



# Beyond DFT-Landauer Quantum Transport: *Ab Initio* GW-NEGF

## in Nano- and Molecular Electronics

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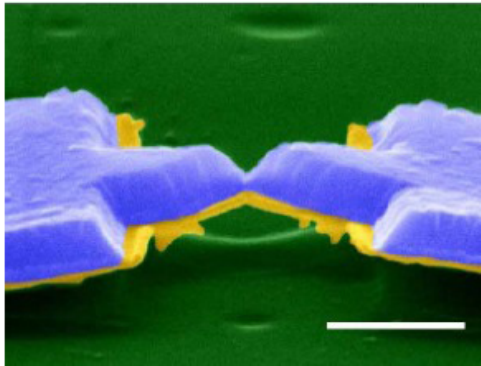
# Outline:

1. Quantum-Transport problem
2. DFT-Landauer Formalism
3. Non-Equilibrium Green's Functions (NEGF) Theory
4. e-e scattering effects and GW
5. Results:
  - Au monoatomic chain
  - BDA / BDT@gold
6. Conclusions

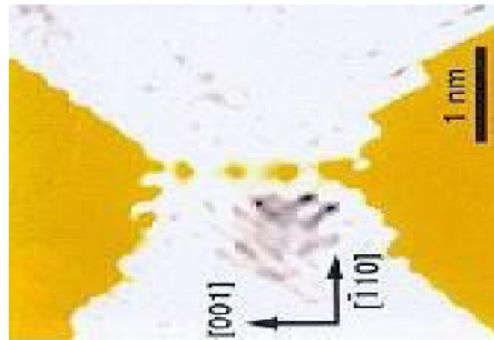
# Molecular and NanoElectronics

## Quantum Transport

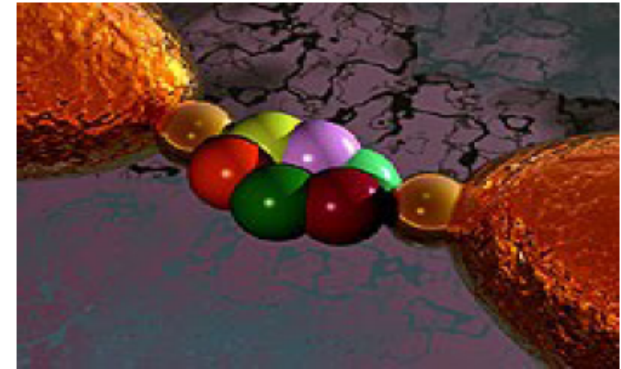
### Nanoscale Electronics Devices



[1] N. Agrait et al.,  
Phys. Rep. (2003)



[2] H. Ohnishi et al.,  
Nature (1998)

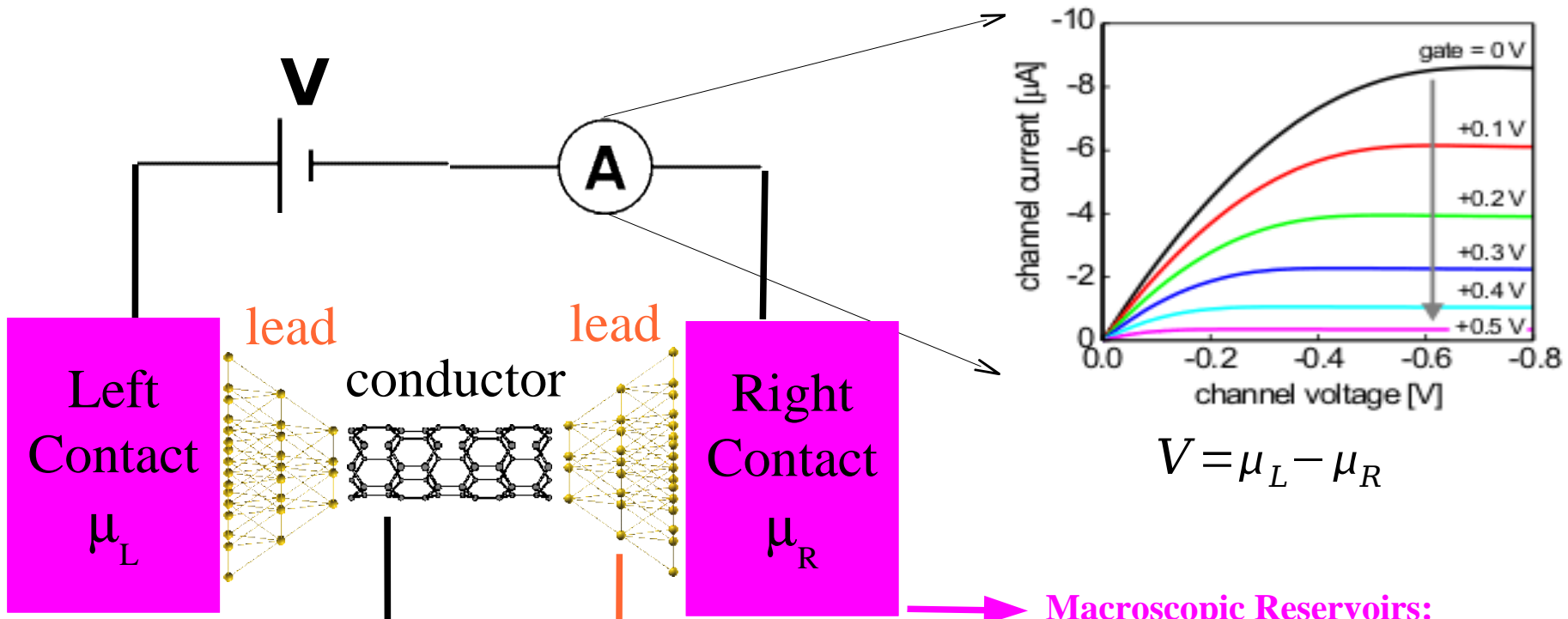


[3] M. Reed et al.,  
Science (1997)

Both an Experimental, a Technological  
and a Theoretical Challenge!

**Real Theoretical challenge:** predict ab initio the I/V Characteristics

# Quantum Transport problem



**Nanoscale Conductor:**  
finite number of states,  
out of equilibrium,  
dissipative effects

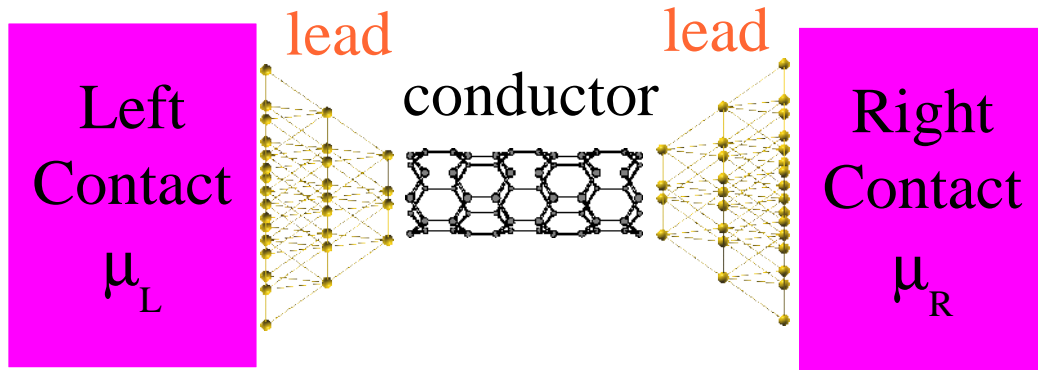
**Mesoscopic Leads:**  
large but finite number of states,  
partial equilibrium,  
ballistic

**Macroscopic Reservoirs:**  
continuum of states,  
thermodynamic equilibrium

We need:

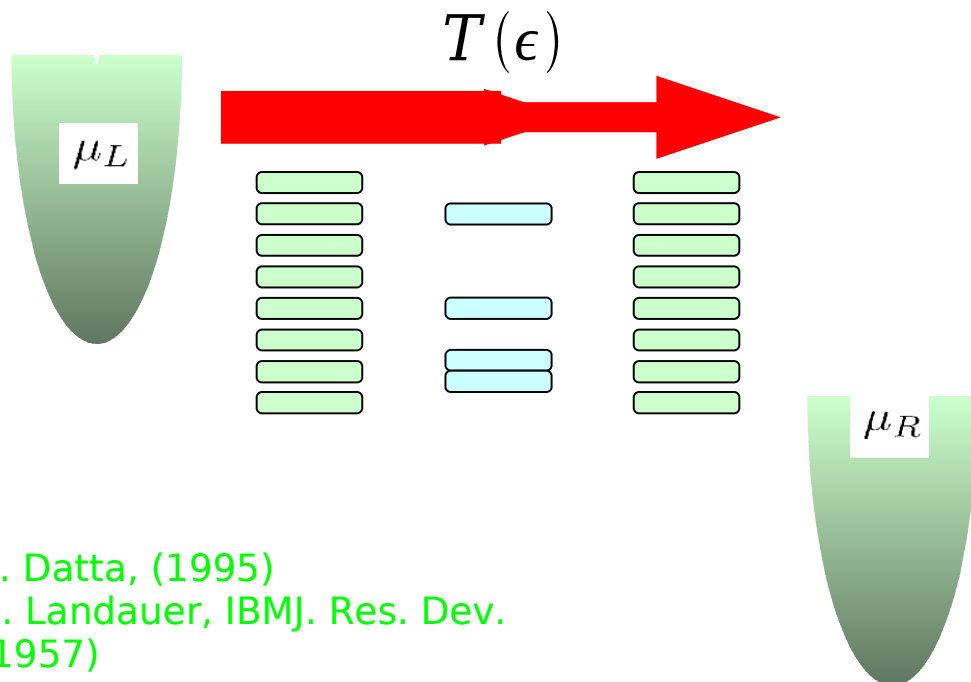
- a First Principle description of the Electronic Structure
- for Finite Voltage: Open System and Out-of-Equilibrium description.

# Landauer Theory

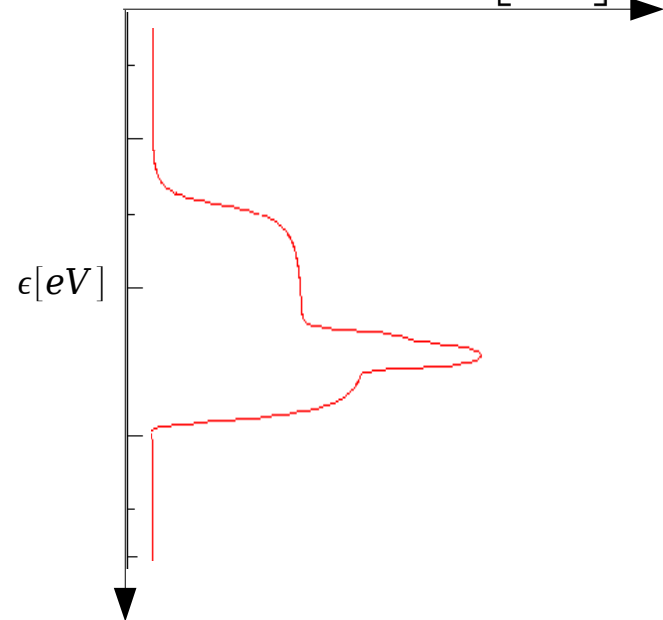


$$C(\epsilon) = \frac{2e^2}{h} M(\epsilon) T(\epsilon)$$

Landauer Formula



Conductance  $\left[ \frac{2e^2}{h} \right]$



# Landauer Theory

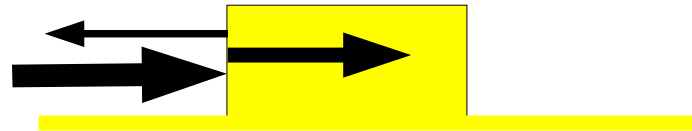
$$C(\epsilon) = \frac{2e^2}{h} M(\epsilon) T(\epsilon)$$

Landauer Formula

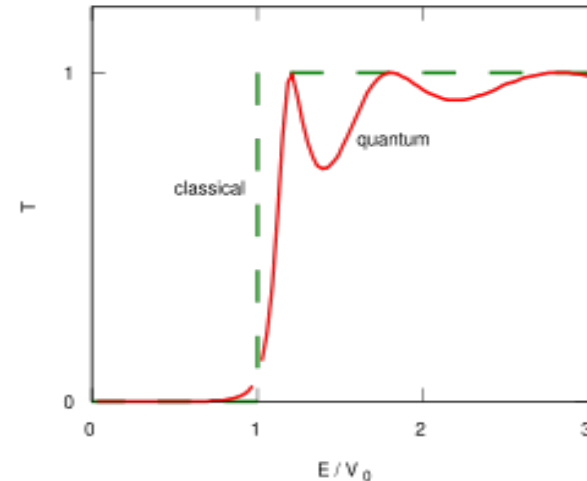
$T(\epsilon)$  Transmittance

1) Calculated via a standard Quantum Mechanics approach:

$$H\psi = \epsilon\psi$$



Example: potential barrier

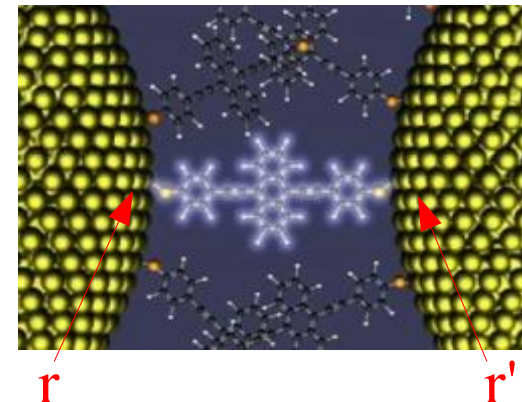


$T(\epsilon)$   $R(\epsilon)$  Transmission and Reflection coefficients

2) Or via a Green's function approach

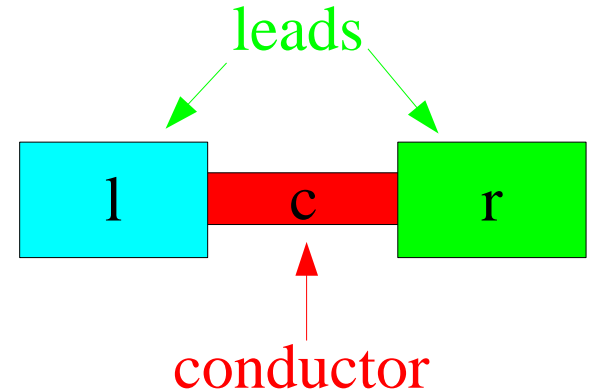
$$(\epsilon - H)G(r, r', \epsilon) = \delta(r, r')$$

probability that an electron of energy  $\epsilon$  injected in  $r$  be transmitted in  $r'$



# Landauer Formula in Green's functions

$$\begin{pmatrix} G_l & G_{lc} & G_{lcr} \\ G_{cl} & G_c & G_{cr} \\ G_{rcl} & G_{rc} & G_r \end{pmatrix} = \begin{pmatrix} (\epsilon - H_l) & -H_{lc} & 0 \\ -H_{lc}^\dagger & (\epsilon - H_c) & -H_{cr} \\ 0 & -H_{cr}^\dagger & (\epsilon - H_r) \end{pmatrix}^{-1}$$



$$G_c = (\epsilon - H_c - \Sigma_l - \Sigma_r)^{-1}$$

conductor  
Green's functions

$$\Sigma_l = H_{lc}^\dagger g_l H_{lc}$$

lead self-energies

$$\Sigma_r = H_{cr} g_r H_{cr}^\dagger$$

$$g_{l,r} = (\epsilon - H_{l,r})^{-1}$$

leads bulk Green's functions

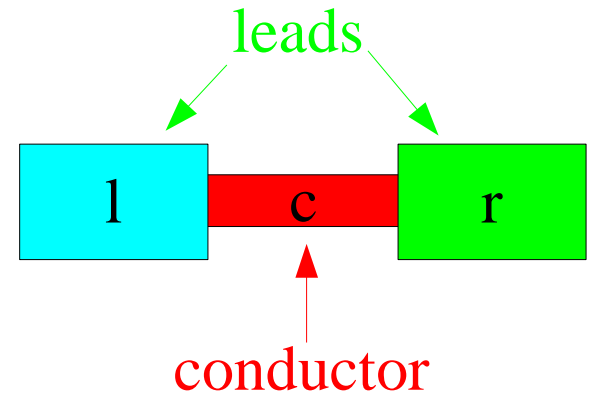
$$\Gamma_{l,r} = i[\Sigma_{l,r}^r - \Sigma_{l,r}^a]$$

conductor-lead coupling

$$\bar{T} = \text{tr}[\Gamma_l G_c^r \Gamma_r G_c^a]$$

Fisher-Lee relation

# Landauer on top of DFT



What to take for the hamiltonian? 
$$H = \begin{pmatrix} H_l & H_{lc} & 0 \\ H_{lc}^\dagger & H_c & H_{cr} \\ 0 & H_{cr}^\dagger & H_r \end{pmatrix}$$

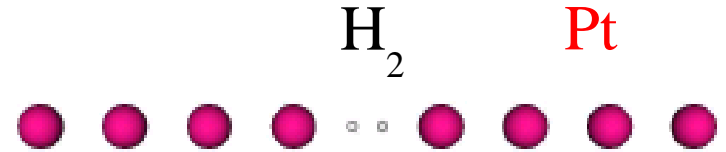
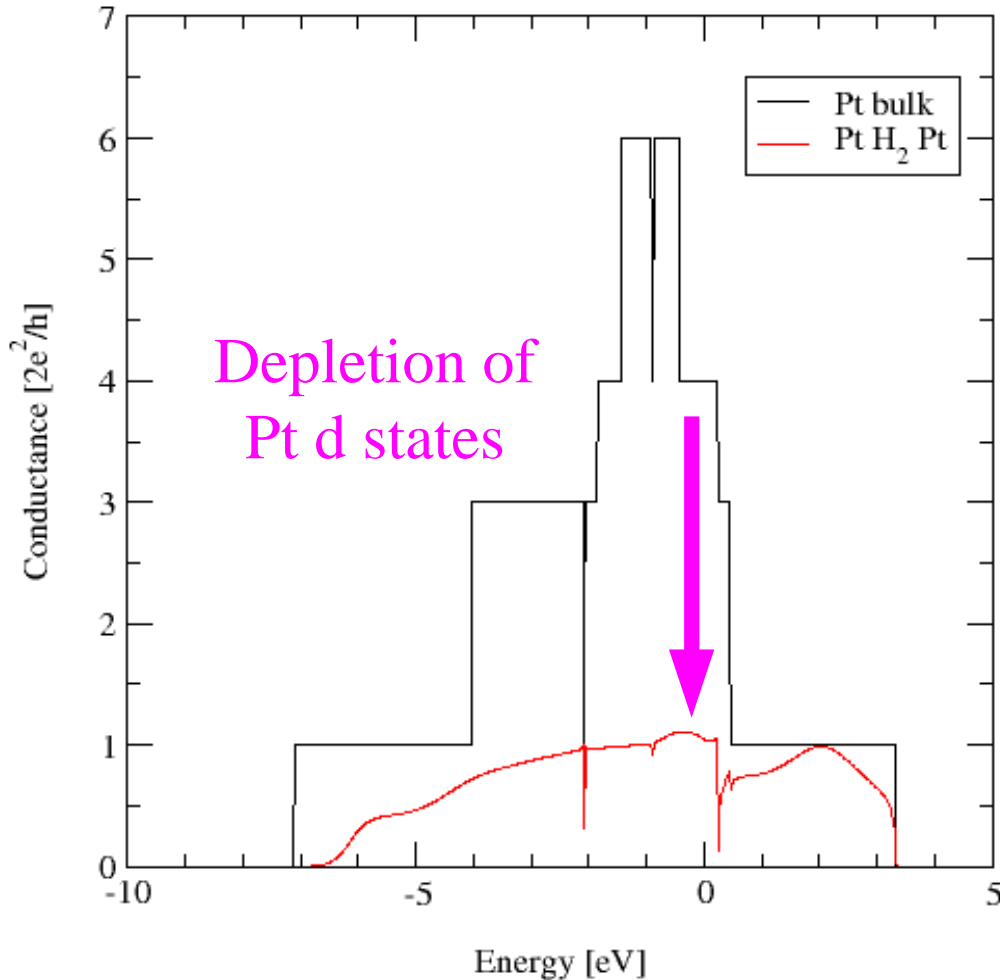
**the DFT Kohn-Sham hamiltonian!**

(represented on a real space basis like atomic orbitals,  
Wannier functions, etc.)

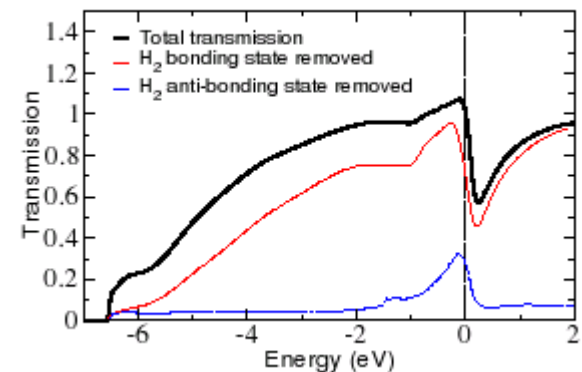


# Example of Landauer conductance

H<sub>2</sub> molecule between Platinum leads



EXP (break junctions):  $C(0) \sim 1$  [ $G_0 = 2e^2/h$ ]  
R.H.M. Smit et al, Nature **419**, 906 (2002)



K.S. Thygesen K.W. Jakobsen,  
Chem. Phys. (2005)

# Landauer approach

Correctly describes:

- ✓ Contact Resistance
- ✓ Scattering on Defects, Impurities
- ✓ Non-commensurability patterns

# DFT-Landauer drawbacks

- ✗ The DFT Kohn-Sham electronic structure is in principle **unphysical**.
- ✗ DFT, no Open Systems, no Out-of-Equilibrium Theory:
  - ✗ only **linear response, small bias**.
- ✗ Non interacting quasiparticles:
  - ✗ only **coherent** part of transport.

 Need to go Beyond!

# Beyond LB-DFT: 2 Possibilities

- TDDFT for Quantum Transport
  - ✓ promising possibility
  - ✗ need a suitable approx for xc
  - ✗ cannot deal with open systems
- NEGF (NonEquilibrium Green's Function theory)
  - ✓ full access to all observables
  - ✓ it has maybe a more intuitive physical meaning

# Non-Equilibrium Green's Function Theory (NEGF)

(improperly called Keldysh theory)

Much more complete framework, allows to deal with:

- **Many-Body** description of **incoherent** transport (electron-electron interaction, electronic correlations and also electron-phonon);
- **Out-of-Equilibrium** situation;
- **Access to Transient** response (beyond Steady-State);
- Reduces to Landauer for coherent transport.

The theory is due to the works of Schwinger, Baym, Kadanoff and Keldysh

# Many-Body Finite-Temperature formalism

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

hamiltonian

many-body

$$\bar{O} = \frac{\sum_i e^{-\beta E_i} \langle \Psi_i | \hat{O} | \Psi_i \rangle}{\sum_i e^{-\beta E_i}} = \text{tr} [\hat{\rho}(\hat{H}) \hat{O}]$$

observable

$$\hat{\rho}(\hat{H}) = \frac{e^{-\beta \hat{H}}}{\text{tr}[e^{-\beta \hat{H}}]}$$

statistical weight

# NEGF formalism

$$\hat{H}(t) = \hat{H} + \hat{U}(t) = \hat{T} + \hat{V} + \hat{W} + \hat{U}(t) \quad \text{hamiltonian}$$

many-body + time-dependence

$$\bar{o}(t) = \text{tr}[\hat{\rho}(\hat{H}) \hat{o}_H(t)] \quad t > t_0 \quad \text{observable}$$

$$\hat{\rho}(\hat{H}) = \frac{e^{-\beta \hat{H}}}{\text{tr}[e^{-\beta \hat{H}}]}$$

statistical weight referred to  
the unperturbed Hamiltonian and  
the equilibrium situation before  $t_0$

# Time Contour

$$\hat{O}_H(t) = \hat{S}(t_0, t) \hat{O}(t) \hat{S}(t, t_0)$$

Heisenberg representation

$$\hat{S}(t, t_0) = T \left\{ \exp \left( -i \int_{t_0}^t dt' \hat{H}(t') \right) \right\}$$

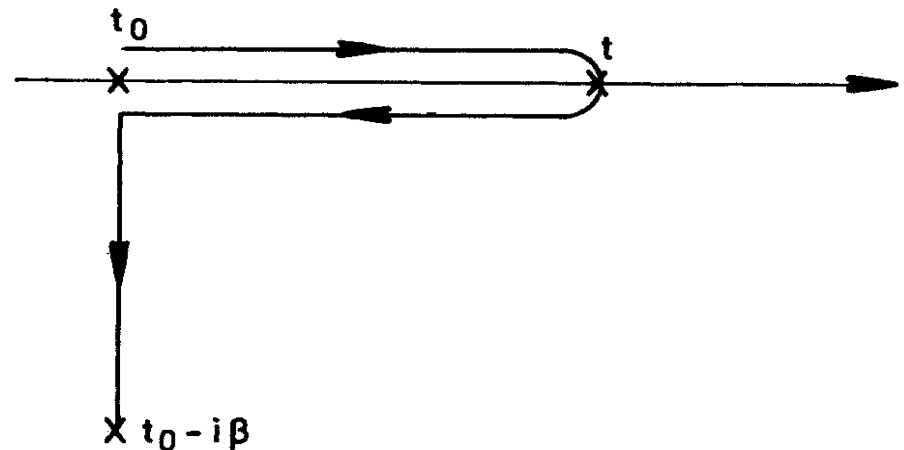
evolution operator

$$\hat{S}(t_0 - i\beta, t_0) = e^{-\beta \hat{H}}$$

trick to put the equilibrium weight into the evolution

$$\bar{O}(t) = \frac{\text{tr}[\hat{S}(t_0 - i\beta, t_0) \hat{S}(t_0, t) \hat{O}(t) \hat{S}(t, t_0)]}{\text{tr}[\hat{S}(t_0 - i\beta, t_0)]}$$

$$\bar{O}(t) = \frac{\text{tr}[T_C[\exp(-i \int_C dt' \hat{H}(t')) \hat{O}(t)]]}{\text{tr}[T_C[\exp(-i \int_C dt' \hat{H}(t'))]]}$$

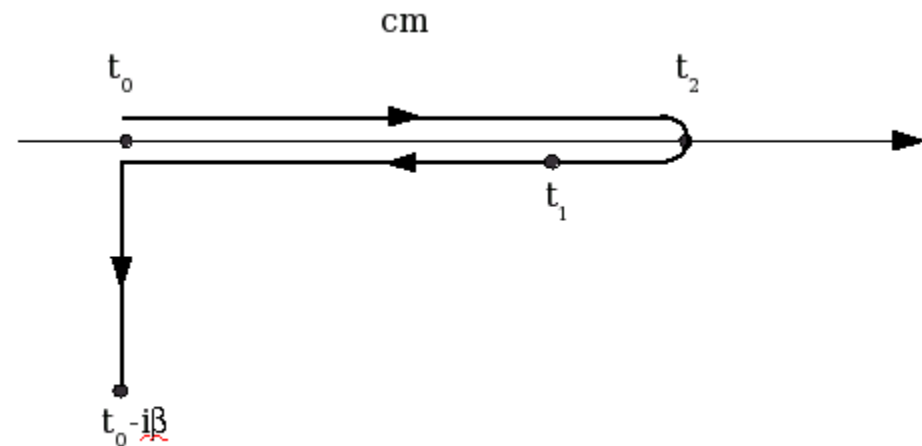




# Contour and Perturbation Theory

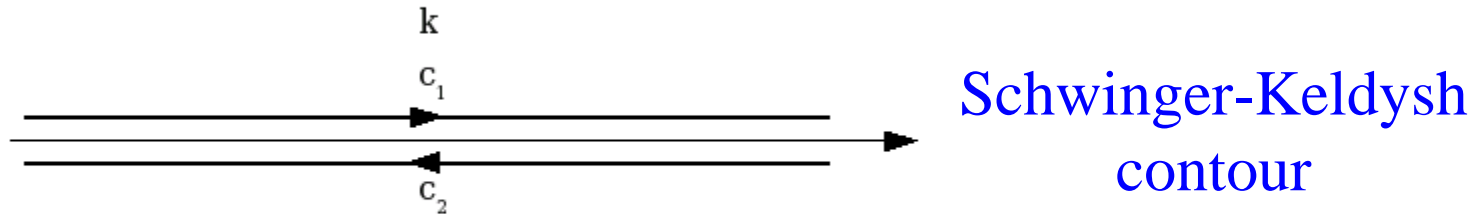
$$G^{co}(x_1, x_2) = (-i) \overline{T_c \{ \psi_H(x_1) \psi_H^\dagger(x_2) \}} \quad \text{contour ordered Green's function}$$

- To recover perturbation theory (Wick's theorem, Feynman diagrams, etc.) you have to declare the Green's function and all the quantities on the Closed Contour.



$$G^{co}(x_1, x_2) = \begin{cases} G^{t_0}(x_1, x_2) & t_1, t_2 \in C_{\rightarrow} \\ G^{<}(x_1, x_2) & t_1 \in C_{\rightarrow}, t_2 \in C_{\wedge} \\ G^{>}(x_1, x_2) & t_1 \in C_{\wedge}, t_2 \in C_{\rightarrow} \\ G^{ato}(x_1, x_2) & t_1, t_2 \in C_{\wedge} \end{cases}$$

# Keldysh Formulation



$$G^{ko} \rightarrow \mathbf{G} = \begin{pmatrix} \mathbf{G}_{11} & \mathbf{G}_{12} \\ \mathbf{G}_{21} & \mathbf{G}_{22} \end{pmatrix}$$

$$\mathbf{G}_{11}(x_1, x_2) = G^{to}(x_1, x_2)$$

$$\mathbf{G}_{12}(x_1, x_2) = G^{<}(x_1, x_2)$$

$$\mathbf{G}_{21}(x_1, x_2) = G^{>}(x_1, x_2)$$

$$\mathbf{G}_{22}(x_1, x_2) = G^{ato}(x_1, x_2)$$

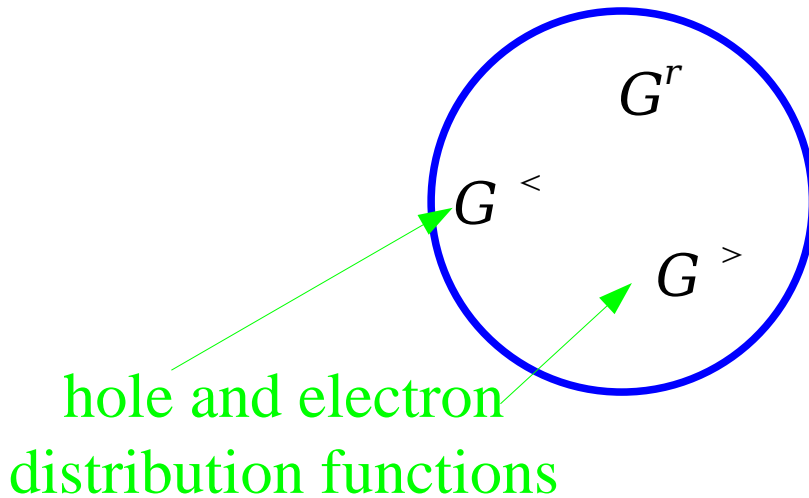
$$\mathbf{G}' = \begin{pmatrix} 0 & G^a \\ G^r & G^k \end{pmatrix} \quad \text{Keldysh formulation}$$

$$G^k = G^{>} + G^{<}$$

Keldysh Green's function

$$\mathbf{G}'' = \begin{pmatrix} G^r & G^k \\ 0 & G^a \end{pmatrix} \quad \text{Larkin-Ovchinnikov formulation}$$

# Green's and Correlation Functions



Out of Equilibrium  
we need to introduce  
at least three unrelated  
“Green's” functions.

Once we know the Green's  
and the Correlation functions,  
the problem is solved!  
They contain all the physics!

$$G^{t^o} = G^r + G^<$$

$$A = i(G^r - G^a) \quad \text{Spectral Function}$$

$$-iG^<(\omega) = f_{FD}(\omega) A(\omega)$$

$$iG^>(\omega) = [1 - f_{FD}(\omega)] A(\omega)$$

At Equilibrium the Correlation  
functions are related to the Green's  
function through the Fermi-Dirac  
distribution.

# NEGF Fundamental Kinetic Equations

$$G^r = [\omega - H_c - \Sigma^r]^{-1}$$

$$G^< = G^r \Sigma^< G^a$$

$$G^> = G^r \Sigma^> G^a$$

Caveat!: in case we want to consider also the transient, then we should add another term to these equations:

$$G^< = G^r \Sigma^< G^a + (1 + G^r \Sigma^r) G^{0<} (1 + \Sigma^a G^a) \quad \text{Keldysh equation}$$

# Self-Energy and Scattering Functions

$\Sigma^r$  Self-Energy

$\Sigma^<$  In-scattering function  
(represent the rate at which the electrons come in)

$\Sigma^>$  Out-scattering function

$$\Gamma = i(\Sigma^r - \Sigma^a) \quad \text{Decay Rate}$$

$$-i \Sigma^<(\omega) = f_{FD}(\omega) \Gamma(\omega)$$

$$i \Sigma^>(\omega) = [1 - f_{FD}(\omega)] \Gamma(\omega)$$

At Equilibrium

# Quantum Transport: composition of the Self-energy

$$\Sigma^{r<>} = \sum_p \Sigma_p^{r<>} + \Sigma_{e-ph}^{r<>} + \Sigma_{e-e}^{r<>}$$

↑ interaction with the leads     
 ↑ electron-phonon interaction     
 ← electron-electron interaction -> ?

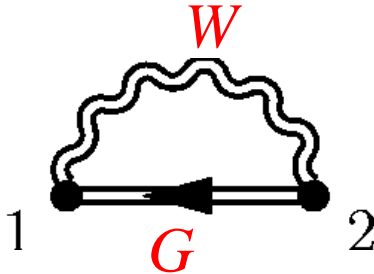
→ SCBA (Frederiksen et al. PRL 2004)

Critical point :

- Choice of relevant approximations for the Self-Energy and the in/out scattering functions

# e-e interactions, our choice: the GW Approximation

$$\Sigma_{GW}(x_1, x_2) = iG(x_1, x_2)W(x_1, x_2) \quad \text{GW Self-Energy}$$

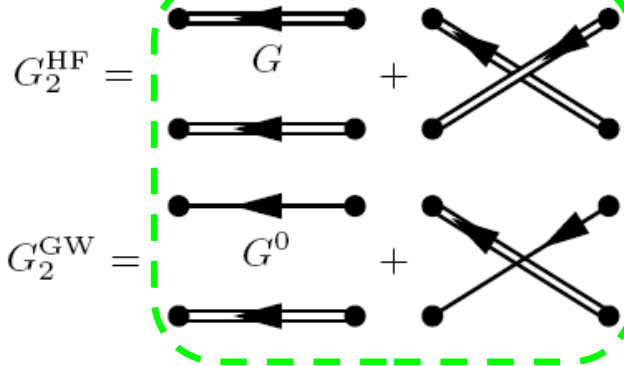
$$\Sigma_M^{GW}(x_1, x_2) = \text{Diagram}$$


# Why GW?

Direct and Exchange terms:

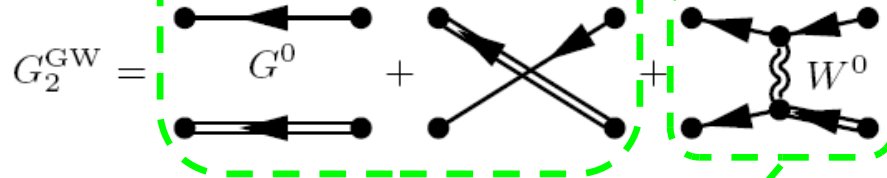
**Band Structure Renormalization**

**Self-consistent Hartree-Fock**



$\Rightarrow \Sigma\{>, <\} = 0$

**$G^0W^0$**



$\Rightarrow \Sigma\{>, <\} \neq 0$

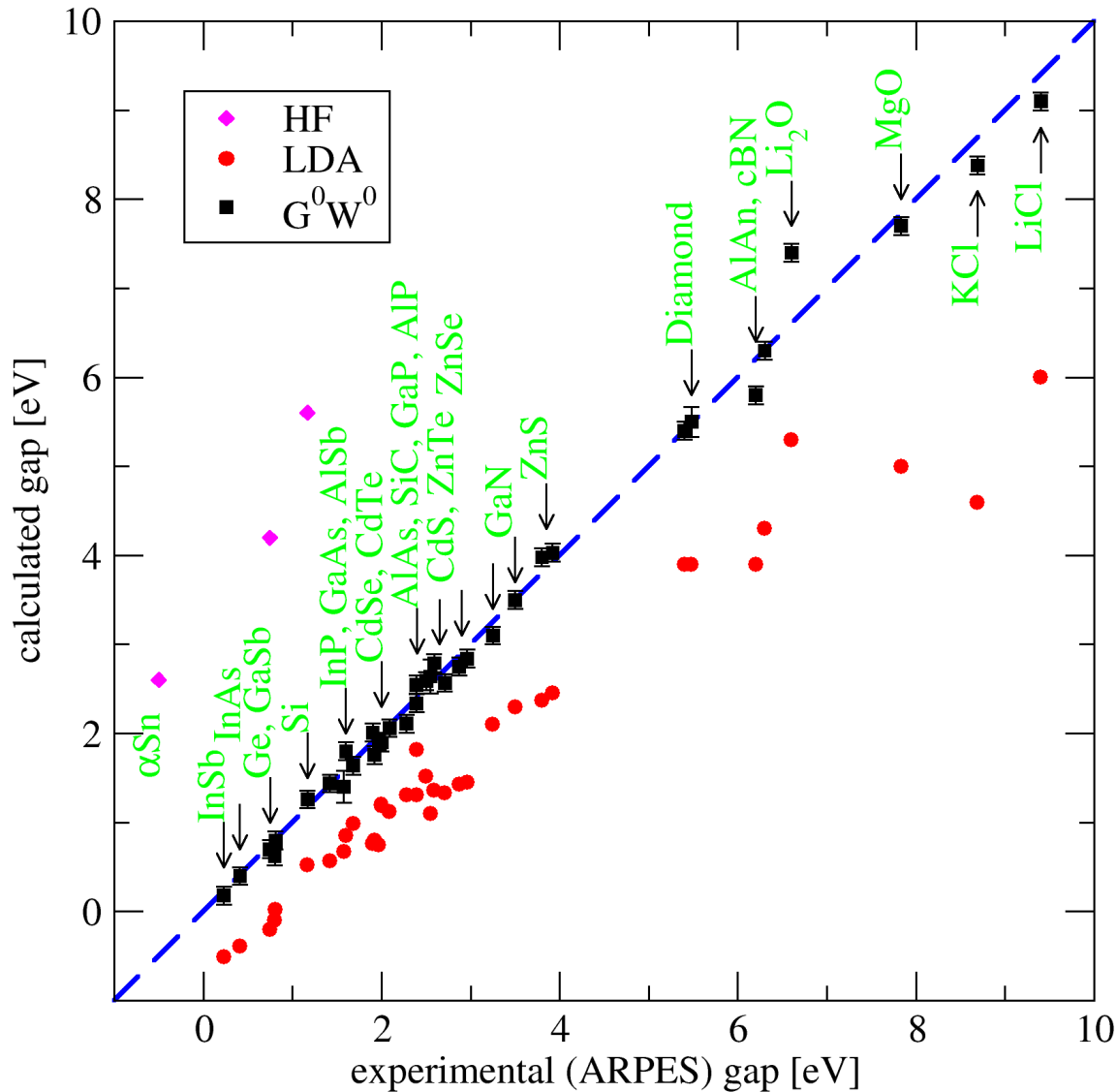
Collisional Term:

Band structure renormalization for Electronic Correlations +  
**e-e Scattering ->**

**Conductance Degrading Mechanisms, Resistance, non-coherent transport**



# Why GW?



**Band renormalization (band gap) in good agreement with the experiment!**

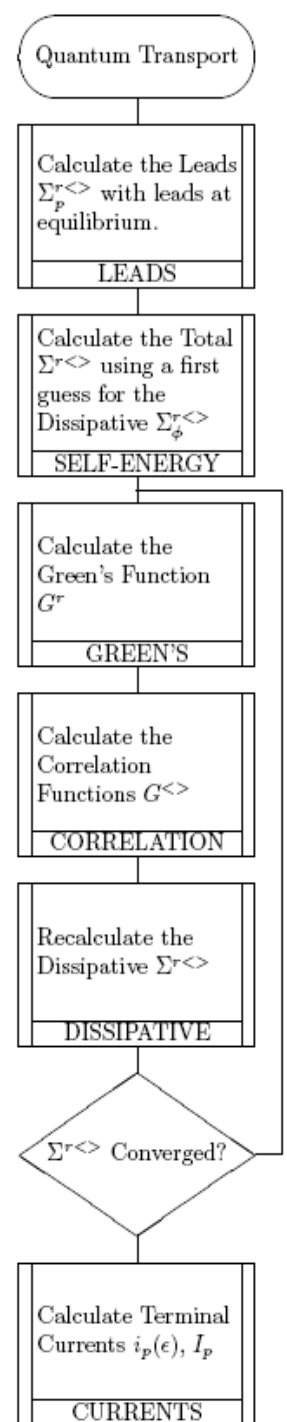
# NEGF Quantum Transport resolution scheme

## Iterating the Kinetic Equations

(G and  $\Sigma$  have to be recalculated at each iteration):

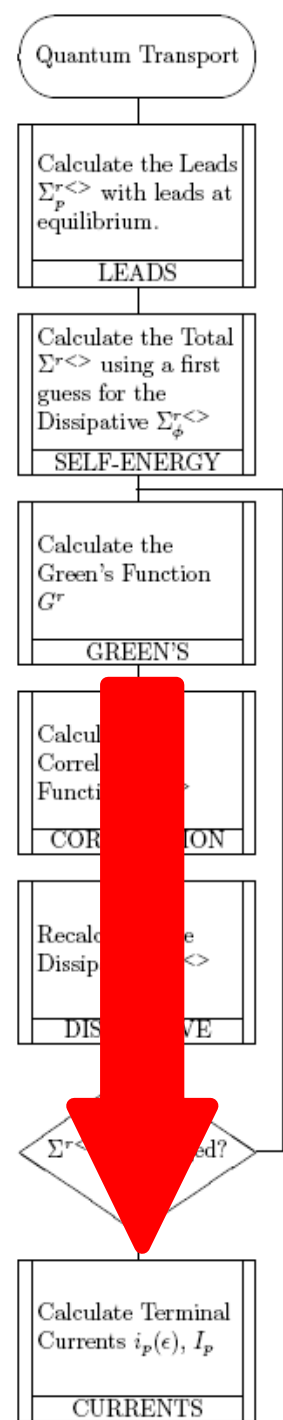
➡ Highly Time-consuming

➡ So far applied to model Hamiltonians (Anderson, Kondo)  
But very few applications for real systems

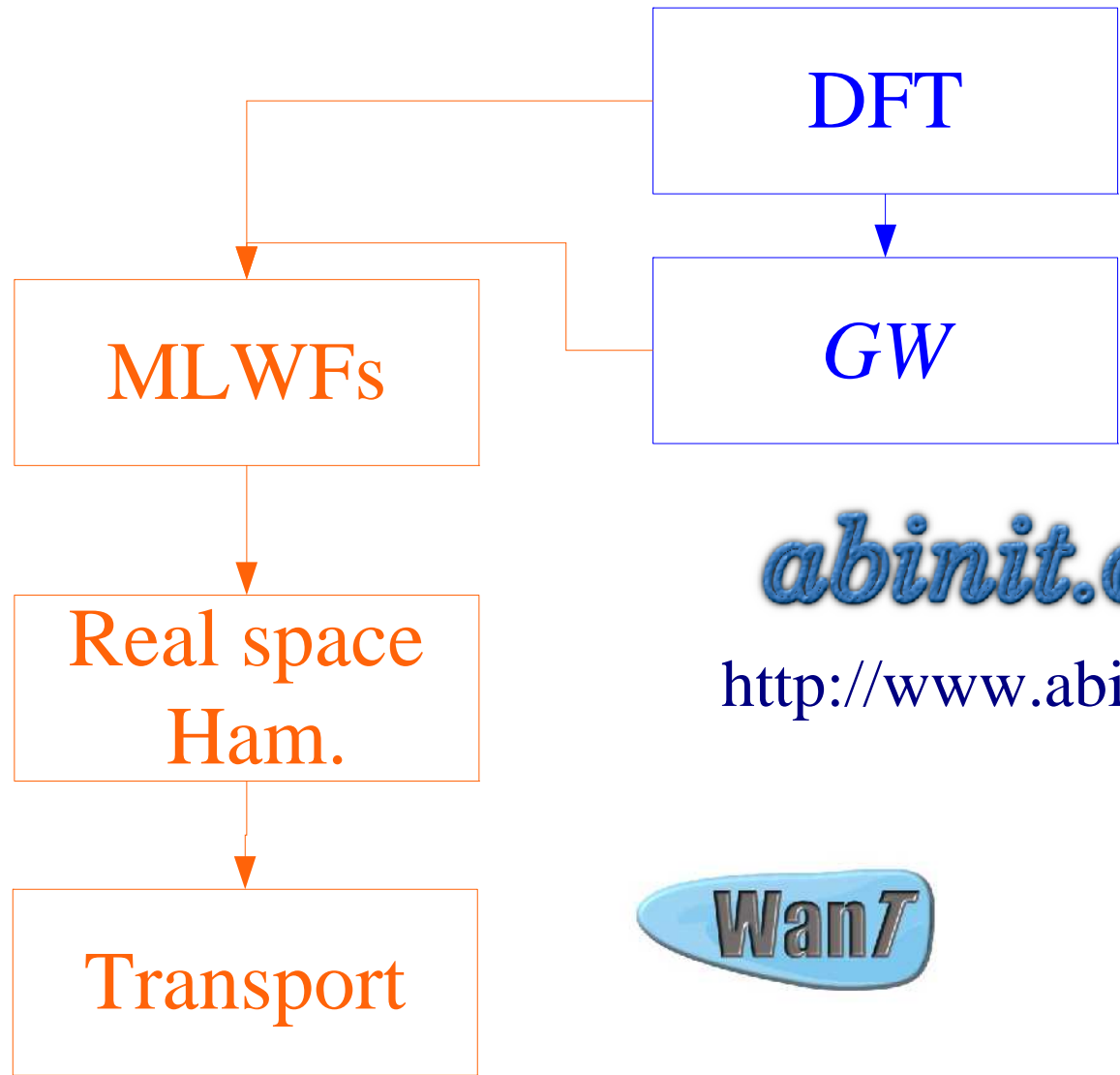


# Our Scheme

- **Approximations:**
  - 1)  $G^0W^0$  Non Self-Consistently
  - 2) Equilibrium (linear response, small bias)
  - 3) Neglect Transient (Steady-State)
- **We take into account:**
  - 1) Many-Body Correlations (Renormalization of the electronic structure)
  - 2) e-e Scattering (appearance of Resistance and Loss-of-Coherence)
  - 3) Finite Lifetime and Dynamical effects (beyond Plasmon-Pole GW)



# Flow diagram



*abinit.org*

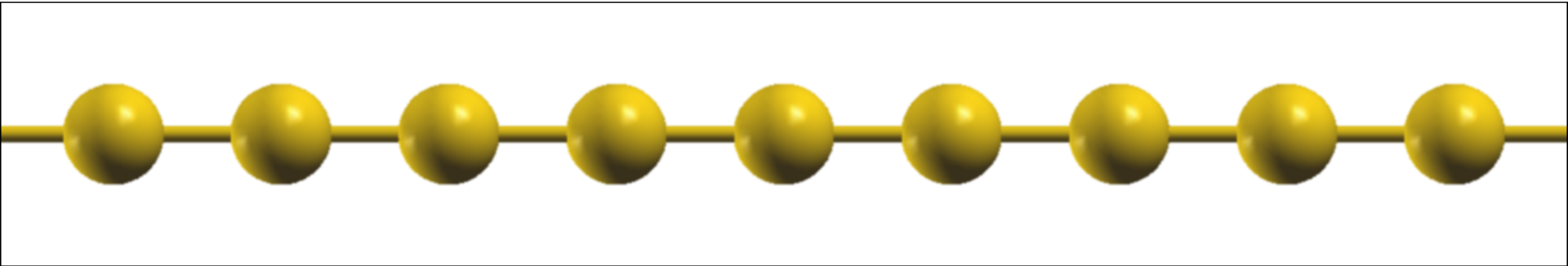
<http://www.abinit.org>



<http://www.wannier.org>

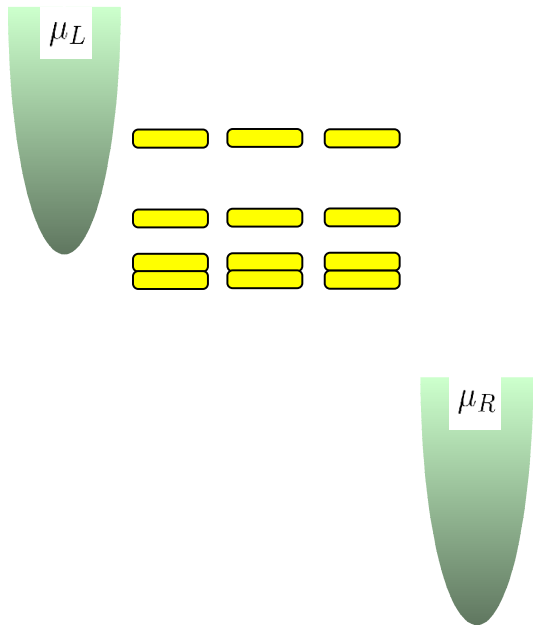
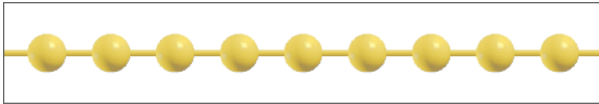
<http://www.wannier-transport.org>

# Results on **Au Monoatomic Chain**



# GW on Au Monoatomic chain: renormalization of the energies

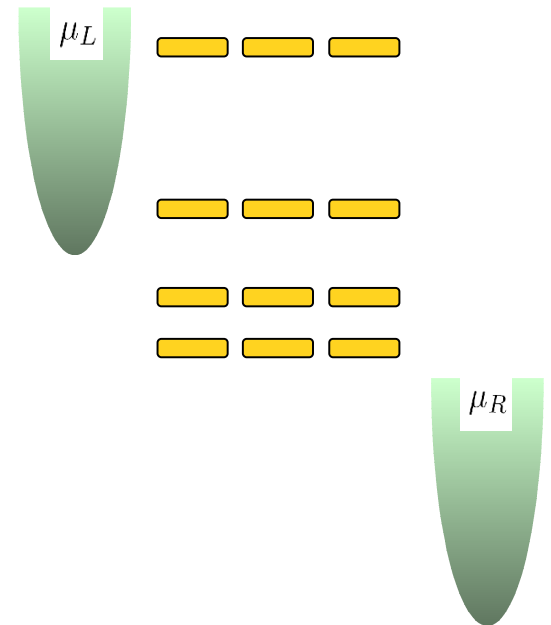
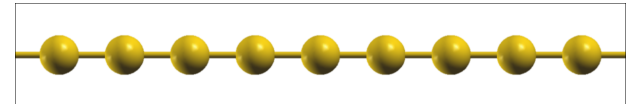
**Kohn-Sham Au chain**



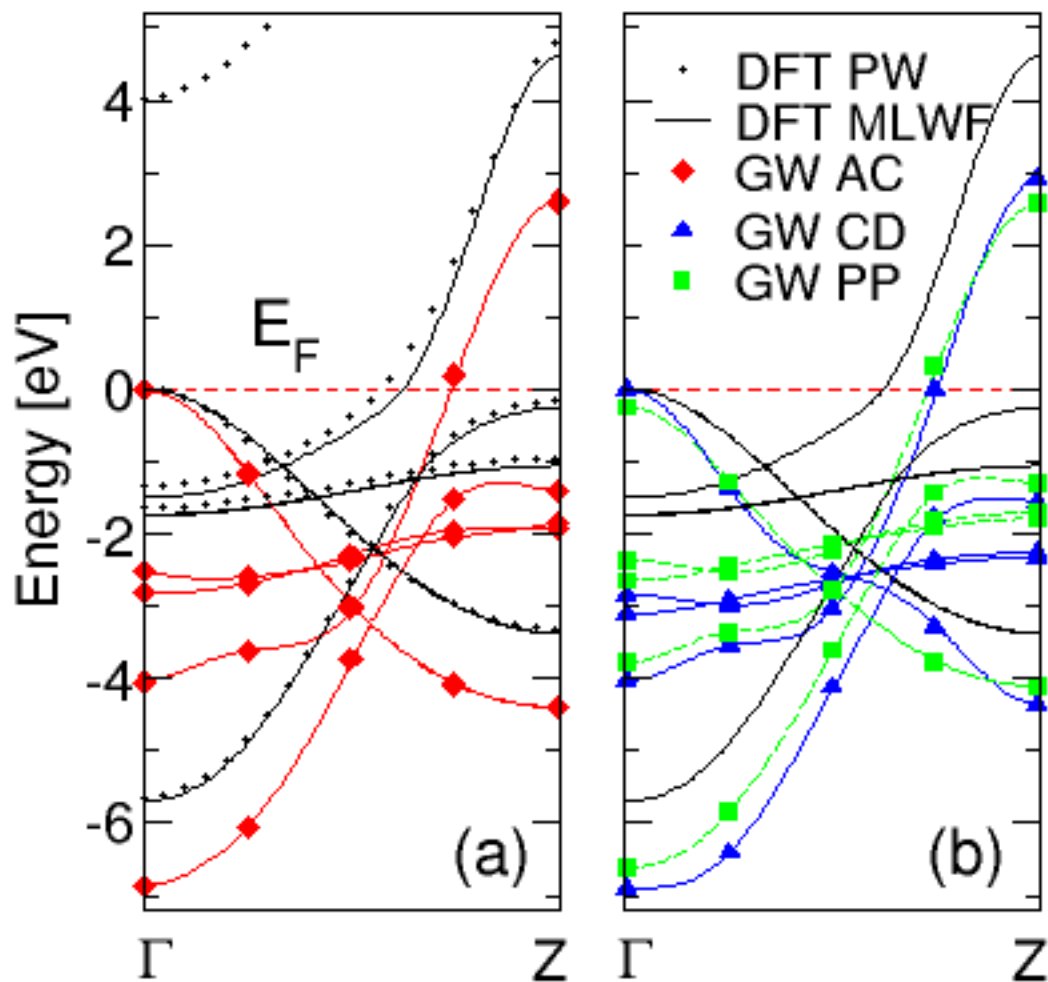
$$\epsilon^{KS} \Rightarrow \epsilon^{GW}$$



**GW Au chain**



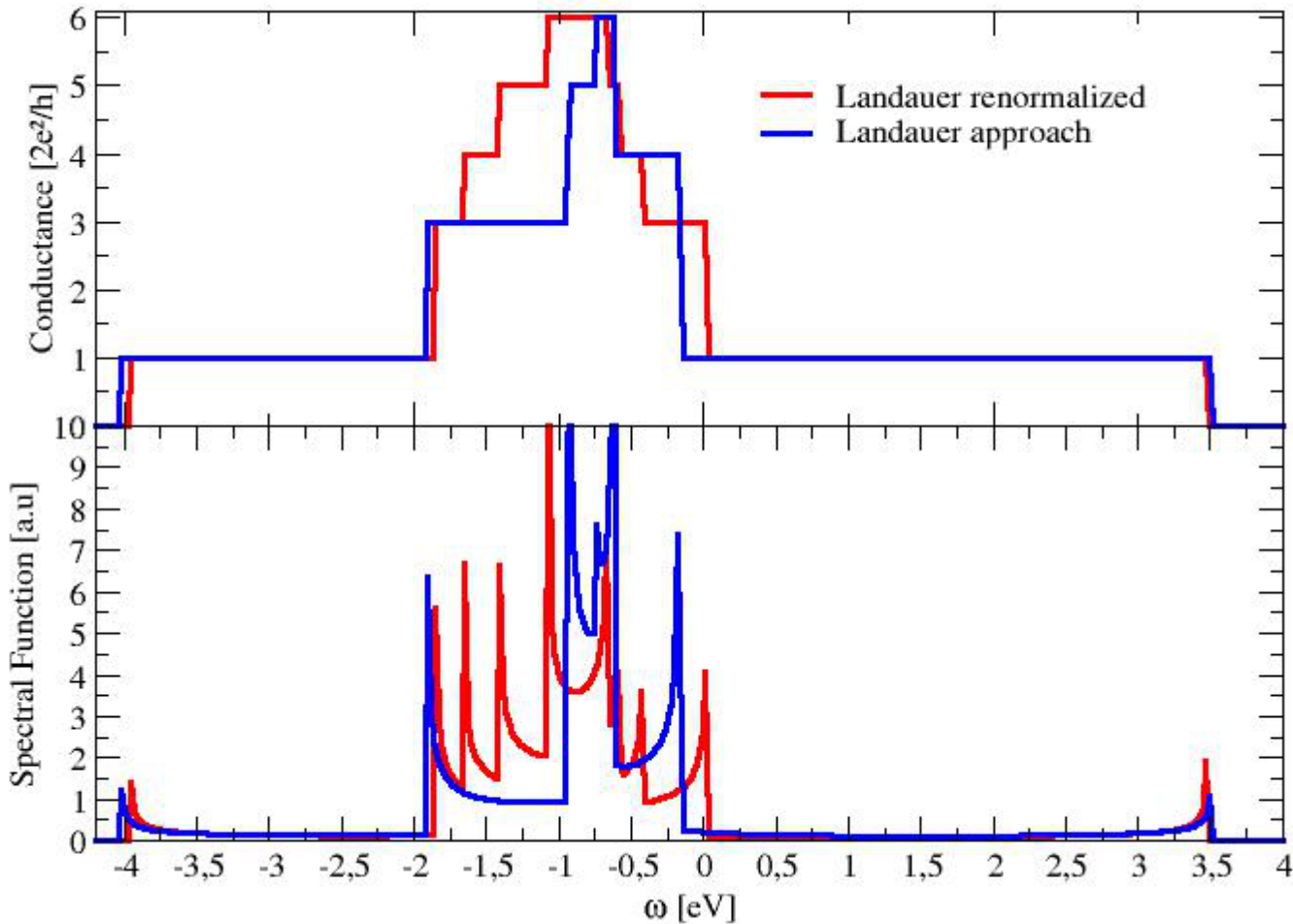
# Monoatomic Gold chain: GW vs DFT bandplot



PPM Plasmon-Pole Model  
AC Analytic Continuation  
CD Contour Deformation  
(more or less the same)

# GW vs DFT

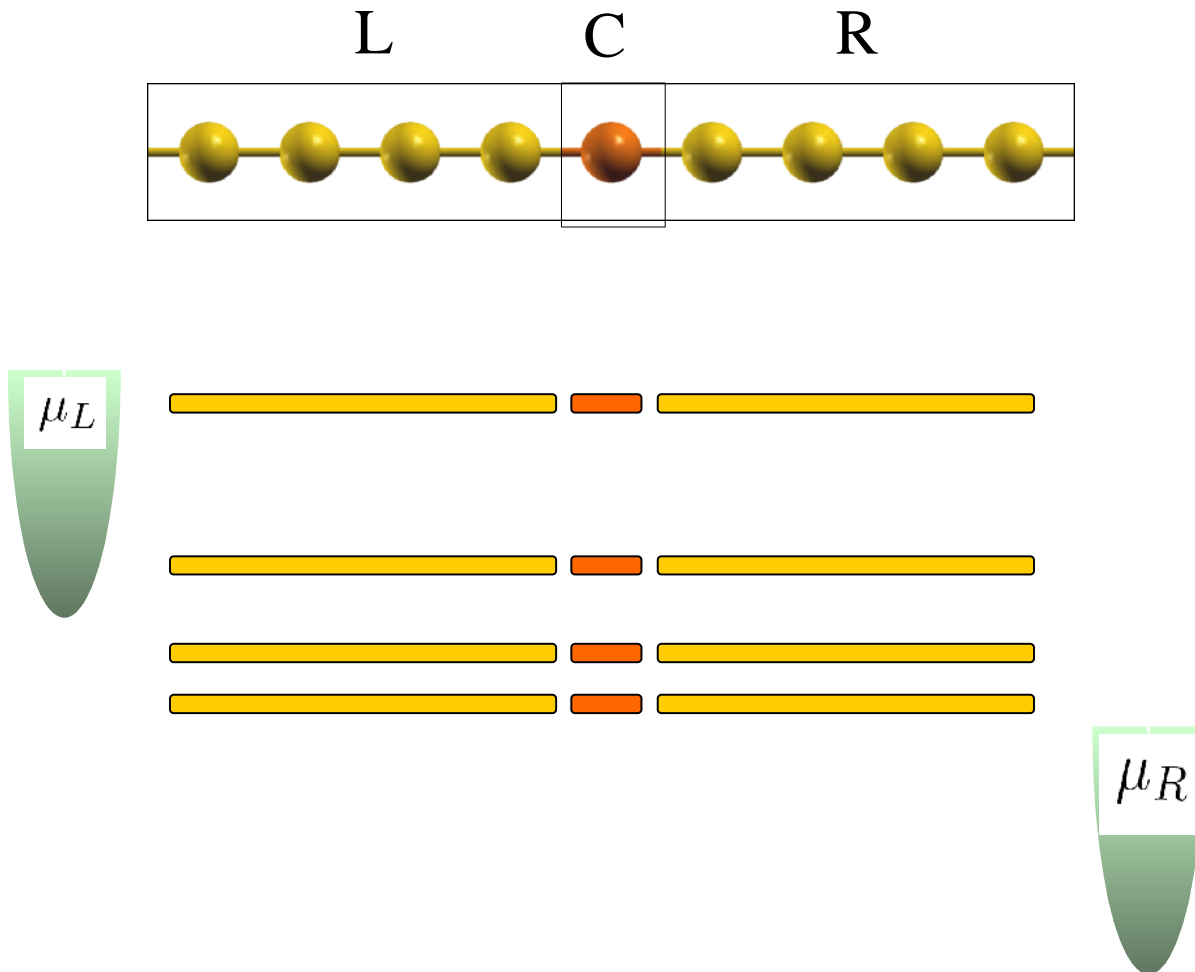
## Landauer Conductance



- non-negligible rearrangement of the conductance channels
- Still **ballistic** conductor (flat plateaus)

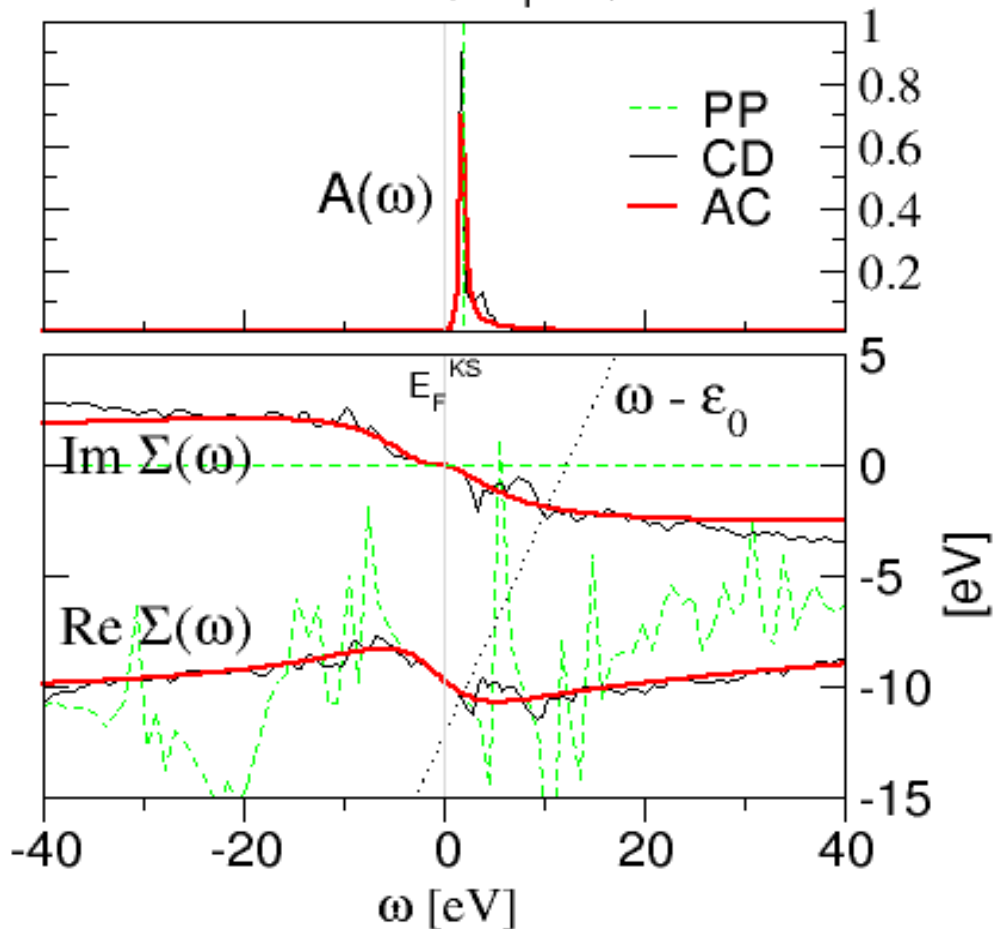


# e-e scattering switched on only in the Central part



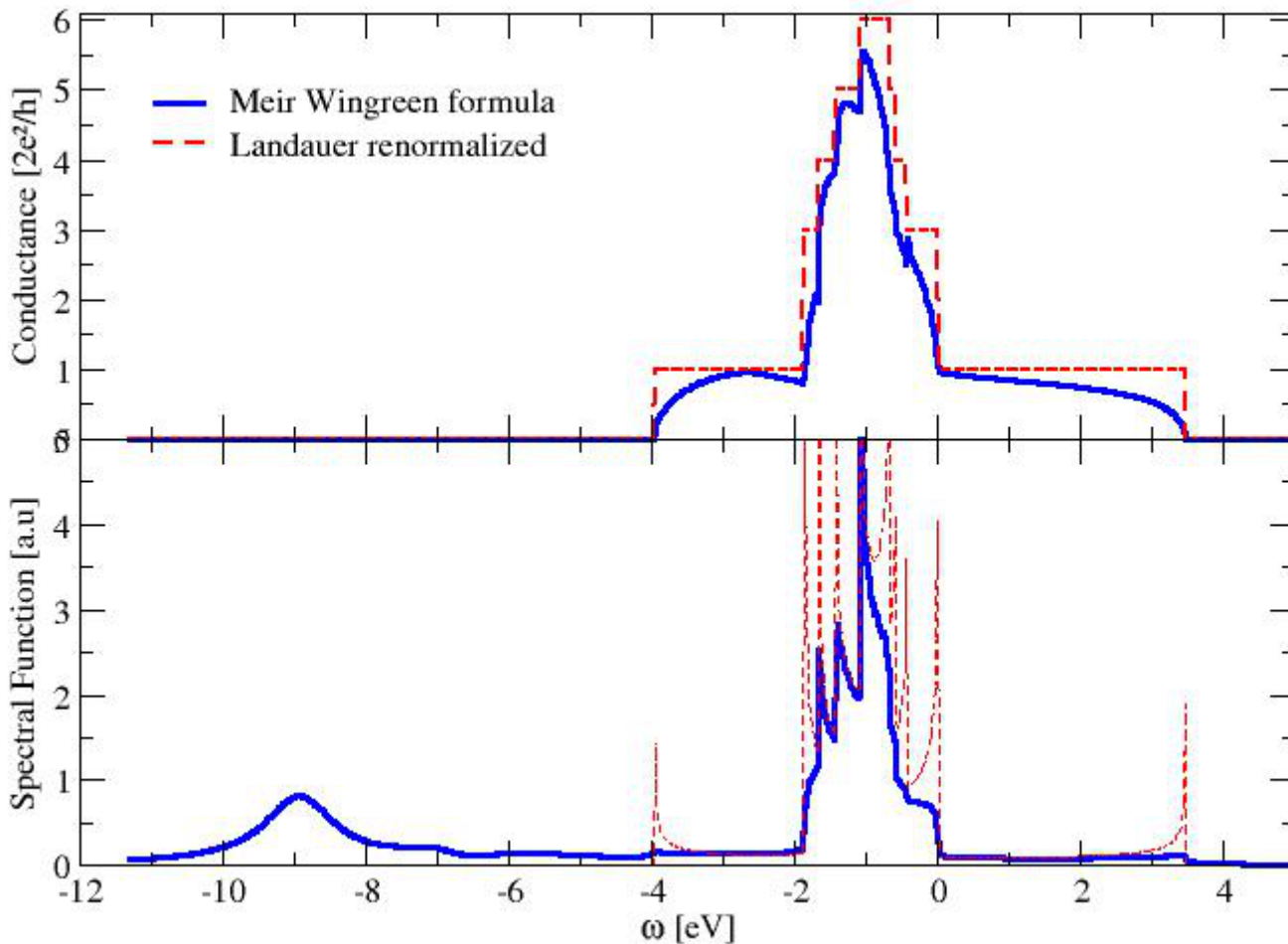
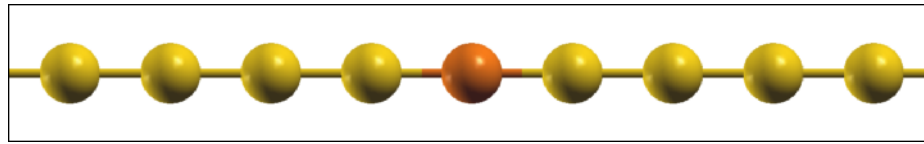
# Self-Energy and Spectral Function

$k=0.375$   
6th band ( $\sim E_F^{GW}$ )



- The Analytic Continuation smooths the more accurate Contour Deformation

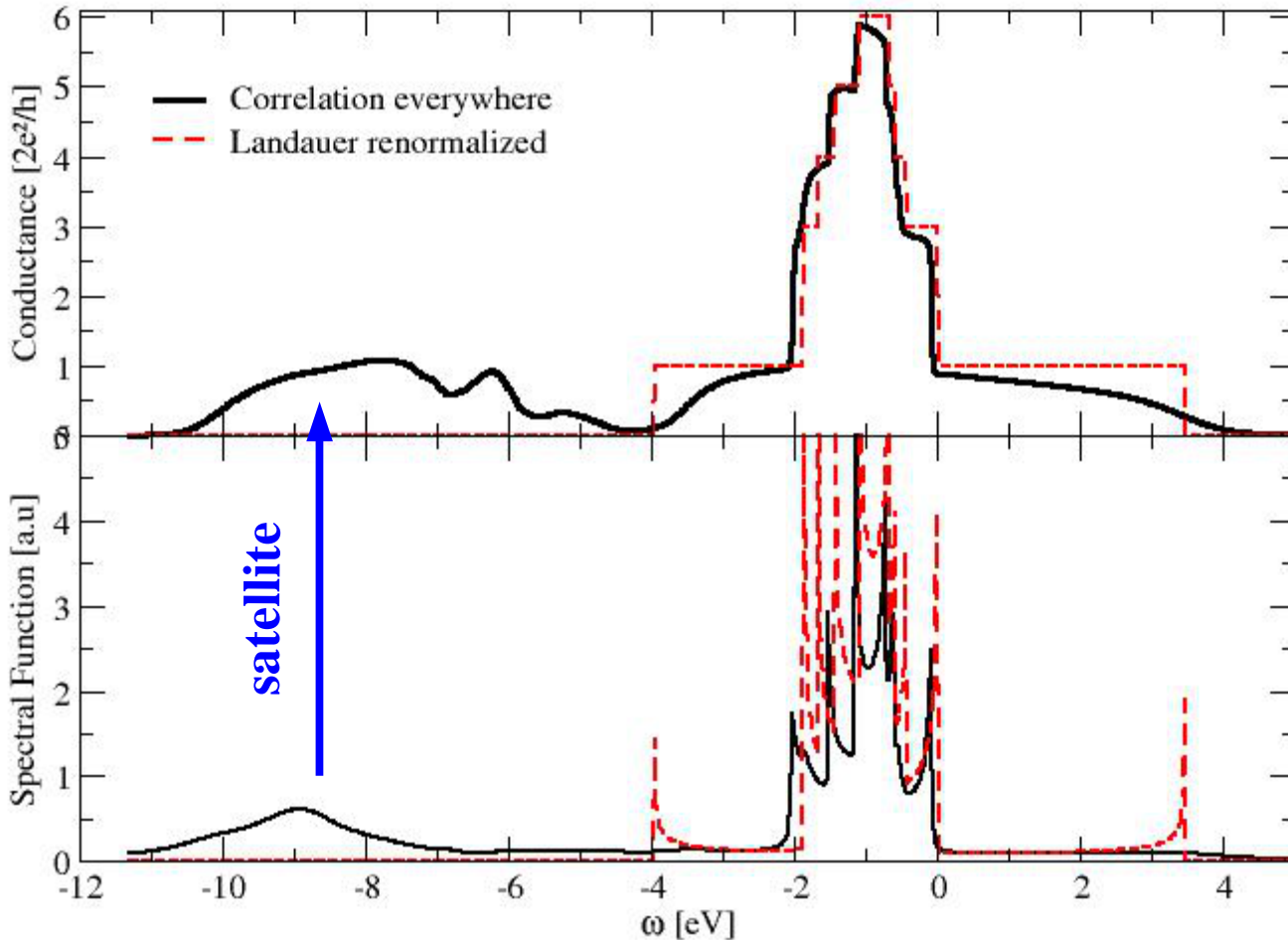
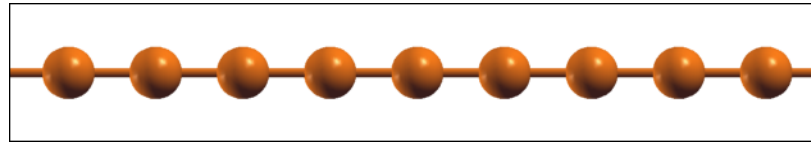
# e-e scattering only in the Conductor



Loss of Conductance:  
→ **Appearance of Resistance**

**Broadening of the peaks:**  
→ **QP lifetime**

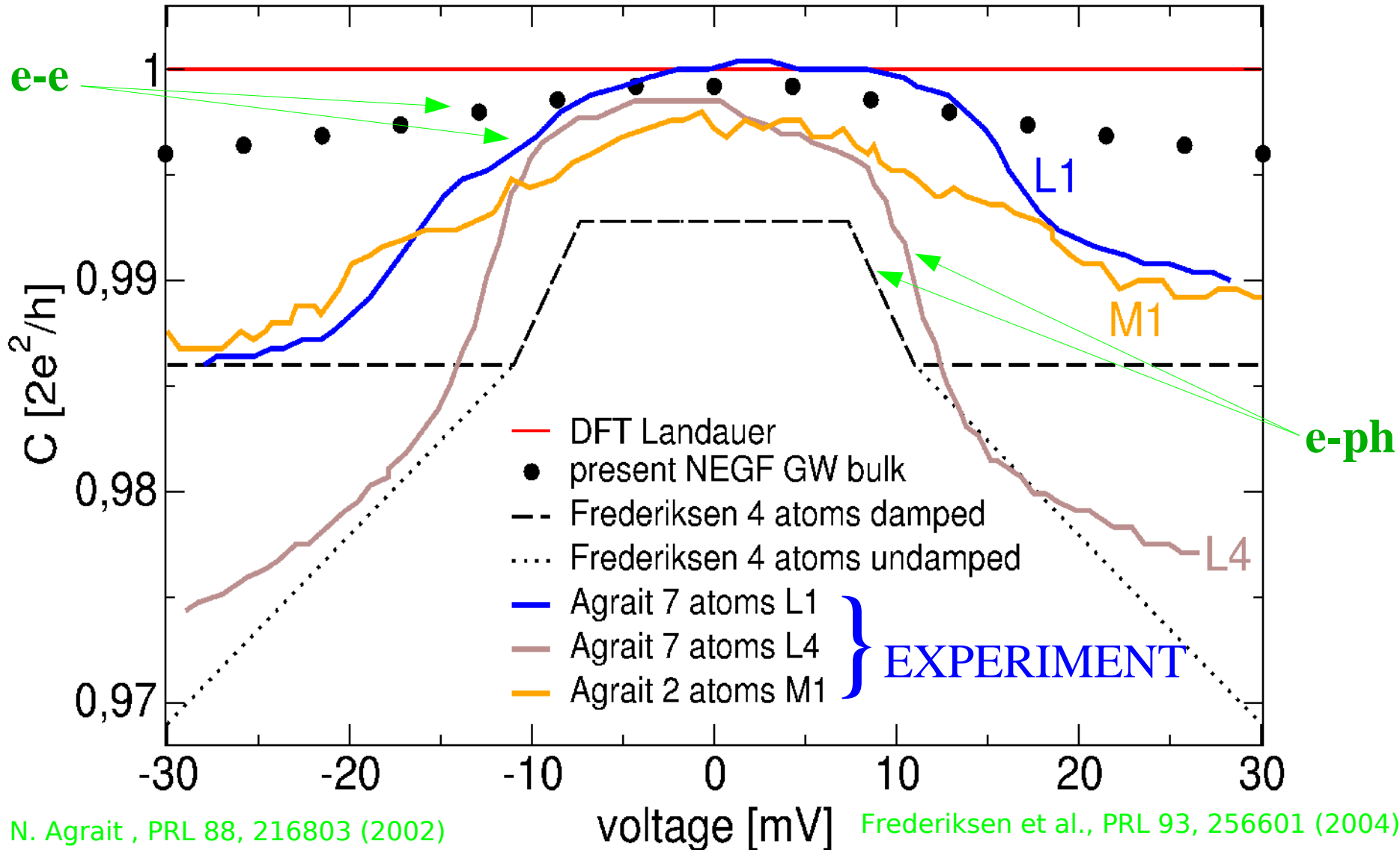
# e-e scattering in conductor and leads



- No contact resistance (small increase in the central part)
- Appearance of Satellite Conductance Channels

# C / V characteristics: GW vs EXP

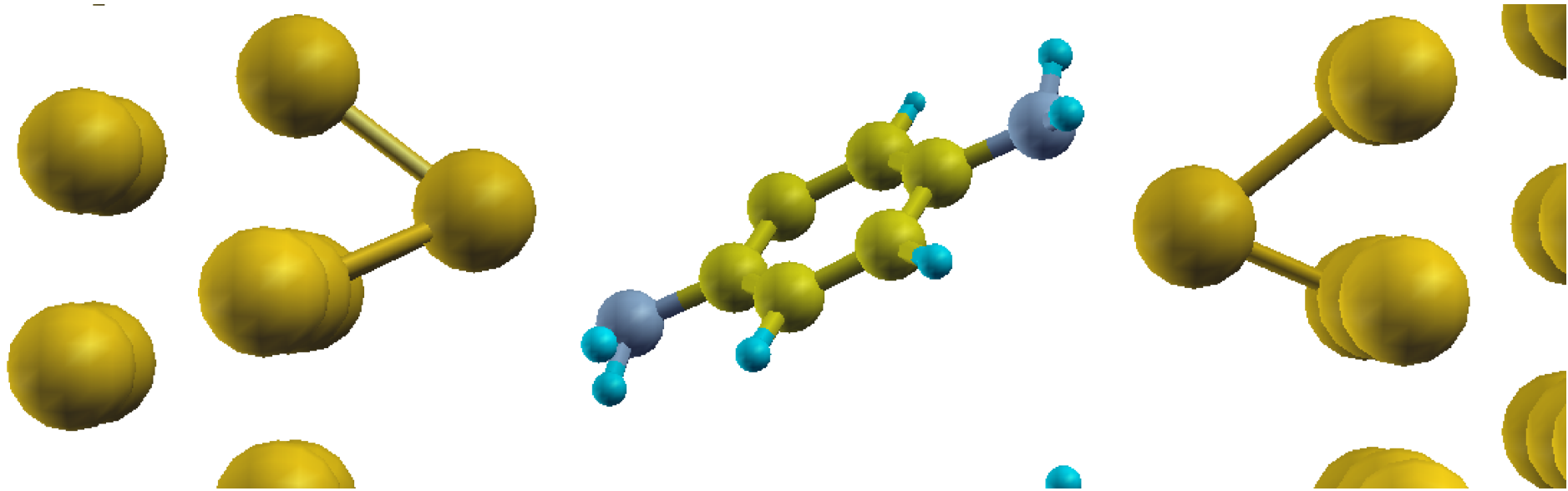
P. Darancet, A. Ferretti, D. Mayou, and V. Olevano, PRB 75, 075102 (2007).



N. Agrait, PRL 88, 216803 (2002)

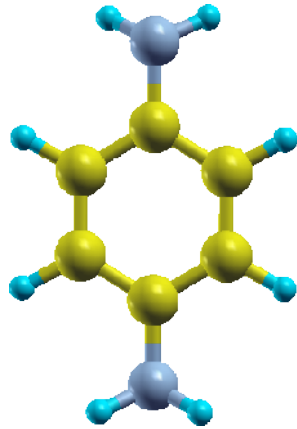
Frederiksen et al., PRL 93, 256601 (2004)

# Results on **Molecular Junctions**

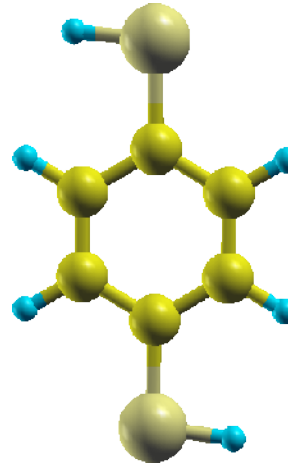


# BDA and BDT

**BDA**

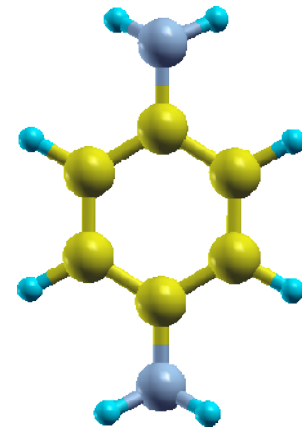


**BDT**



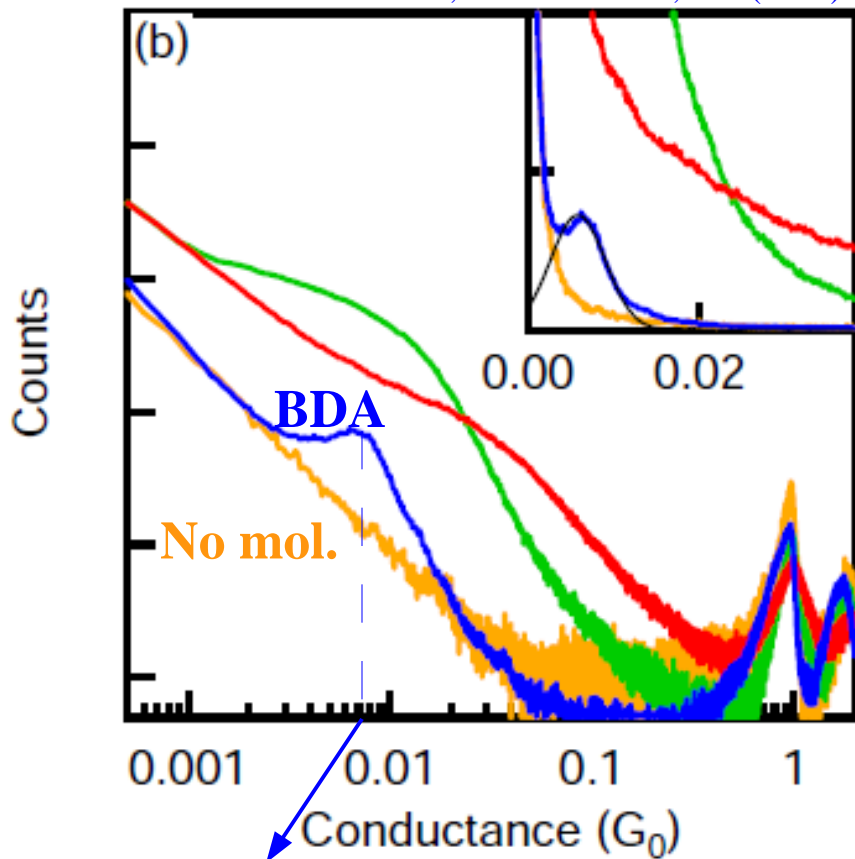
- Benzene Dithiol/Diamine @ Au(111) are among the most studied systems.

# Experiment vs DFT on BDA



Break Au junctions:

L. Venkataraman et al., Nano Letters **6**, 458 (2006)



zero-bias conductance [ $G_0$ ]

EXP 0.007

DFT 0.018

**DFT overestimate of the conductance!**

$G = 0.007$

Is it due to e-e many-body effects?

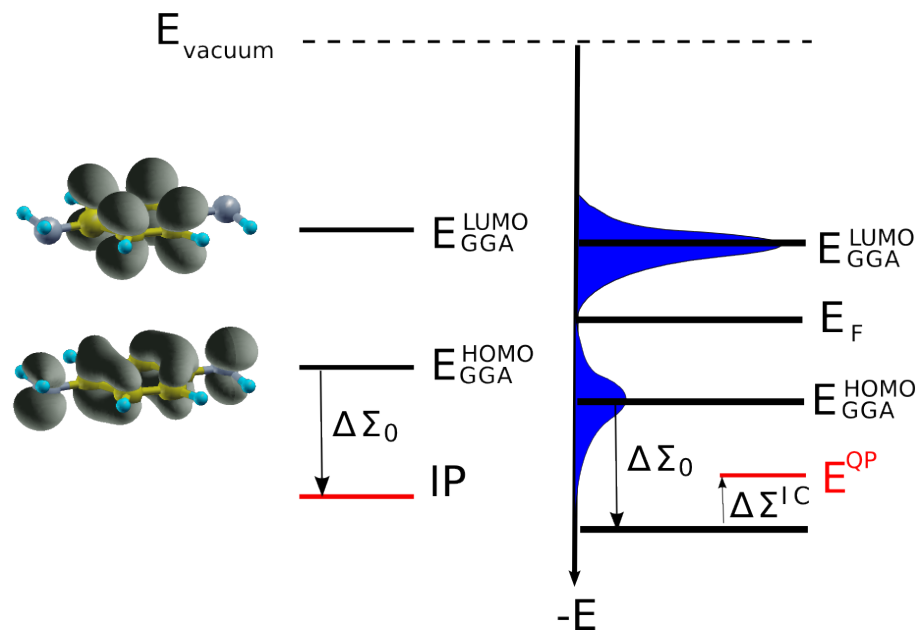


# First essays: 1PM-IC model

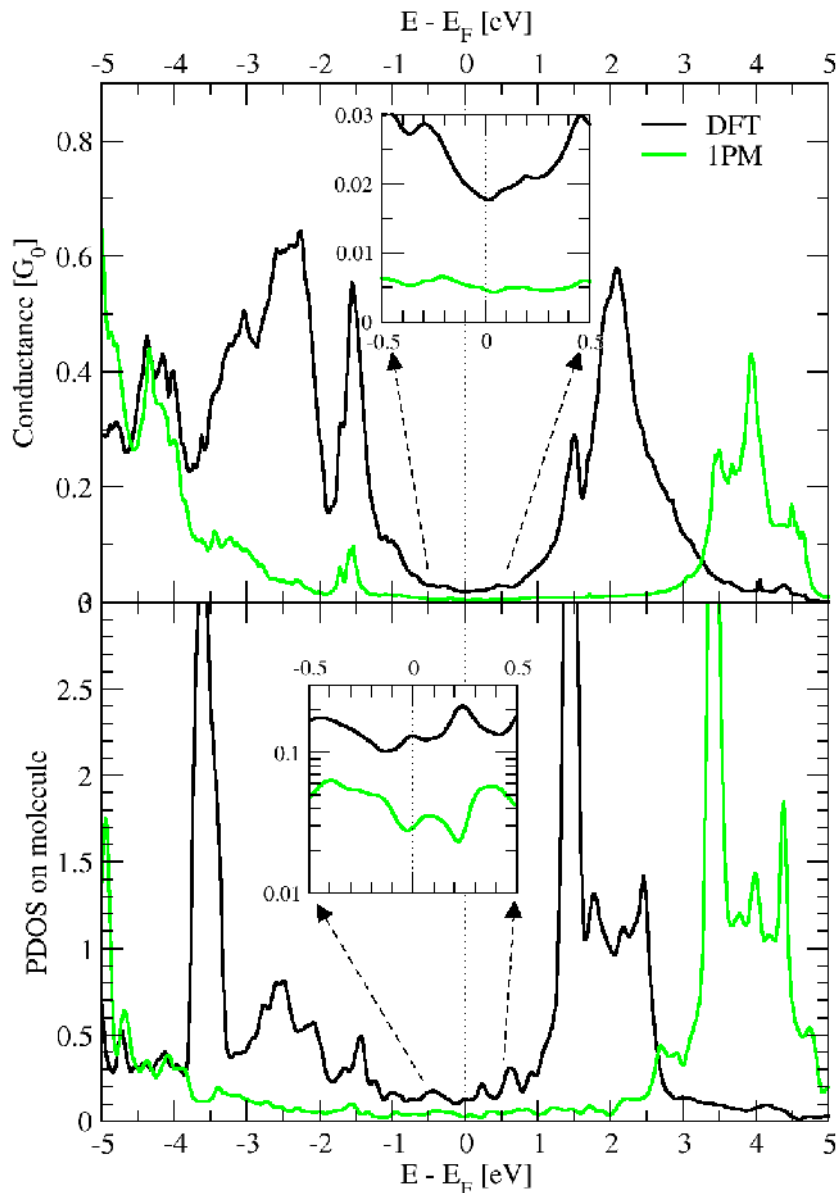
- The self-energy is modeled by a simple one-projector (on molecular orbitals) model (1PM):

$$\Sigma^{1\text{PM}} = \sum_m \Delta_m \left| \phi_m^{\text{mol}} \right\rangle \left\langle \phi_m^{\text{mol}} \right|$$

- The  $\Delta_m$ , simplified to a HOMO-LUMO shissor operator, are adjusted on the experiment or on another model: the Image-Charge (IC) model



# 1PM vs DFT vs Experiment



zero-bias conductance [ $G_0$ ]

DFT 0.018

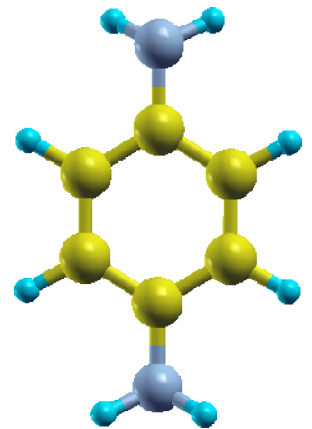
EXP 0.007

1PM 0.004

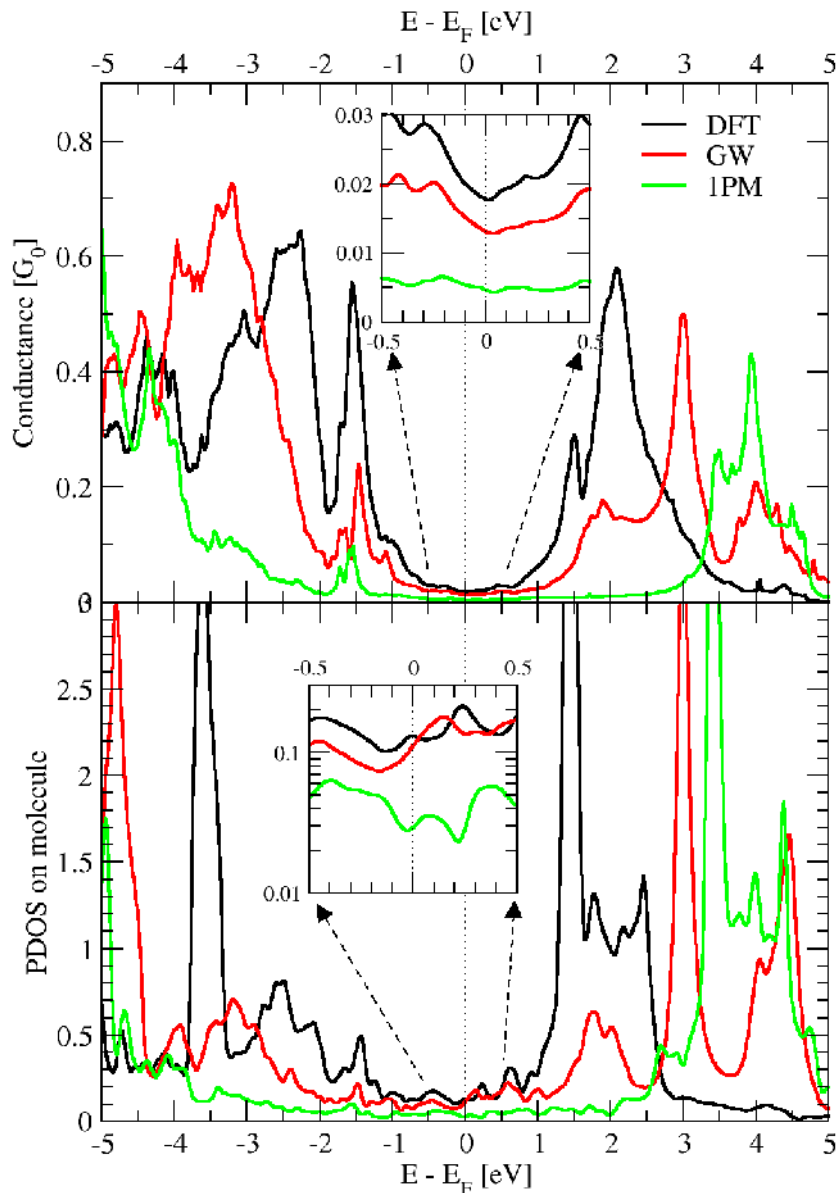
- The 1PM model reduces the conductance

# Our GW calculation on BDA@gold

- Approximations:
  - ✗ neglect of the non-hermitian  $\Sigma$  component  
→ real quasiparticles, no lifetimes
  - ✗ neglect of the dynamic  $\Sigma(\omega)$  behavior
- Fully accounted:
  - ✓ non diagonal  $\Sigma$  elements
- Cost of 1 iteration in BDA:
  - ~ 250 bands → 250 x 250 matrix elements
  - 96 irreducible  $\mathbf{k}$ -points, 11463 plane waves
  - ~ **1 month on 32 processors.**



# Ab Initio GW conductance



zero-bias conductance [ $G_0$ ]

DFT 0.018

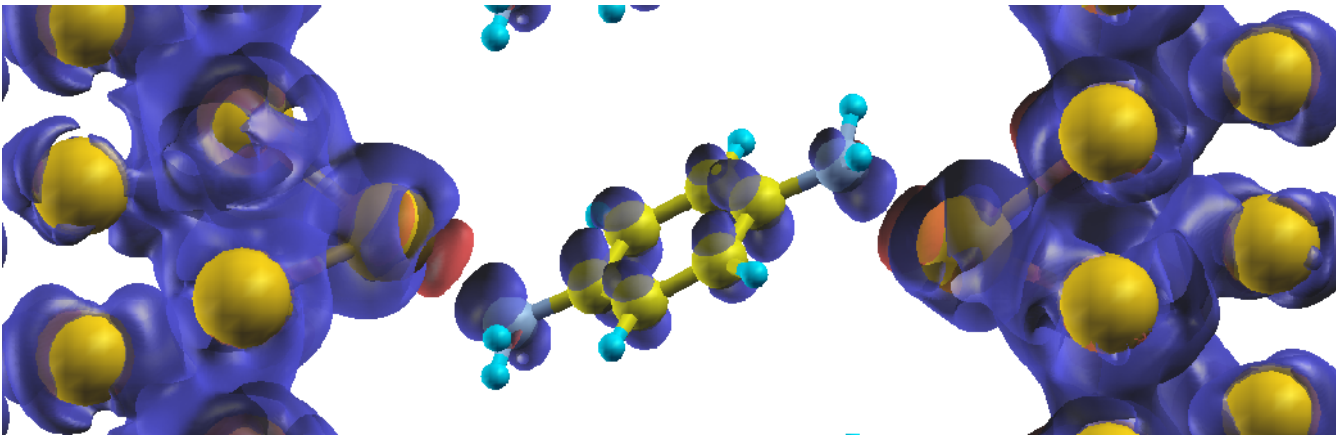
GW 0.013

EXP 0.007

1PM 0.004

- **Ab initio GW reduces the conductance**
- GW is still half-way → further SC iterations?
- 1PM is beyond

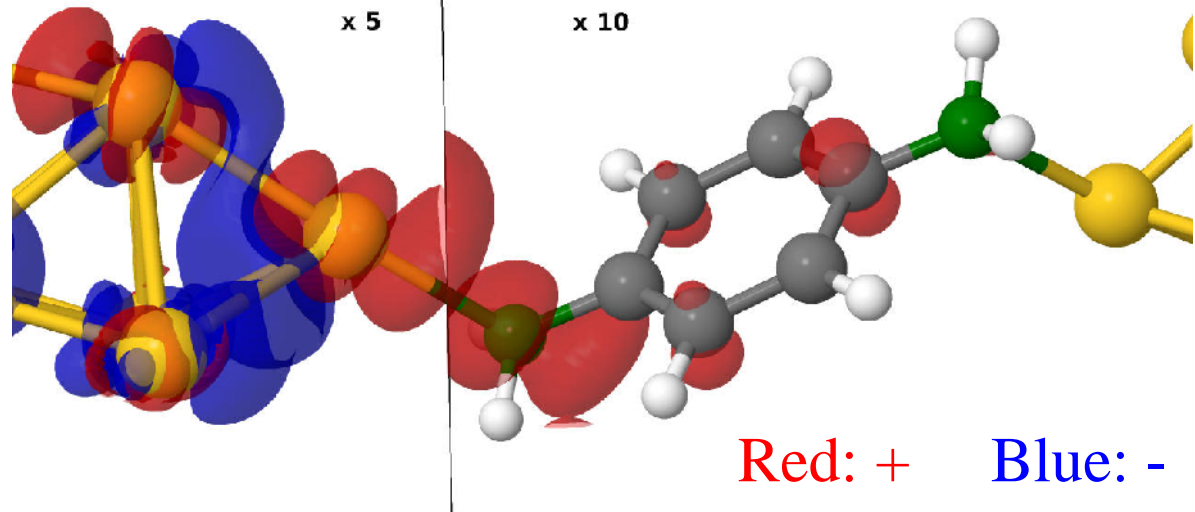
# Conductance reduction mechanism



**LDOS difference: GW - DFT**

**Important changes**  
both on the leads and  
on the molecule

## Eigenchannel difference: GW - 1PM

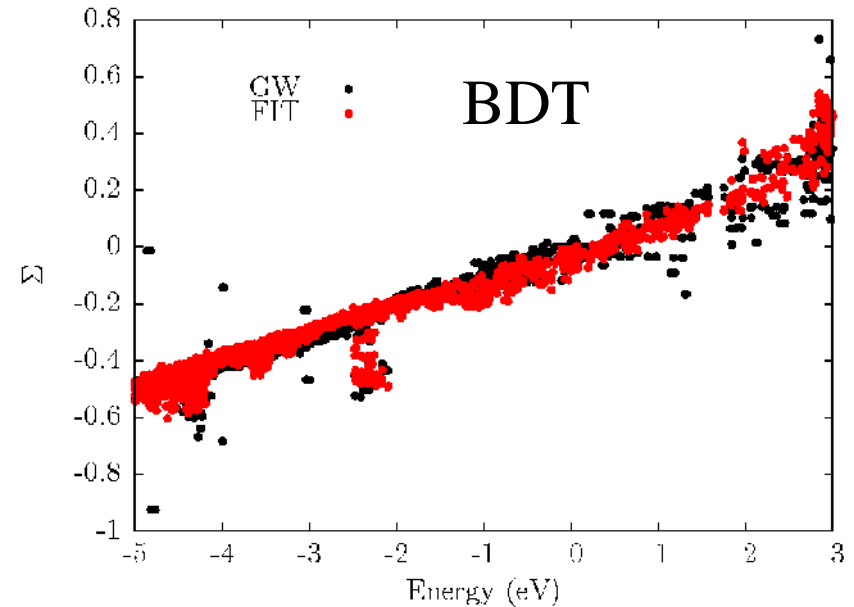
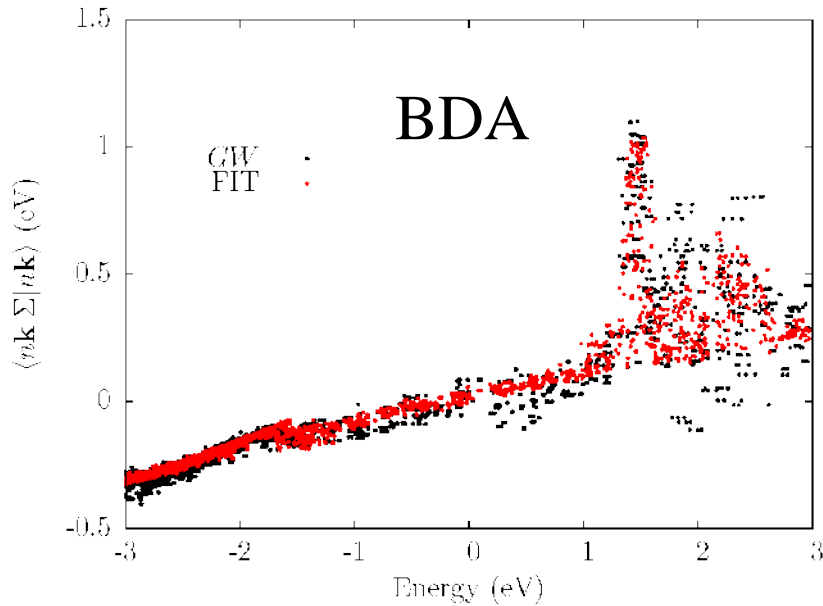


**Red: +**    **Blue: -**

**Important differences**  
between the 1PM model  
and the *ab initio* GW  
→ the 1PM model  
reduces the conductance  
**but does not reproduce**  
**the correct physics.**

# 3PM model

$$\Sigma^{3PM} = \sum_m \Delta_m^{mol} |\phi_m^{mol}\rangle \langle \phi_m^{mol}| + \sum_l \Delta_l^{Au-sp} |\phi_l^{Au-sp}\rangle \langle \phi_l^{Au-sp}| + \sum_l \Delta_l^{Au-d} |\phi_l^{Au-d}\rangle \langle \phi_l^{Au-d}|$$



	BDA	BDT-H	BDT-h	BDT-p
DFT	0.018	0.034	0.28	0.37
GW	0.013	In progress		
3PM	0.011	0.010	0.25	0.36
1PM	0.004	In progress	NA	NA
EXP	0.007	0.010		

3PM model:

- More physical
- Promising results

# Conclusions

- GW e-e correlations in quantum transport:
  - Static real part of self-energy (GW-LB)
    - **modification** of the conductance profile.
    - **reduction** of the 0-bias conductance
  - Non-hermitean part of the self-energy (NEGF-GW)
    - loss-of-coherence, **dissipative** effects.
  - Full dynamical self-energy (NEGF-GW)
    - appearance of **satellites**
- GW in **good agreement** with the Experiment both on:
  - the smooth drop in the Au-chain conductance
  - the absolute 0-bias conductance in BDA@gold

# GW instead then KS leads

