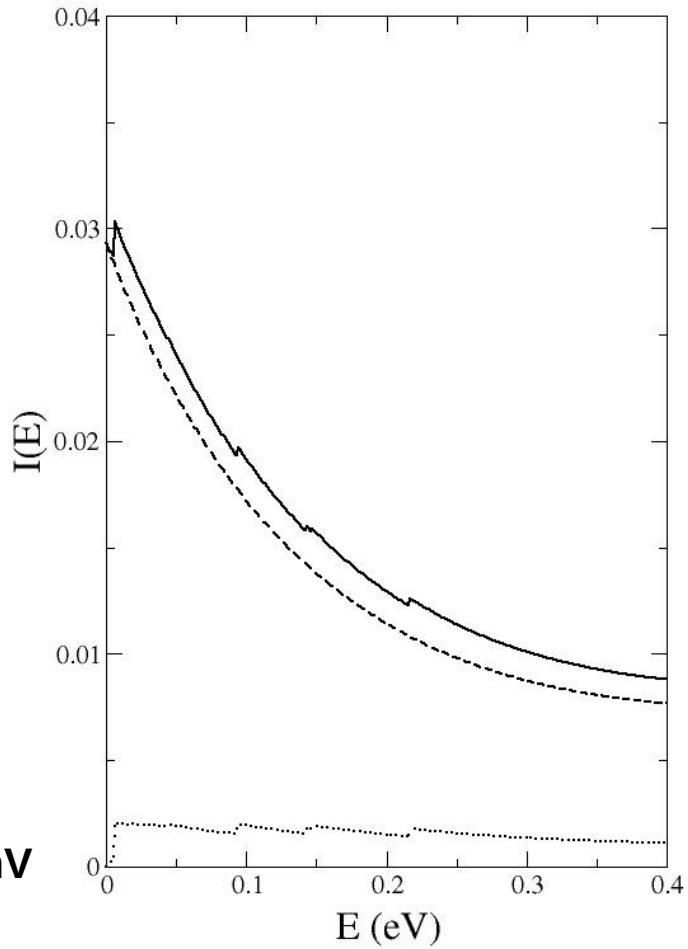




Application to benzene



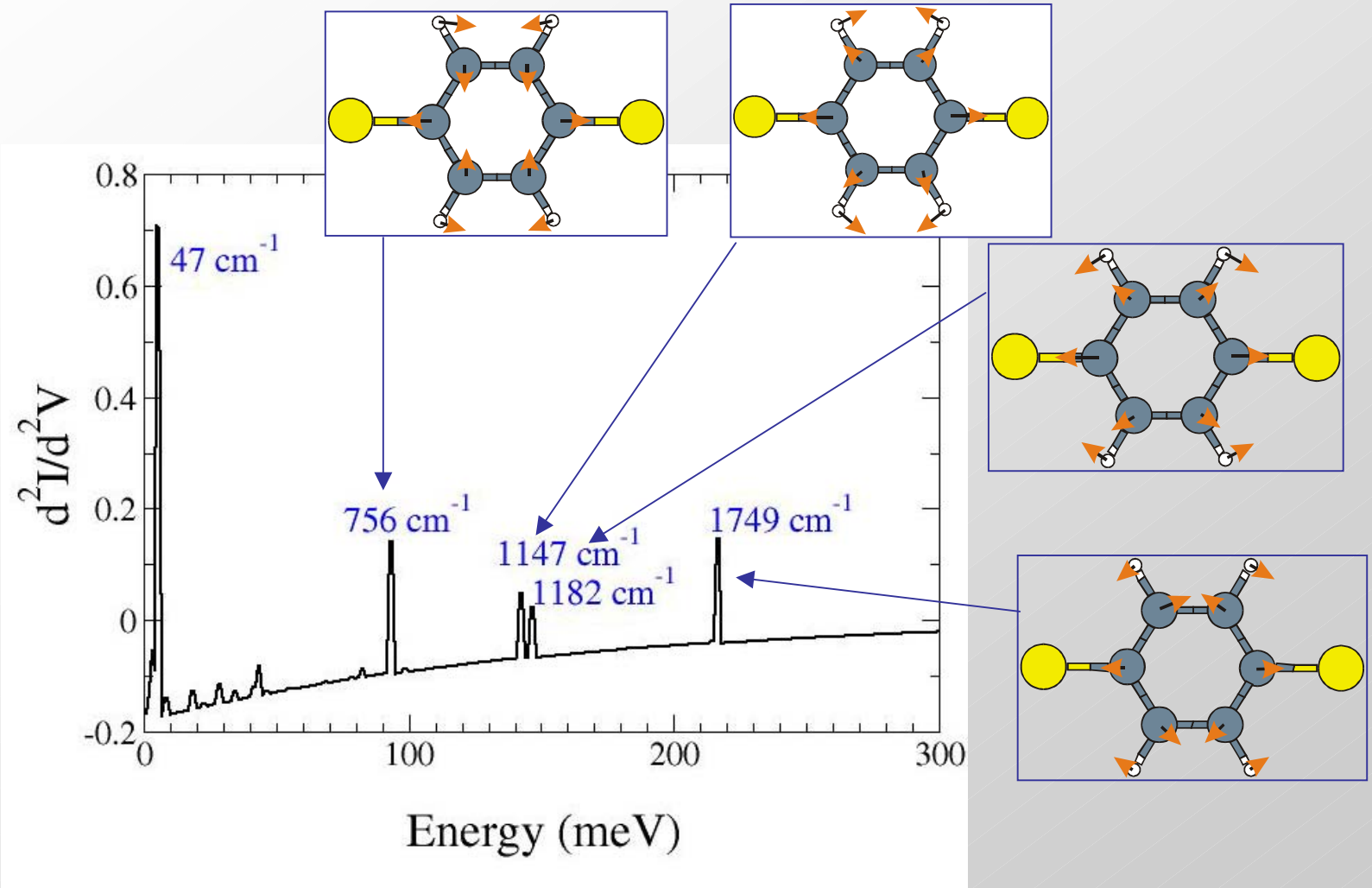
36 vibrational modes



Current density vs Energy for an applied bias of 400 mV

Pecchia *et al.*, J. Comp. Elect. (2005)

Inelastic peaks

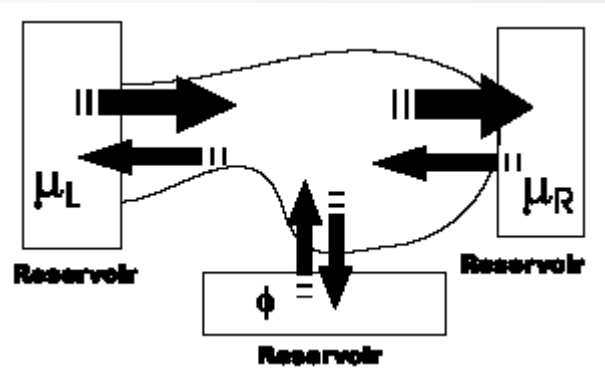


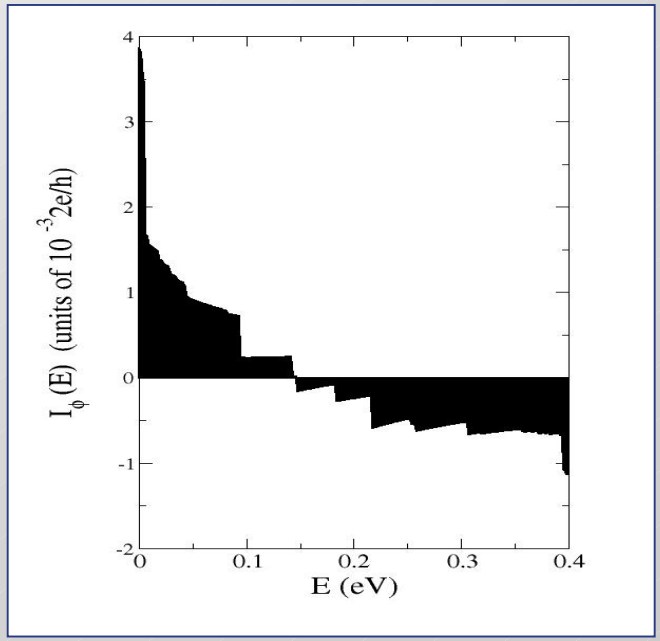
Power emitted

Power emitted is computed using:

$$W = \frac{2}{h}\int Tr[\Sigma_{\phi}^{<}(E)G^{>}(E) - \Sigma_{\phi}^{>}(E)G^{<}(E)]EdE$$

Virtual contact current

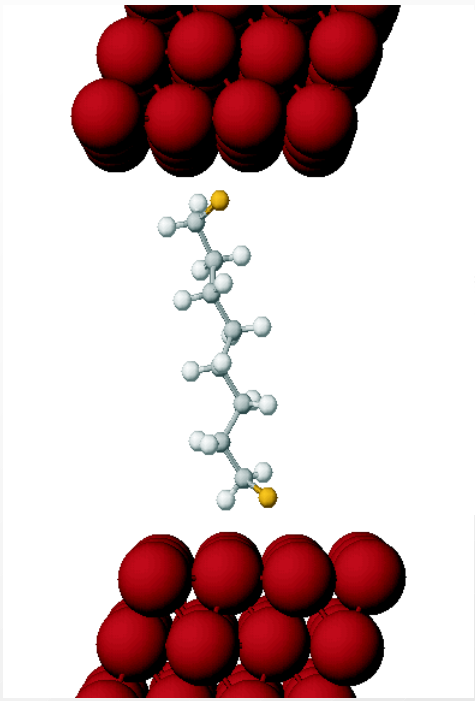


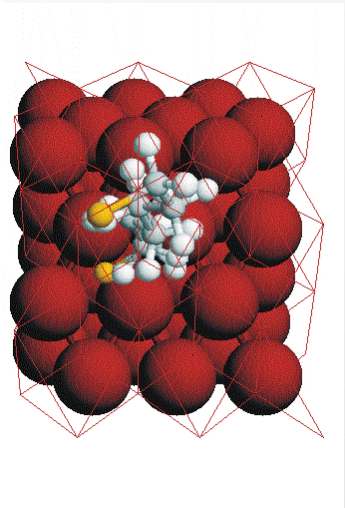


Power released at 0.4 V **11 nW**

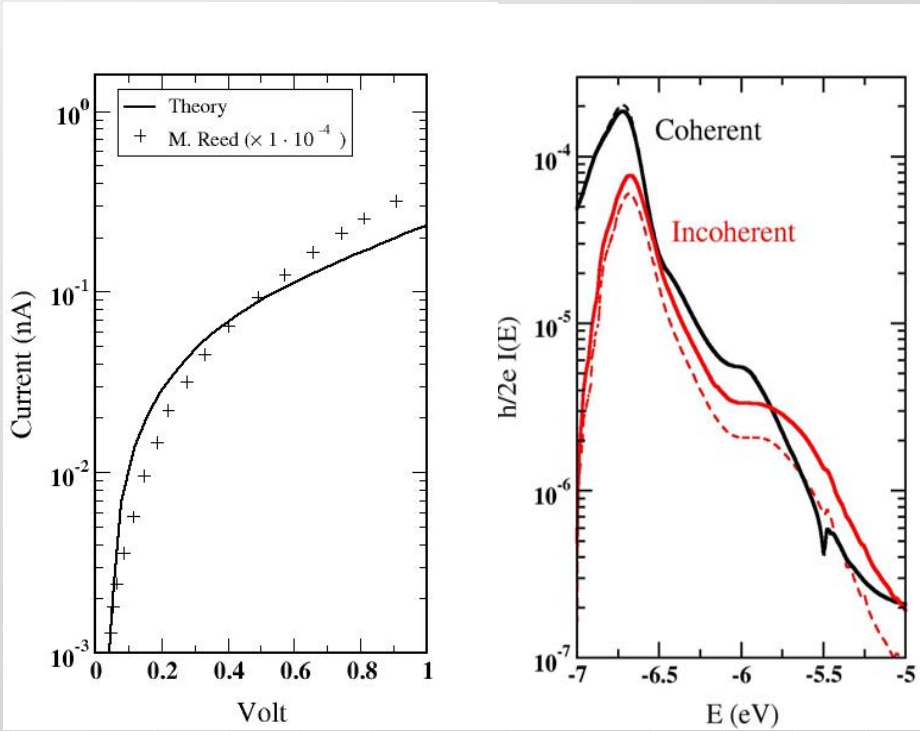
Power released at 1.0 V **33 nW**

Au/octanethiol/Au



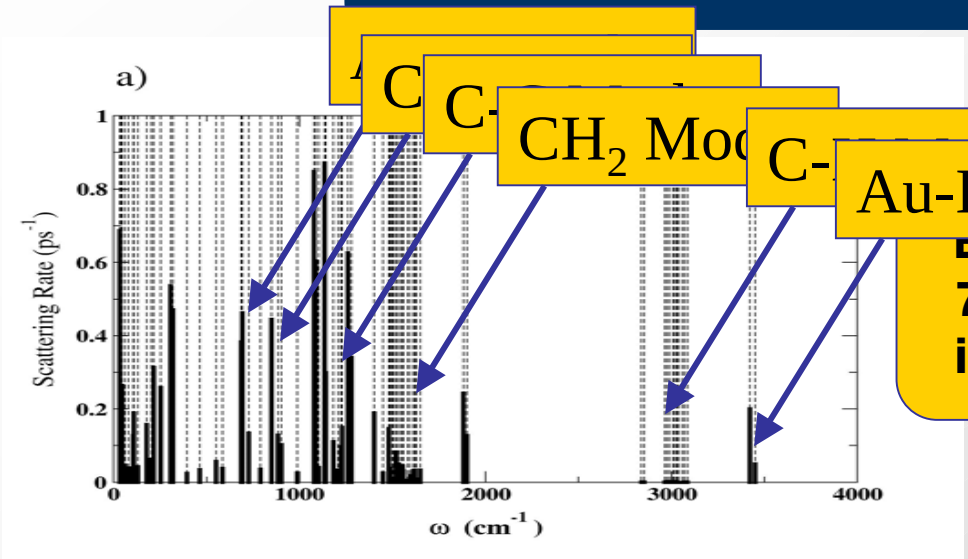


Pecchia *et al.*, Nano Letters 4, 2125 (2004)

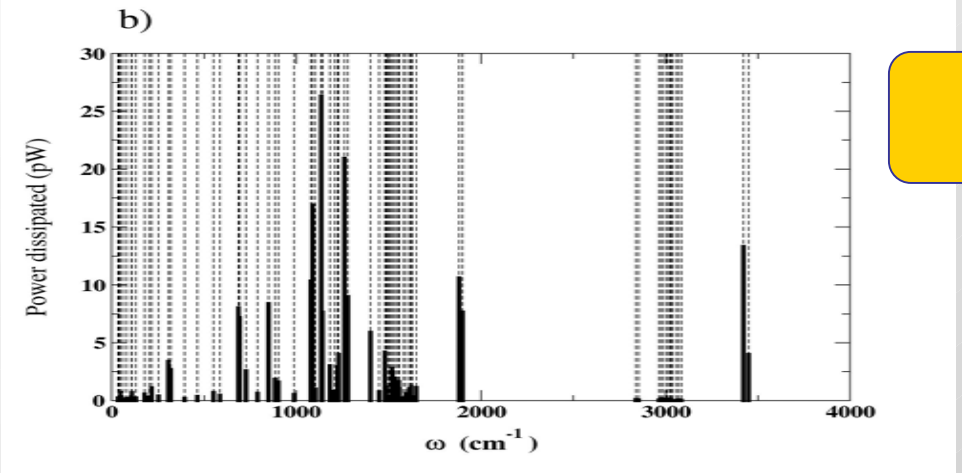


Tunneling and I-V characteristics

Emission rate analysis



Emission rate for each one of the 72 vibrational modes considered independently



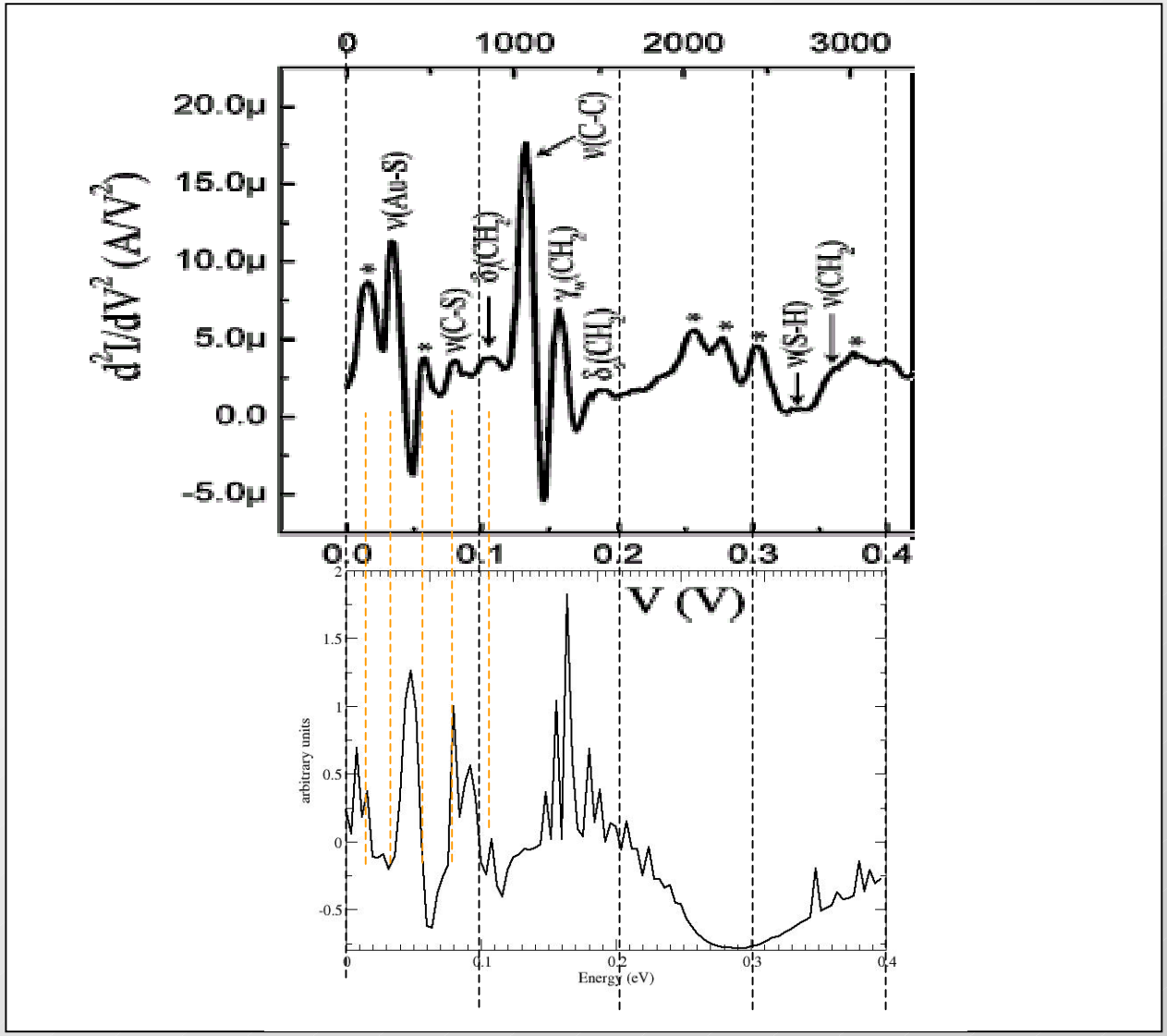
Power released in each mode

Total Power emitted at 2.0 V

W=0.16 nW

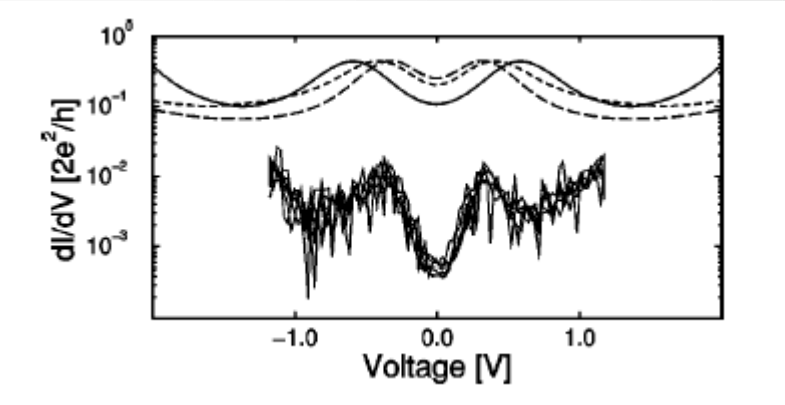
The power is mostly released in the C-C stretch modes

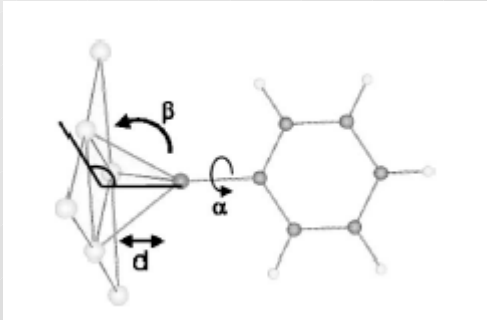
Comparison with our result



Limitations of DFT

Tunneling is usually calculated using DFT spectrum





In principle we should include corrections beyond DFT in order to address this problem.

(Exact exchange, CI, TD-DFT, GW)

Correlations: GW

Screened electron-electron potential to include correlations beyond DFT(B)

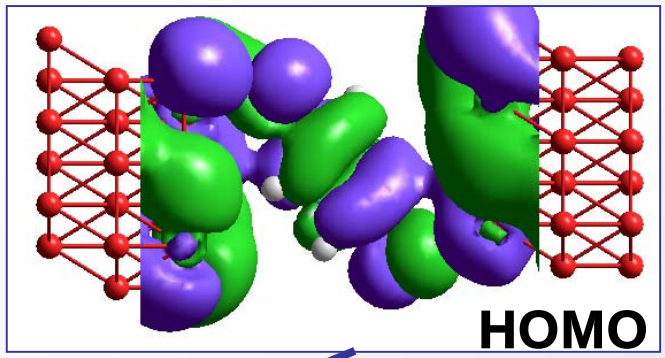
$$\Sigma^{GW}(E) = \frac{i}{2\pi}\int G(E-E')W(E')dE' \quad \Rightarrow \quad W(E) = \varepsilon^{-1}(E)v$$

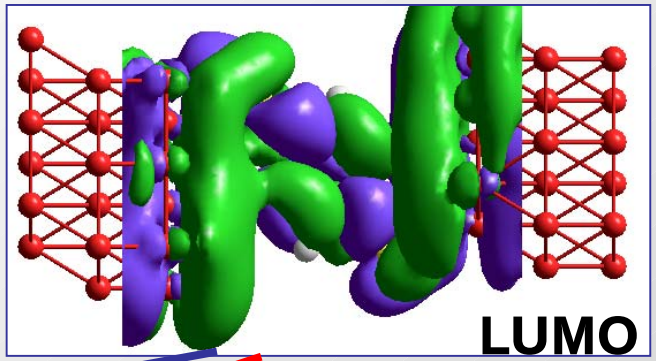
Key approximation on products of DFTB AO wavefunctions:

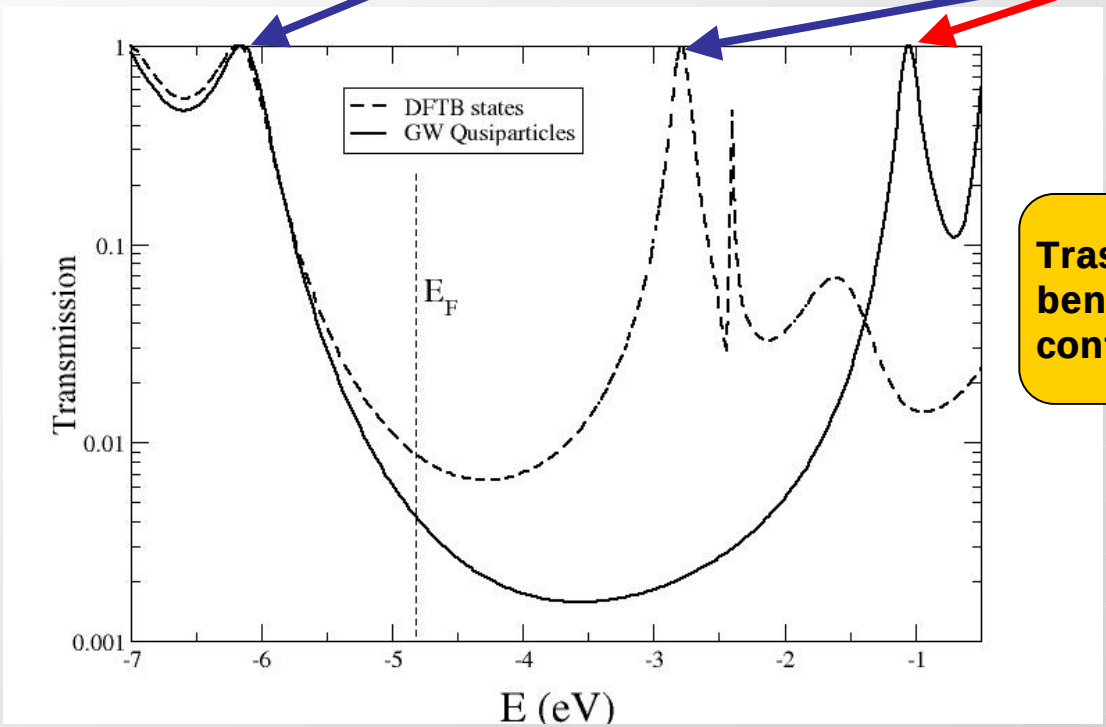
$$\phi_\mu(r)\phi_\nu(r) \approx S_{\mu\nu}\left[\left|\phi_\mu(r)\right|^2 + \left|\phi_\nu(r)\right|^2\right]$$

T.A. Niehaus et al., Cond-matt/0411024

Effect of QP Corrections







Trasmission function for a single benzene molecule between copper contactsincluding QP correction

Pecchia *et al.*, J. Comp. Elect. (2005)

Future Work

- **Implement real part on the self-energy to account for polaronic formation**

- **Construct a model for phonon relaxations in order to study heat dissipation into the contacts.**