

# Tutorial on Electronic Transport

Roberto Car  
Princeton University



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# Contents

- **Basic background**
- **Quantum master equation approach**
- **Linear response formulation**
- **Some challenges**

# Boltzmann's equation: the standard approach to electric transport in the bulk

$$\frac{df}{dt} = \left( \frac{\partial f}{\partial t} \right)_{field} + \left( \frac{\partial f}{\partial t} \right)_{collisions}$$

Steady State:

$$\left( \frac{\partial f}{\partial t} \right)_{field} = - \left( \frac{\partial f}{\partial t} \right)_{collisions}$$

$f \equiv f(x, p; t)$  is a classical probability distribution

# Can it be derived from quantum mechanics?

$$f \rightarrow S = \sum_i |\psi_i\rangle p_i \langle \psi_i|$$

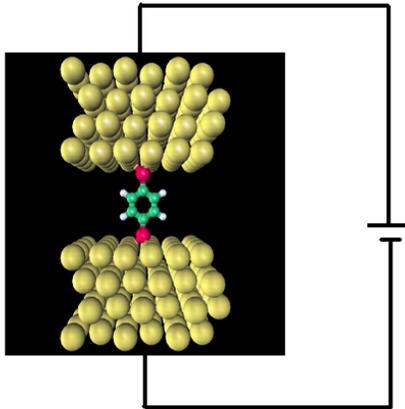
The answer is yes if Joule heating can be neglected (linear regime with the applied field) and collisions with diluted impurities are considered

Kohn and Luttinger, *Phys. Rev.* **108**, 590 (1957)

This paper also contains the idea that ring geometry and gauge invariance can be used to apply an electric field to a periodic crystal

The resistance in the Ohmic regime is due to impurity and/or phonon scattering. This resistance leads to energy dissipation

# Electric transport at the nanoscale: molecular electronics



A nano device (e.g. molecule + contacts) is part of a circuit under an applied electromotive force.

Experiments measure the current  $I$  versus the applied bias  $V$ . This gives the *conductance*  $g = \frac{I}{V}$

Macroscopically:  $g = \sigma \frac{A}{L}$  (Ohm's law)

Microscopically this formula is not valid and should be replaced by:

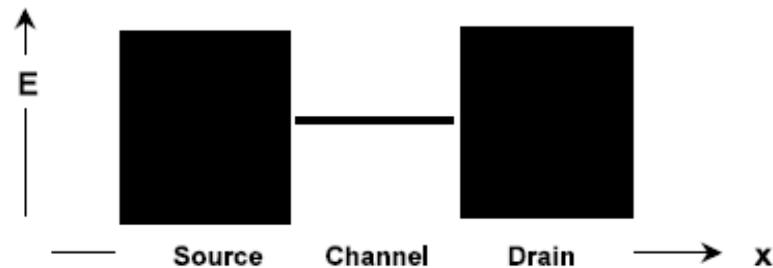
$$g = \frac{e^2}{h} \text{Tr}(TT^\dagger) \quad \text{Landauer's formula}$$

This is a consequence of Quantum Mechanics

# Level quantization is a source of resistance. Ballistic (dissipationless) conductance

$$g = \frac{e^2}{h} \text{Tr}(TT^\dagger)$$

$$G_0 = e^2/h = 38.7 \mu\text{S} = (25.8 \text{ k}\Omega)^{-1} \quad \text{quantum of conductance}$$

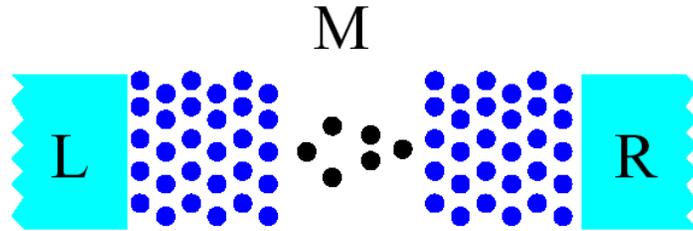


If the channel contains 1 electron level, the *maximum* possible conductance, taking spin degeneracy into account is  $2G_0$

This should be contrasted with  $g = \sigma \frac{A}{L}$  (Ohm's law)

Can ballistic and ohmic effects be treated in a unified way?

# The standard approach to molecular electronics focuses on ballistic transport



Steady state: 
$$I = \frac{2e}{h} \int_{\mu_L}^{\mu_R} dE T(E)$$
 Landauer formula

The transition probability  $T$  is calculated with scattering formulations, i.e. by solving the Lippmann-Schwinger equation

$$\psi_{\varepsilon, k_{\parallel}}(r) = \psi_{\varepsilon, k_{\parallel}}^0(r) + \int d^3r' d^3r'' G_{\varepsilon}^0(r, r') V(r', r'') \psi_{\varepsilon, k_{\parallel}}(r'')$$

or by using Green's function techniques.

(ground-state) DFT formulations map the problem into an effective single particle problem making numerical calculation possible

Dynamic evolution:

Starting with the system in thermal equilibrium an electromotive force

is applied  $\lambda(t)\mathcal{E}$   $\mathcal{E} = -\nabla\phi$

This can be done using the technique of non-equilibrium Green's functions (Keldysh (1964))

In order to be tractable in a finite segment of the device the potential must reach a constant value inside the two metallic electrodes

This is an approximation although a good one for practical purposes

It amounts to assuming constant (and different) chemical potentials in an electrically connected system out of equilibrium (due to current flow)

# Quantum Master Equations (QME)

- QMEs describe relaxation to equilibrium of a system coupled to a heat bath
- They involve dynamics on a coarse grained time scale (kinetics), possible because on the time scale of the relaxation some details of the microscopic dynamics are irrelevant
- The quantum system is open (exchanges of heat with the bath are allowed) and is generally in a mixed quantum state described by a density operator (matrix)  $S$
- Typically they assume that the equilibrium solution is known, it is the relaxation to equilibrium which is not

# Lindblad QME

Harmonic bath, weak coupling  $V_{e-ph}$ ,  $\tau_C \ll \tau_S$   $H_0 + R + V_{e-ph}$

$$\frac{\partial S(t)}{\partial t} = -\frac{i}{\hbar} [H_0, S(t)] + \mathcal{C}S(t)$$

$$\mathcal{C}S(t) = 2 \sum_i \Gamma_i Q_i S(t) Q_i^\dagger - \sum_i \Gamma_i \{Q_i^\dagger Q_i, S(t)\}$$

Jump operators:  $Q_i |\Psi_m\rangle = |\Psi_n\rangle \quad i \equiv (n, m)$

$$\Gamma_{n,m} = \begin{cases} g(E_m - E_n) |\langle \Psi_n | V_{e-ph} | \Psi_m \rangle|^2 (\bar{n}_{E_m - E_n} + 1), & E_n < E_m \\ g(E_n - E_m) |\langle \Psi_n | V_{e-ph} | \Psi_m \rangle|^2 (\bar{n}_{E_n - E_m}) & E_n > E_m \end{cases}$$

Detailed balance:  $\frac{\Gamma_{n,m}}{\Gamma_{m,n}} = e^{\frac{E_m - E_n}{k_B T}}$

# Lindblad QME with time dependent bias

$$\frac{\partial S(t)}{\partial t} = -\frac{i}{\hbar} [H(t), S(t)] + \mathcal{C}S(t)$$

System relaxes to *steady state*:  $\frac{i}{\hbar} [H(t), S] = \mathcal{C}S$

Analogy with semi-classical Boltzmann equation:

$$\frac{df}{dt} = \left( \frac{\partial f}{\partial t} \right)_{field} + \left( \frac{\partial f}{\partial t} \right)_{collisions} \qquad \left( \frac{\partial f}{\partial t} \right)_{field} = - \left( \frac{\partial f}{\partial t} \right)_{collisions}$$

$$f \equiv f(x, p; t)$$

classical probability distribution

# Difficulty (exponentially hard)

$H$  is the electronic many-body Hamiltonian

$S$  is the electronic many-body density operator

Can we make this problem tractable?

Map to a fictitious non-interacting system having the same current evolution of the interacting system

This involves extending TDDFT to dissipative systems (K Burke, RC, R Gebauer, *PRL* 2005)

Knowing the current evolution we also know the density evolution via the continuity equation

# Non-interacting QME

$$\frac{\partial S}{\partial t} = -\frac{i}{\hbar} [H_{KS}(t), S(t)] + C_{KS} S(t)$$

Tracing out  $N - 1$  electronic degrees of freedom we obtain an equation for the reduced single-particle density matrix:

$$S_{nm} = \text{Tr} (S c_m^\dagger c_n) \quad m, n \text{ label KS (equilibrium) eigenstates}$$

The jump operators are now given by  $Q_{nm} = c_n^\dagger c_m$

$$\text{Tr} (S(t) c_i^\dagger c_j^\dagger c_k c_l) \approx S_{l,i} S_{k,j} \quad \text{Hartree approximation in the collision operator}$$

Bury what is left out in the KS potential!

# KS QME

$$\frac{\partial S}{\partial t} = -\frac{i}{\hbar} [H(t), S(t)] + C[S(t)] \quad S \text{ is now } \textit{single-particle}$$

$$\begin{aligned} \dot{S}_{n,m} = & -i \sum_p \left( H_{n,p}(t) S_{p,m} - S_{n,p} H_{p,m}(t) \right) \\ & + (\delta_{n,m} - S_{n,m}) \sum_p (\Gamma_{n,p} + \Gamma_{m,p}) S_{p,p} - S_{n,m} \sum_p (\Gamma_{p,n} + \Gamma_{p,m}) (1 - S_{p,p}) \end{aligned}$$

$$\Gamma_{n,m} = \begin{cases} |\langle n | V_{e-ph} | m \rangle|^2 (\bar{n}(\omega_{mn}) + 1) \rho(\omega_{mn}) & \text{if } e_n < e_m \\ |\langle n | V_{e-ph} | m \rangle|^2 \bar{n}(\omega_{nm}) \rho(\omega_{nm}) & \text{if } e_n > e_m \end{cases} \quad \bar{n}(\omega) = \frac{1}{e^{\omega/T} - 1} \quad \text{Implied again detailed balance}$$

At equilibrium  $S$  becomes diagonal and its diagonal elements are given by the Fermi-Dirac distribution, i.e. the finite  $T$  generalization of DFT

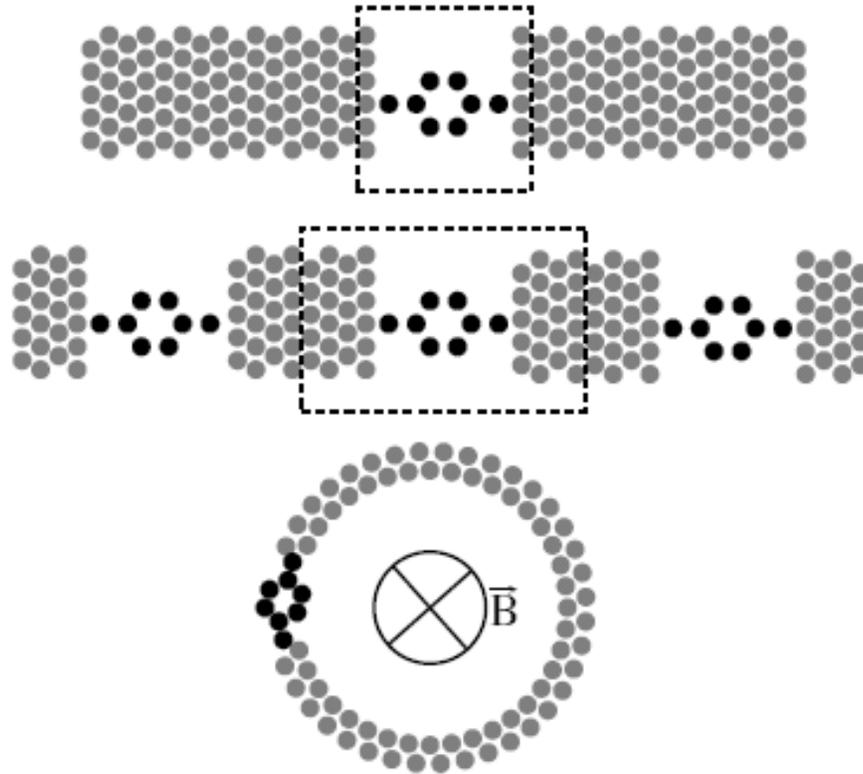
# Canonical vs Grand-canonical

The QME conserves the particle number  $N$ , thus cannot describe fluctuations of  $N$  (canonical ensemble at equilibrium)

It does not allow to treat a system with open boundaries that can exchange electrons with the environment (grand-canonical ensemble at equilibrium)

This implies that in transport situations a whole circuit or something mimicking it has to be used

# Open and Closed Boundary Conditions



A ring geometry, which allows current flow with close boundaries, can be realized with a proper choice of the *gauge*

**x-gauge**      $\mathcal{E} = -\nabla \varphi, \quad \varphi = -\mathcal{E} \cdot x$

**v-gauge**      $\mathcal{E} = -\frac{\partial A}{c\partial t}, \quad A = -c\mathcal{E}t$

The  $v$ -gauge corresponds to a *ring geometry* in which an electric current is induced by a magnetic flux

The electrons are then subject to a steady electromotive force. Coupling to a heat bath prevent them from accelerating indefinitely

## The Liouville-Master equation

$$\dot{S}_{n,m} = -i \sum_p \left( H_{n,p}^\varepsilon(t) S_{p,m} - S_{n,p} H_{p,m}^\varepsilon(t) \right) \\ + \left( \delta_{n,m} - S_{n,m} \right) \sum_p \left( \Gamma_{n,p} + \Gamma_{m,p} \right) S_{p,p} - S_{n,m} \sum_p \left( \Gamma_{p,n} + \Gamma_{p,m} \right) \left( 1 - S_{p,p} \right)$$

Here: 
$$H^\varepsilon(t) = \frac{(p - \varepsilon t)^2}{2} + U_0(x) + \delta V_{HXC}[n]$$

In the numerical implementation the electric field is systematically “gauged” away to avoid indefinite “growth” of the Hamiltonian with time. The result is that the effect of the electric field is transferred from the Hamiltonian to the density matrix

R. Gebauer and R.C. (PRB 2004), S. Piccinin, R. Gebauer, RC, K. Burke (in preparation)

# Gauge transformation

$$\mathbf{A}(t) = -c\mathcal{E}t$$

$$A(t + \Delta t) \rightarrow A'(t + \Delta t) = A(t)$$

$$S(t+\Delta t) \rightarrow S'(t+\Delta t) = \exp(ic\Delta t\mathcal{E}\cdot\hat{\mathbf{r}})S(t+\Delta t)\exp(-ic\Delta t\mathcal{E}\cdot\hat{\mathbf{r}})$$

For a finite ring of length  $L$  the following condition needs to be imposed to keep  $S$  single-valued on the ring

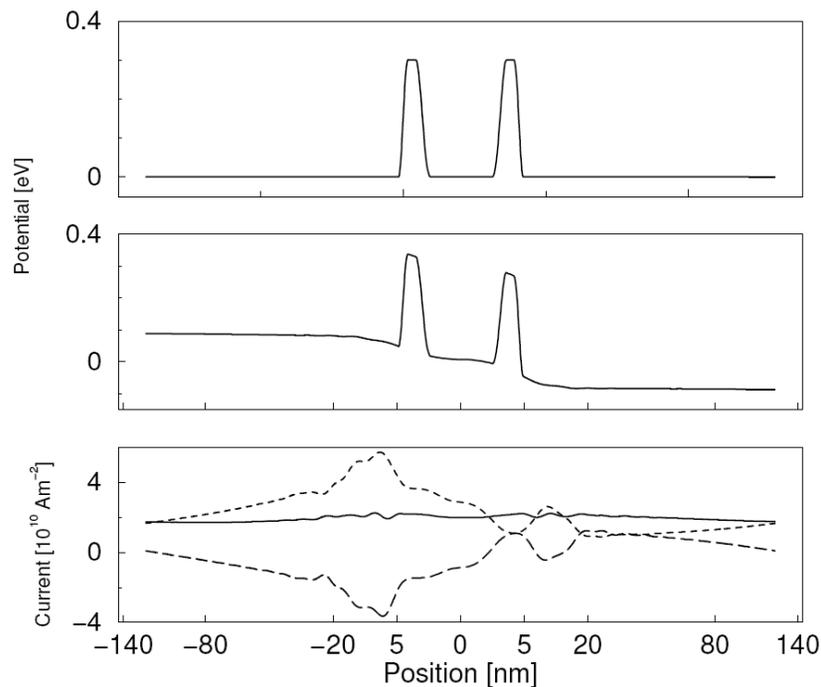
$$c\Delta t\mathcal{E}L = 2\pi$$

Then  $\Delta t$  involves an additional coarse graining in time but it can be made as small as required by exploiting Bloch's theorem

Generalized continuity equation (R. Gebauer and RC, *PRL* 2004)

$$\frac{dS}{dt} = -i[H, S] + \mathcal{C}[S] \quad \frac{d\rho(r)}{dt} = -\nabla \cdot j_H(r) - \nabla \cdot j_C(r)$$

The collision current is a *quantum effect*: collisions that change momentum also change position (density distribution).



Because of the collision current the power dissipated in the circuit obeys:

$$W > \mathcal{E}LI$$

The additional resistance comes from the coupling to the bath and is different from Landauer's residual resistivity dipole (both effects however originate from microscopic inhomogeneity) (Gebauer, Piccinin, RC, *CPC* 2005)

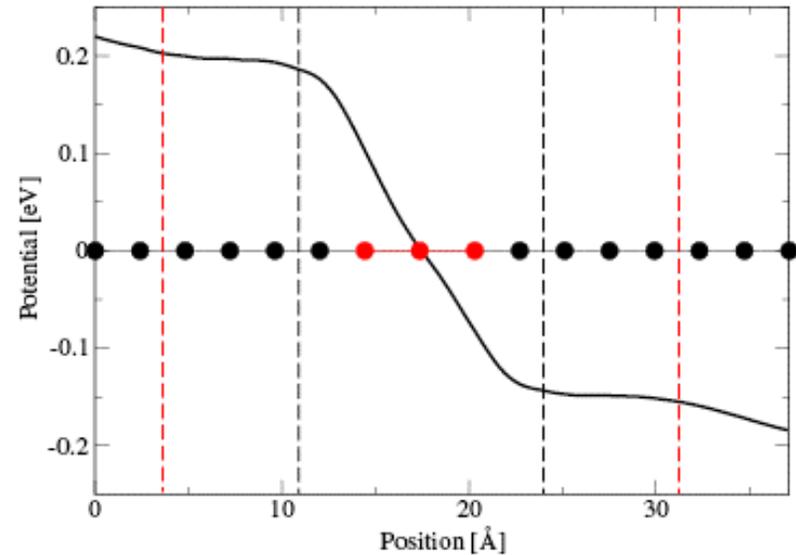
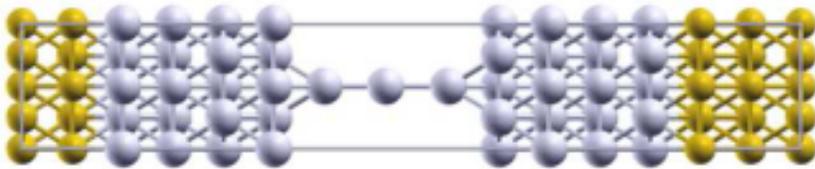
In actual calculations on small systems it is better to neglect the collision current that would be unphysically large

# Pseudopotential plane wave calculations on molecular junctions within DFT-GGA

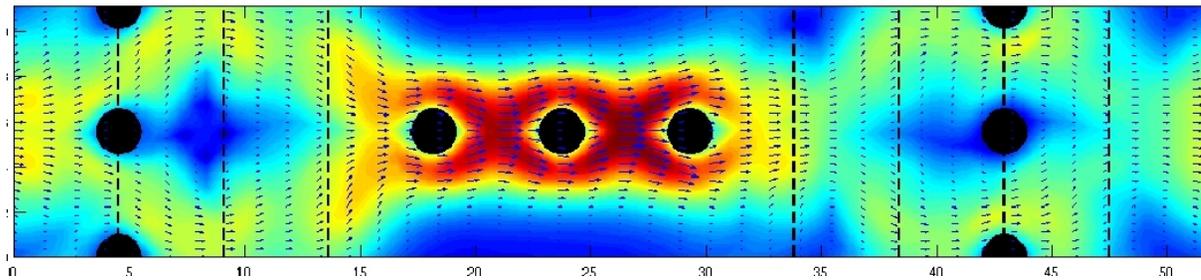
From S. Piccinin, R. Gebauer, R.C., K. Burke, in preparation

# A 3-atom gold wire

Calculations using pseudopotentials and plane waves in a supercell geometry

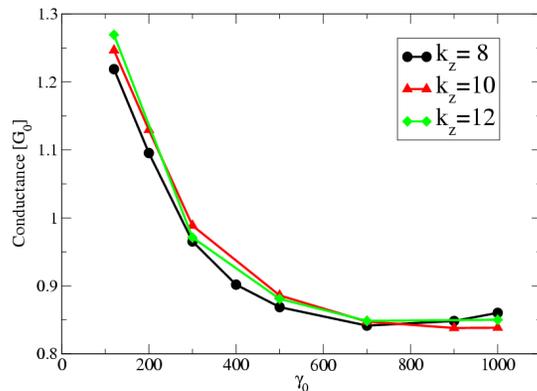


Potential drop in the position gauge



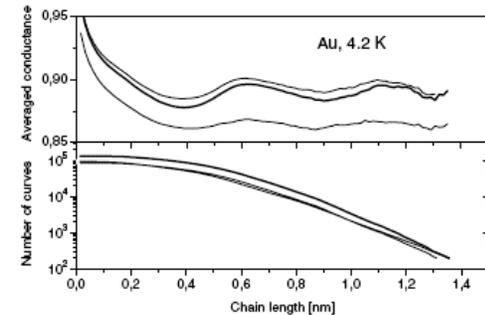
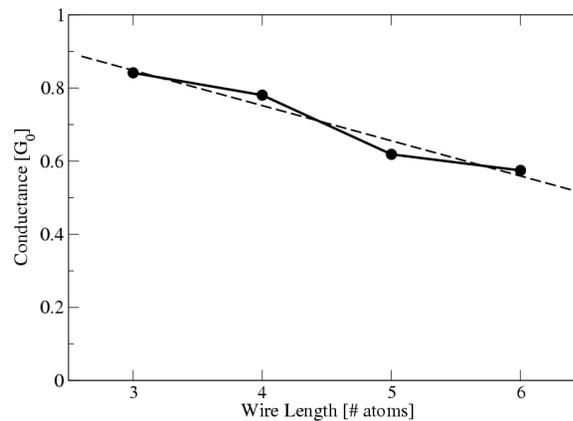
Visualization of the electronic current flow

# Issues: current contribution due to the bath; effect of dissipation on current characteristics



At sufficiently large dissipative coupling the conductance measured across the “ballistic” junction shows saturation, becoming “independent” of the dissipative coupling

Conductance fluctuations with the number of atoms in the wire (as found in NEGF calculations, but out of phase with experiment). The conductance in our calculation decreases with the number of atoms in the wire: an ohmic proximity effect.



Experiments: Smit et al. *PRL* (2003)

# Benzene dithiolate (BDT) between gold slabs

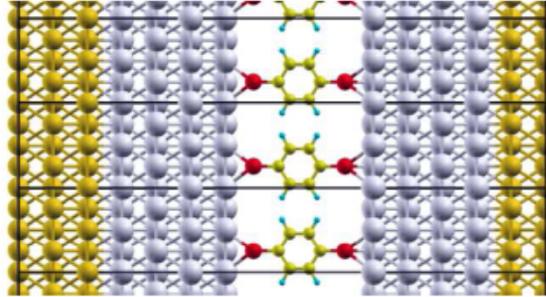


FIG. 8: Unit cell used for the study of the electronic structure of the Au(111)-BDT-Au(111) system. The molecule is adsorbed as a thiolate diradical on the FCC hollow site of the Au surface. The atomic positions have been relaxed.

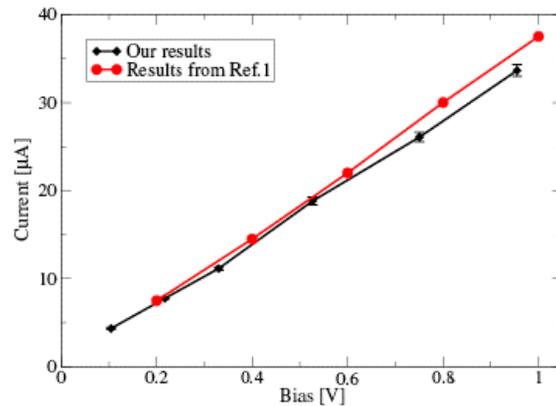


FIG. 11: Comparison between our results and the ones obtained using the NEGF approach<sup>17</sup>. A linear fit of our results gives a low bias conductance of  $0.45 G_0$ .

Calculations at saturation for dissipative coupling. Ref.1: Transiesta calculation reported in:

K. Stokbro, J. Taylor, M. Brandbtge, J.-L. Mosoz, and P. Ordejon, *Comp. Mat. Sc.* **27** (2003).

## **A difficulty**

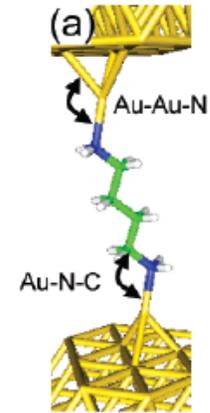
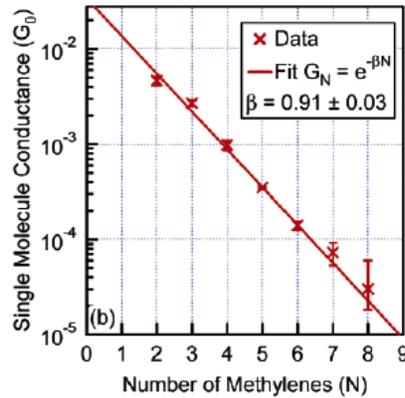
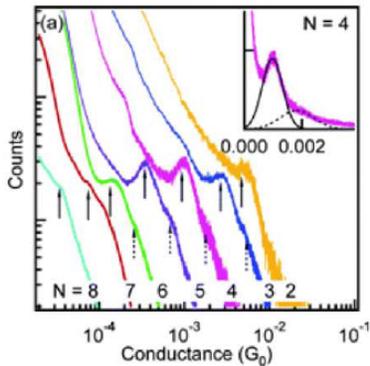
Setting aside issues of system size and issues related to the presence of a fictitious bath, the master equation works well numerically in resonant or near resonant situations when the conductance is relatively large. In off-resonant situations when the conductance (due to tunneling) is extremely small it is much more convenient to use linear response theory

# Experiments on insulating molecules at weak bias

## Single-Molecule Circuits with Well-Defined Molecular Conductance

Latha Venkataraman,<sup>\*,†,||</sup> Jennifer E. Klare,<sup>‡,||</sup> Iris W. Tam,<sup>‡,||</sup> Colin Nuckolls,<sup>‡,||</sup>  
 Mark S. Hybertsen,<sup>§,||</sup> and Michael L. Steigerwald<sup>‡</sup>

NANO  
 LETTERS  
 2006  
 Vol. 6, No. 3  
 458-462



Zero bias conductance

$$G = G_c e^{-\beta N}$$

Why such behavior?

How do  $G_c$  and  $\beta$  depend on the electronic properties of the molecule, the metallic electrodes and the chemical contacts?

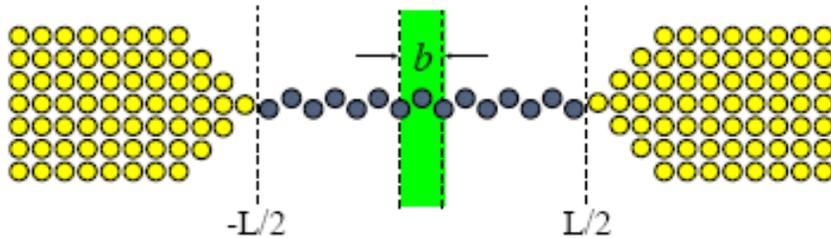
At zero bias the conductance is conveniently calculated from **Linear Response Theory**

In the static limit within the adiabatic approximation of TDDFT

$$G = \int d\mathbf{r}_\perp \int d\mathbf{r}'_\perp \hat{\sigma}_{zz}^{\text{KS}}(\mathbf{r}_\perp, z; \mathbf{r}'_\perp, z')$$
$$\sigma_{zz}(\mathbf{r}, \mathbf{r}') = -\frac{e^2 \hbar^3}{8\pi m^2} \Delta G_{\epsilon_F}(\mathbf{r}, \mathbf{r}') (\overrightarrow{\partial}_z - \overleftarrow{\partial}_z) \Delta G_{\epsilon_F}(\mathbf{r}', \mathbf{r})$$
$$\Delta G_{\epsilon_F}(\mathbf{r}, \mathbf{r}') = G_{\epsilon_F + i\delta}(\mathbf{r}, \mathbf{r}') - G_{\epsilon_F - i\delta}(\mathbf{r}, \mathbf{r}')$$
$$G_\epsilon = (\epsilon - H)^{-1}$$

Thus only an *equilibrium* Kohn-Sham calculation is required in this limit

It is convenient to model the system as a strictly periodic molecular chain (an infinite polymer) *strongly* perturbed by the metallic leads



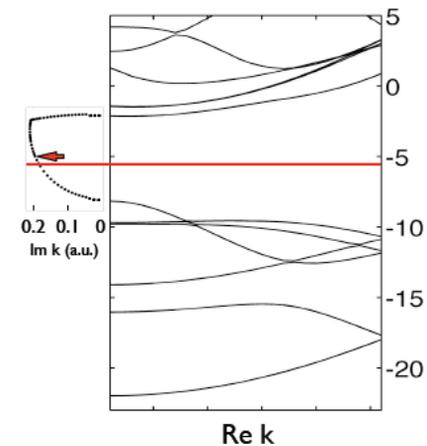
$$H = -\nabla^2 + V_0(\mathbf{r}) + \Delta V(\mathbf{r}) \equiv H_0 + \Delta V(\mathbf{r})$$

$$\Delta V = \Delta V_L + \Delta V_R$$

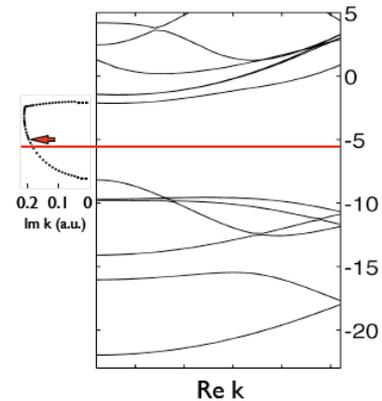
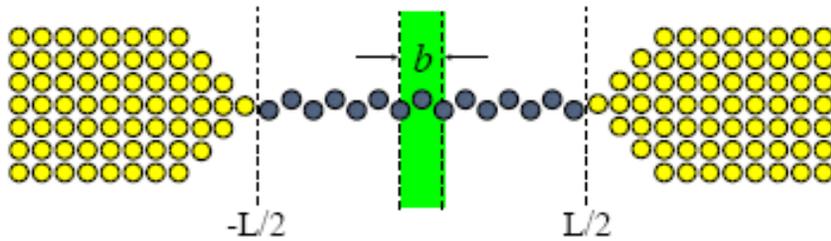
$$G_\epsilon = G_\epsilon^0 + G_\epsilon^0 T_\epsilon G_\epsilon^0$$

$$T_\epsilon = \Delta V + \Delta V G_\epsilon \Delta V$$

$$T_{LR} = [1 + o(e^{-2\beta_{\min} L})] T_L G_\epsilon^0 T_R$$



## Exact asymptotic formula (E. Prodan and R.C., *PRB* (2007))

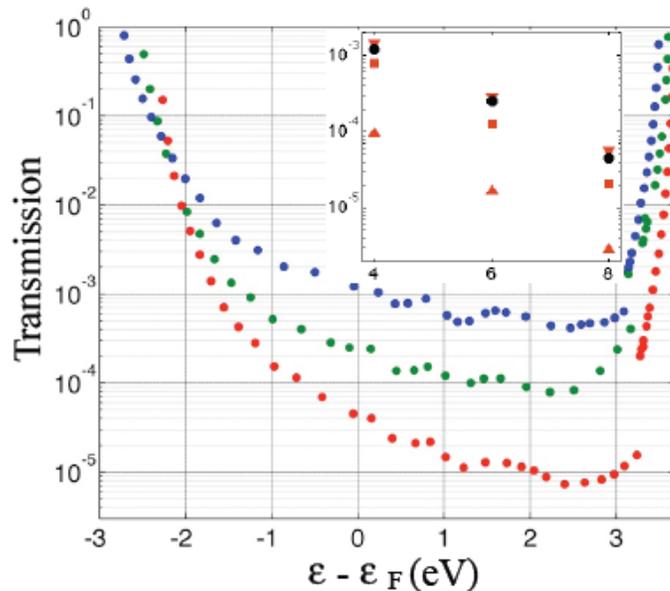


$$G = \Theta_L \Theta_R e^{2ikL} \quad \beta = 2\text{Im}[k]b$$

$$\Theta_L = \frac{2\pi i}{W(\psi_k, \psi_{-k})} \int d\mathbf{r} \int d\mathbf{r}' \psi_{-k}(\mathbf{r}) \Delta V_L(\mathbf{r}) \rho_{\epsilon_F}(\mathbf{r}, \mathbf{r}') \Delta V_L(\mathbf{r}') \psi_{-k}(\mathbf{r}')$$

$$W(\psi, \phi) = \int d\mathbf{r}_\perp \psi(\mathbf{r}_\perp, z) (\vec{\partial}_z - \overleftarrow{\partial}_z) \phi(\mathbf{r}_\perp, z)$$

Link between electronic structure and experiment:  $G = G_c e^{-\beta N}$



$$g = g_c e^{-\beta N} [1 + O(e^{-\beta N})]$$

$e^{-\beta N}$  is equal to 0.04, 0.007, and 0.001, respectively, for  $N = 4, 6,$  and  $8.$

Reference	$\beta$	$g_c$ (k $\Omega$ )
our work (theory)	0.82	388
Ref. 1 (experiment)	$0.91 \pm 0.03$	430
Ref. 2 (HC, experiment)	$0.81 \pm 0.01$	350
Ref. 2 (LC, experiment)	$0.88 \pm 0.03$	4044
Ref. 27 (theory)	0.98	140

Table 1.  $\beta$  and  $g_c$  from our work and the previously reported experimental and theoretical values.

Agreement between theory and experiment is good ....but

How do the results depend on the numerical and physical approximations?

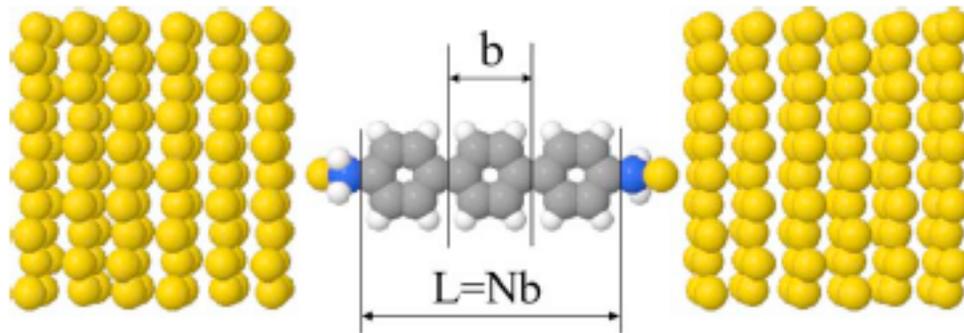
Ref.1: Venkataraman et al, *Nanolett.* (2006)

Ref.2: Chen et al., *JACS* (2006)

Ref.27: Fagas and Greer, *Nanotechnology* (2007)

From Prodan and Car, *Nanolett.* (2008)

# Phenyl Chains (E. Prodan and RC, *PRB* 2009)



In this case the same approach leads to conductances that are  $\sim 1$  order of magnitude larger than experimental values: why?

The problem has to do with the Kohn Sham levels and particularly the alignment of the molecular levels with the Fermi level of the electrodes in presence of a relatively small KS gap in the molecule

# (Some) Challenges

- Level alignment. Use GW approaches: at the static COHSEX level one still has a Hamiltonian formulation and calculations should be feasible, particularly for linear response calculations...
- Dissipation effects (with “realistic” phonon and el-ph couplings): in principle possible but require large systems (feasible with simplified electronic structure models - should allow to study the T dependence
- Approach to equilibrium not just steady state
- Beyond Markov approximation
- More subtle correlation effects (e.g. Kondo problem): how to deal with them?
- Polaronic effects
- .....

# Acknowledgements

Collaboration with K. Burke, E. Prodan, R. Gebauer and S. Piccinin

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