Atomistic simulation of electronic transport in organic nanostructures: electron-phonon and electron-electron interactions

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Outline

- Heat relaxation in molecular wires can be of crucial importance for future molecular electronic devices.

- Calculations based of a first-principle DFT Hamilonian for the electron-phonon coupling, applied to **octanethiols** and **benzenethiols**

- Limits or the DFT Theory (gap underesitimate) Application of GW quasiparticle corrections to **benzenedithiol**

The DFTB method

- **Tight-binding expansion of the wave functions**
  [Porezag, et al Phys. Rev. B 51 (1995) 12947]

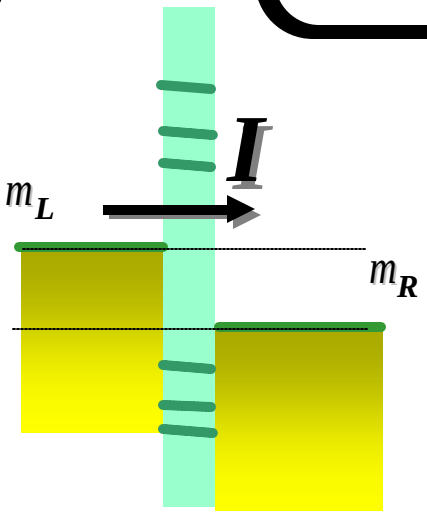
- **Calculation of the matrix elements in the two-centers approx from ab-initio DFT calculations.**

- **II order-expansion of Kohn-Sham energy functional**
  [Elstner, et al. Phys. Rev. B 58 (1998) 7260]

$$E^{(2)} = \sum_i n_i \langle y_i | H_0 | y_i \rangle + \frac{1}{2} \sum_{m,n} g_{mn} \Delta q_m \Delta q_n + E^{rep}$$

- **Short-range repulsion energy, E^{rep}, expanded in atomic pair-potentials computed with ab-initio DFT.**

Current calculations



$$I = \frac{2e}{h}\int Tr\left[\Sigma^{<}(E)G^{>}(E) - \Sigma^{>}(E)G^{<}(E)\right]dE$$

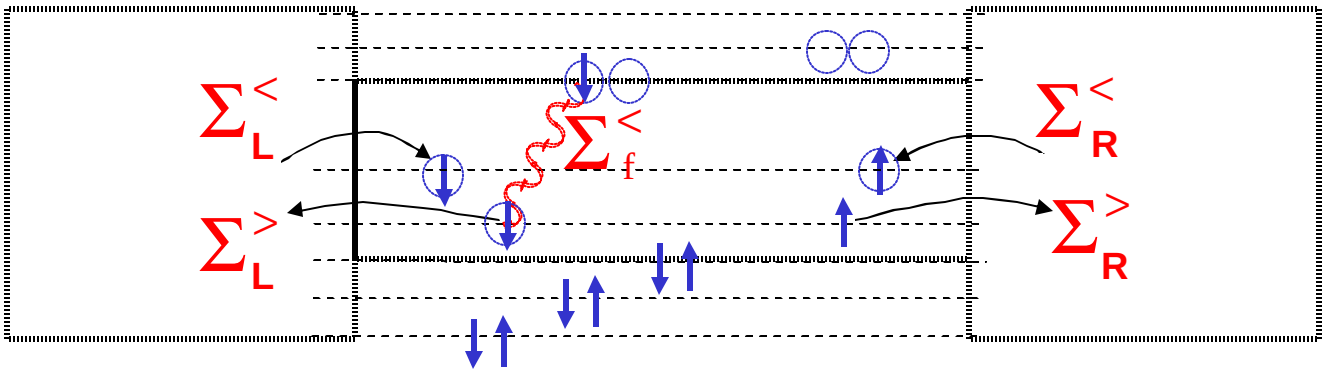
$$G^{<}(E) = G^{r}(E)\Sigma^{<}(E)G^{a}(E) \qquad \textbf{Kinetik equation}$$

○ ⟷ $G^{>}$ **hole density**

$\Sigma^{<}$ **electron inscattering**

↑ ⟷ $G^{<}$ **electron density**

$\Sigma^{>}$ **hole inscattering**



Electron-phonon coupling

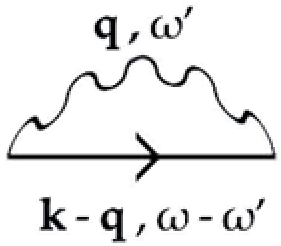
$$dH = \sum_{m,n} \sum_{q} g^{q}_{mn} c^{\dagger}_{m} c_{n} \left(a^{+}_{q} + a_{q}\right)$$

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

$$g^{q}_{mn} = \frac{\partial H_{mn}}{\partial x_q} - \sum_{l,s} H_{ml} S^{-1}_{ls} \frac{\partial S_{sn}}{\partial x_q} - \frac{\partial S_{ms}}{\partial x_q} S^{-1}_{sl} H_{lm}$$

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

Phonon self-energy



$$:\quad \Sigma_f^<(E) = \frac{i}{2p}\sum_q g_q^2 \int dE'\, G^<(E - E')D_q^<(E')$$

Approximation for the phonon self-energy:

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

Dyson's equation:

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

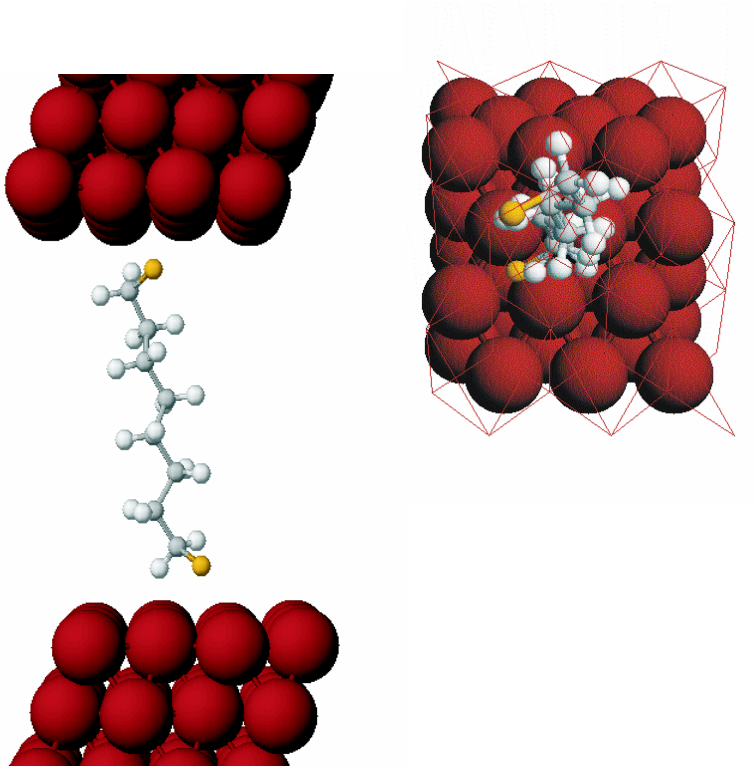
Kinetic equation:

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

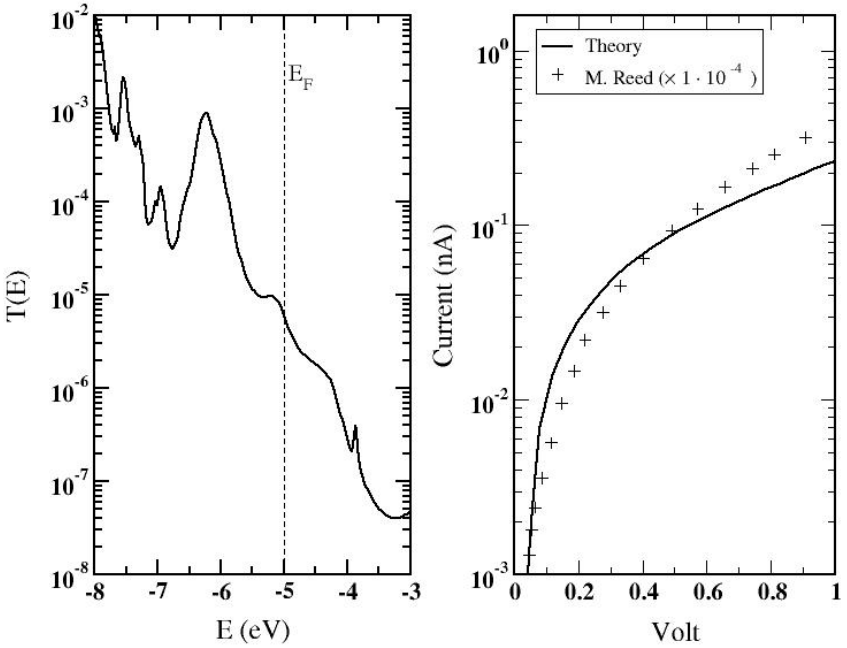
Self-consistent Born approx.

Au/Octanethiol/Au system

(Pecchia *et al.*, Nano Letters, In Press)

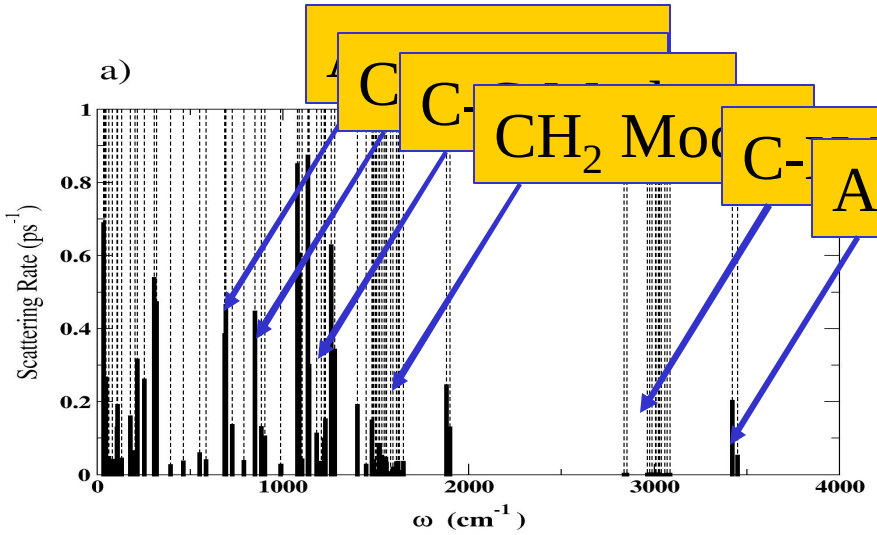


Structure of $S_2C_8H_{16}$ relaxed between gold contacts with the DFTB code.

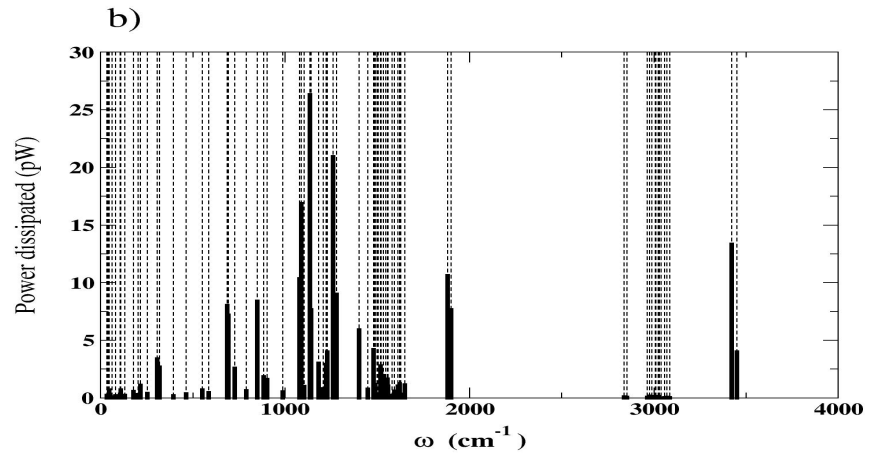


Tunneling and I-V characteristics

Emission rate analysis



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

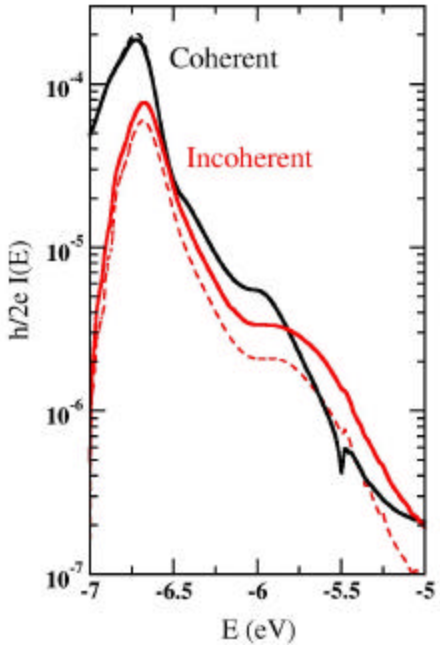


Power released in each mode

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

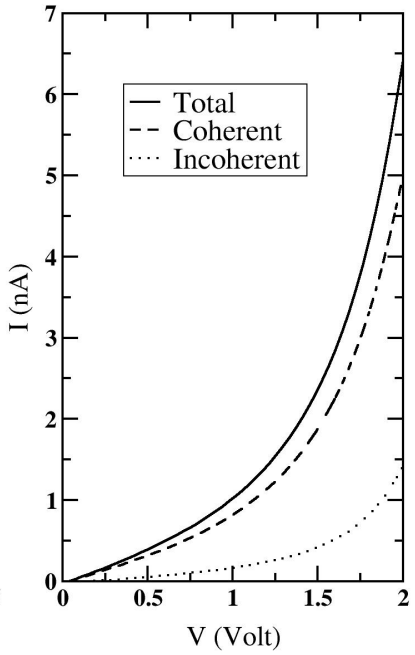
Incoherent current

All modes are considered



Coherent and Incoherent components.

Dashed lines are First order, Solid lines are Self-consistent Born approximations.



I-V characteristics:

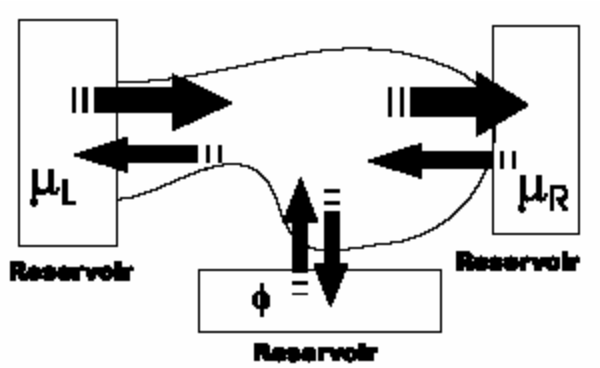
coherent and incoherent components

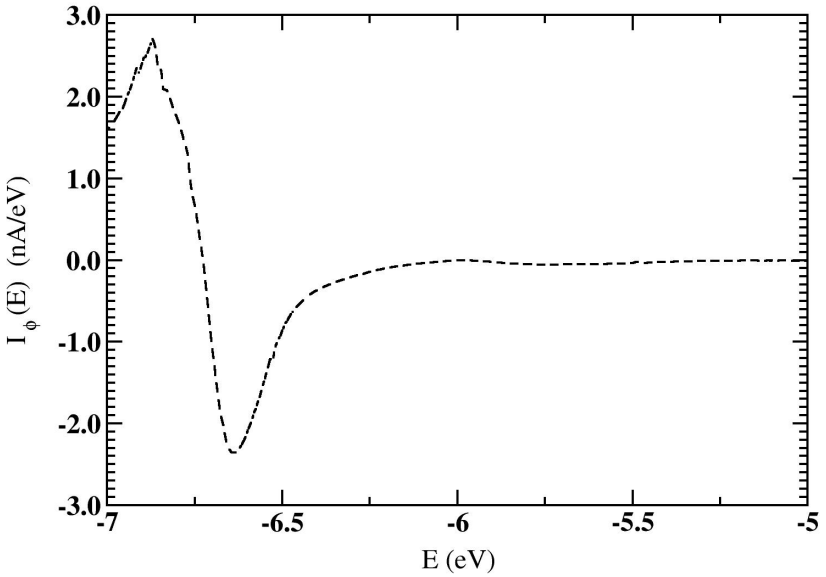
Power emitted

Power emitted is computed using:

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

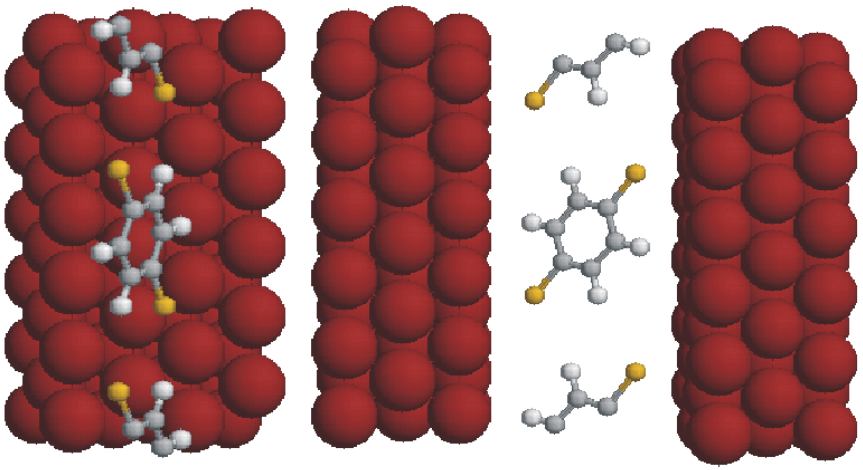
Virtual contact current



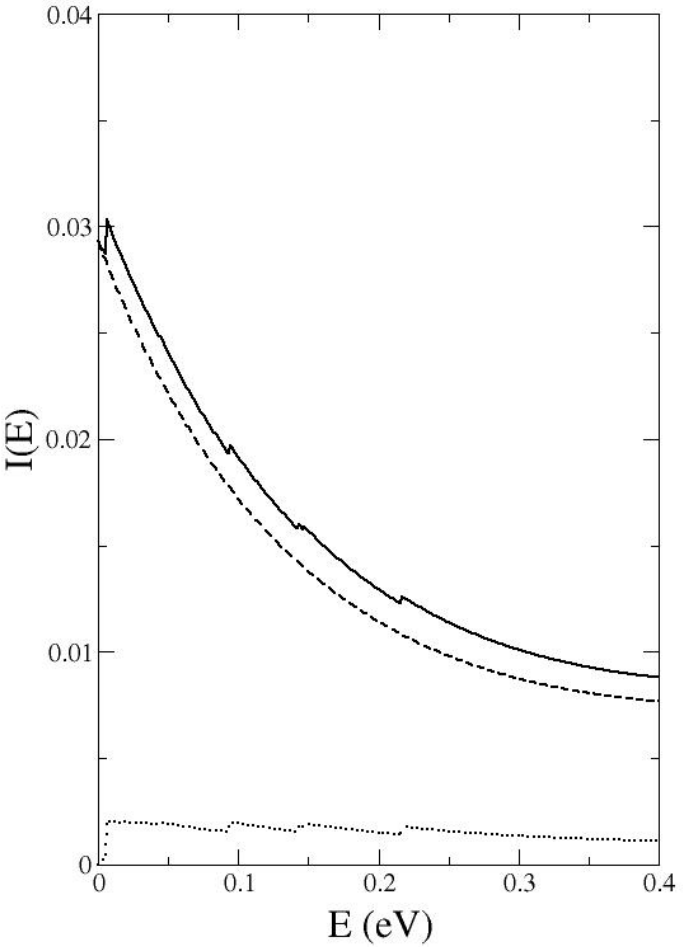


Power emitted at 2.0 V **W=0.16 nW**

Application to benzene



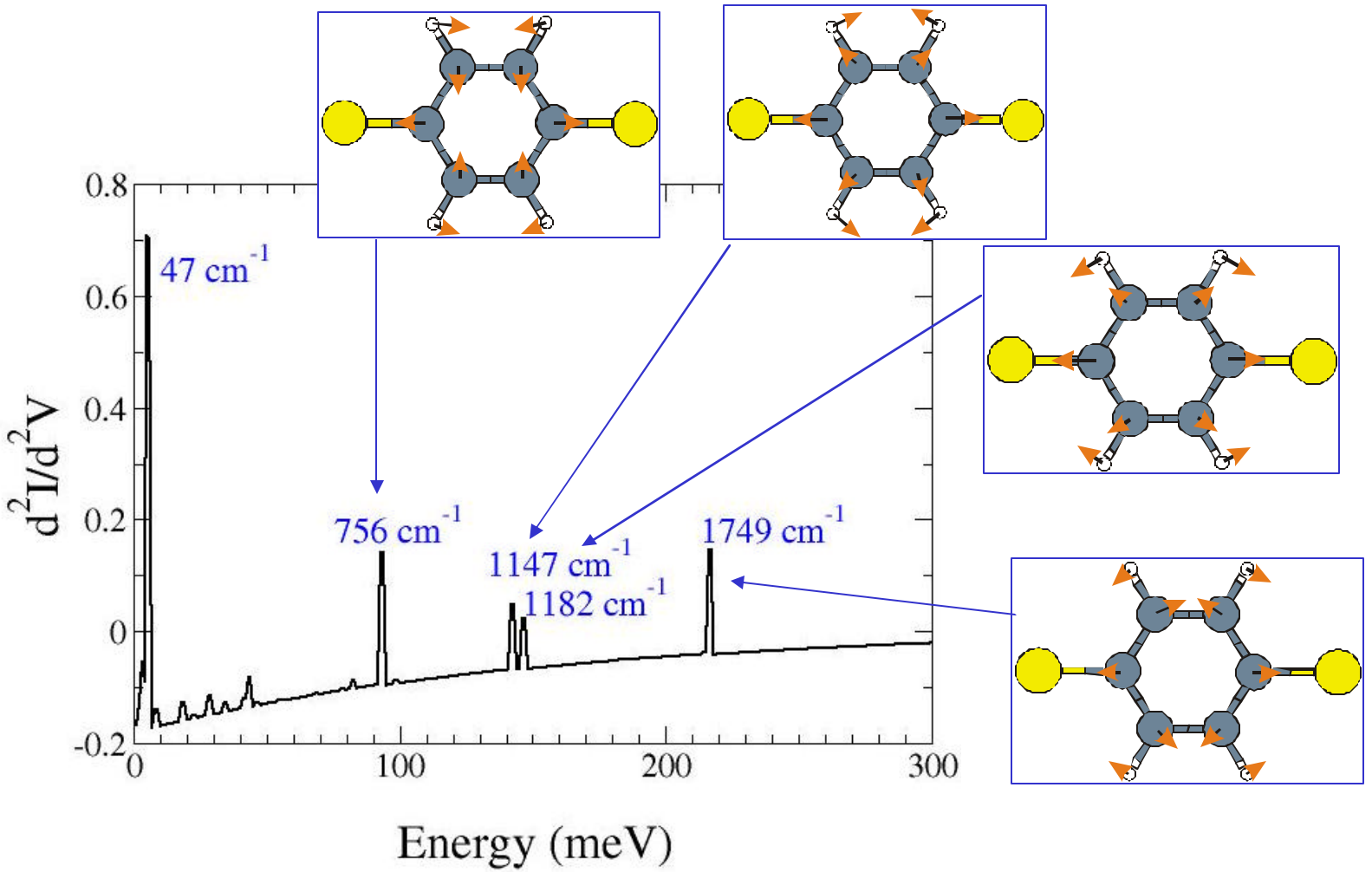
36 vibrational modes



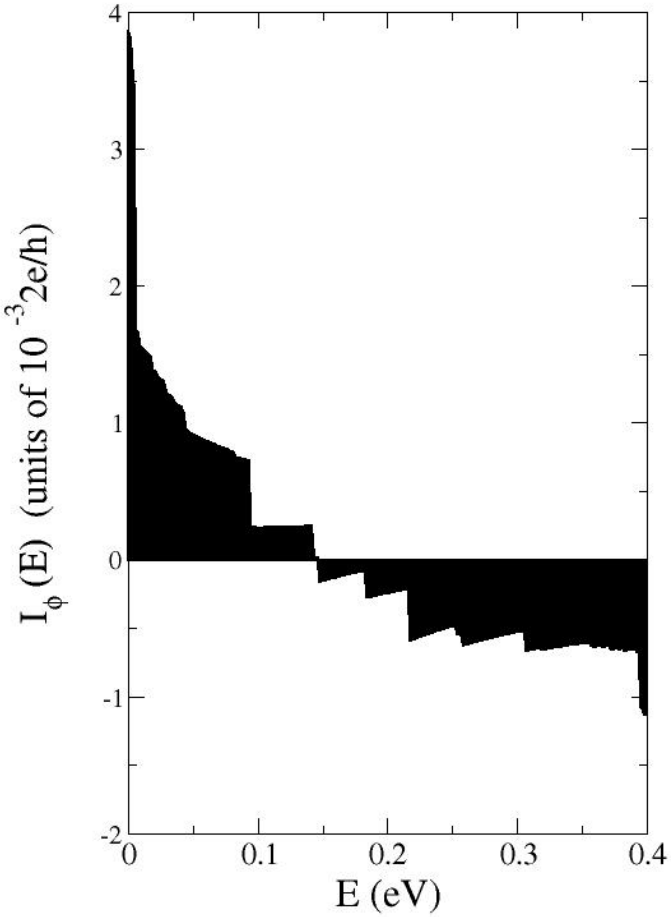
Current density vs Energy

For an applied bias of 400 mV

Inelastic peaks



Power dissipated



Power released at 0.4 V **11 nW**

Power released at 1.0 V **33 nW**

DFT limits

Tunneling is usually calculated using DFT spectrum

DFT theory tends to underestimate Energy gap and HOMO-LUMO gaps in molecules (approx. XC)

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

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

GW QP corrections

Implementation of an approximated GW into DFTB to allow corrections of large systems

GW self-energy:

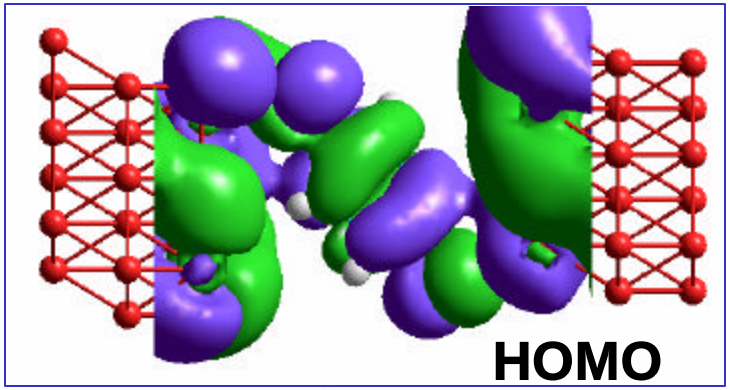
$$\Sigma(r,r',E)=\frac{i}{2p}\int dw G_0(r,r',E-w)W(r,r',w) \quad W=e^{-1}u$$

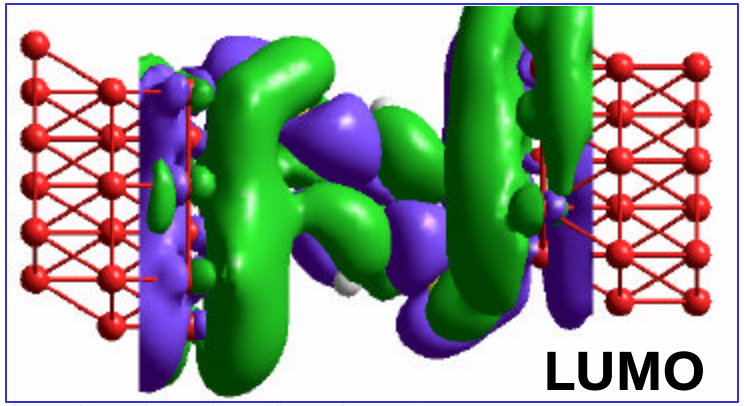
Key approximation:

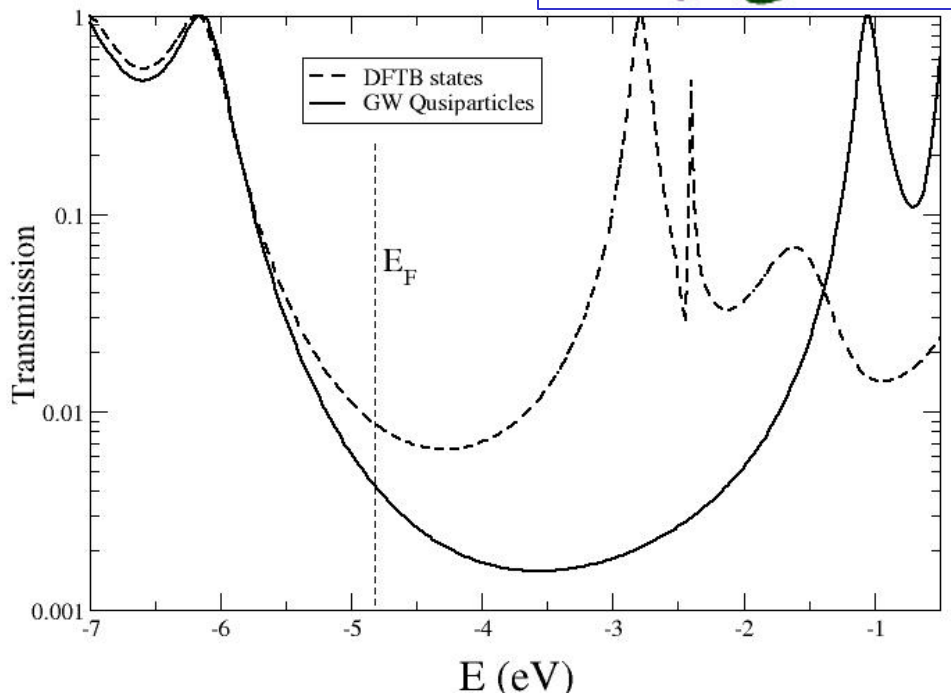
Products of DFTB AO wavefunctions are expressed as:

$$f_m(r)f_n(r)\approx S_{mn}\left[\left|f_m(r)\right|^2+\left|f_n(r)\right|^2\right]$$

Effect of QP


HOMO


LUMO


DFTB states
GW Qusiparticles
E_F
Transmission
E (eV)
1
0.1
0.01
0.001
-7
-6
-5
-4
-3
-2
-1

Conclusions

A method based on NEGF and DFT-TB for coherent and incoherent tunneling in molecular wires has been developed

The method was applied to the realistic molecular systems between Au contacts

We have calculated the total power emitted on molecular wires and made a detailed mode analysis

A first calculation of GW quasiparticle correction and tunneling in Cu-benzene-Cu has been shown