

# ***Rigorous Density Functional Theory Approach to Single Molecule Transport***

**Kieron Burke and friends**

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*Department of Physics and Astronomy*

***Rutgers** University and*

*Princeton Materials Institute*

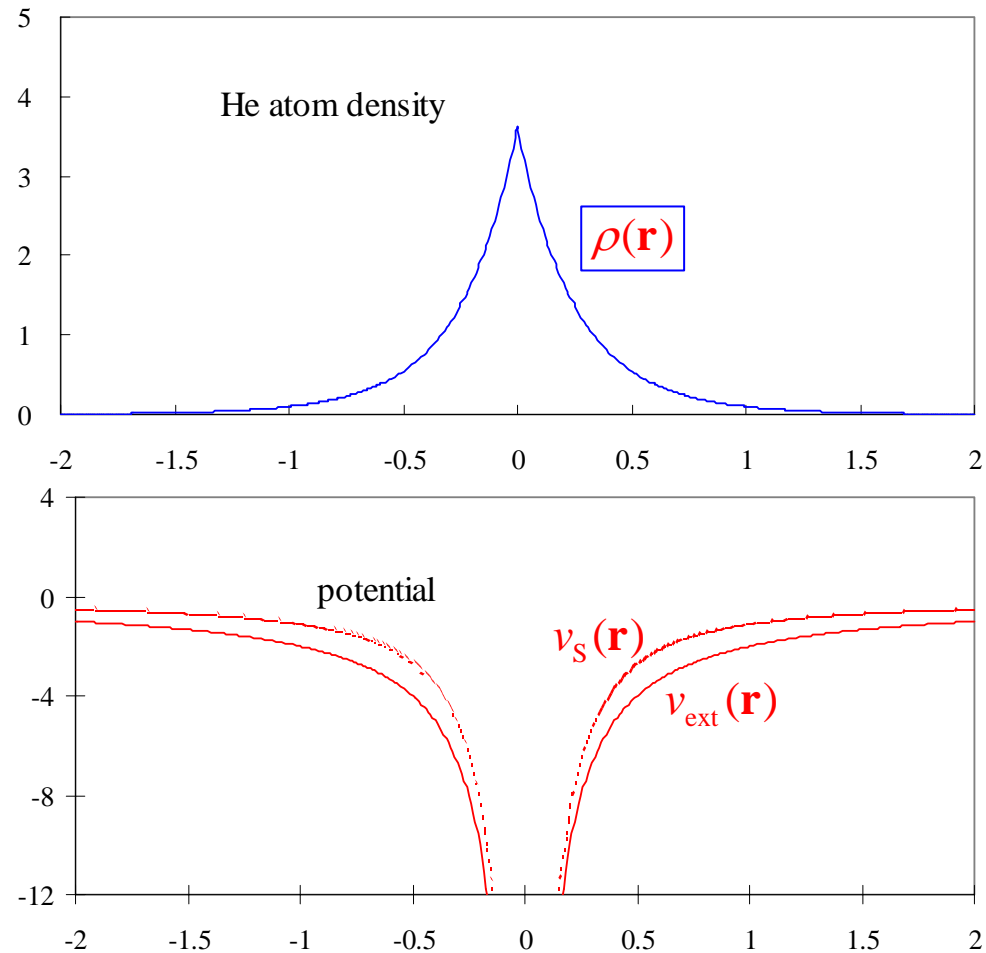
<http://dft.rutgers.edu/grp.html>

(Santa Fe summer school and DFT book)

# *Outline*

- Basics and overview of DFT work at Rutgers
- Weak bias limit of conductance of single molecule (with Evers)
- Building dissipation into TDDFT for finite bias (with Car)

# Exact ground-state DFT

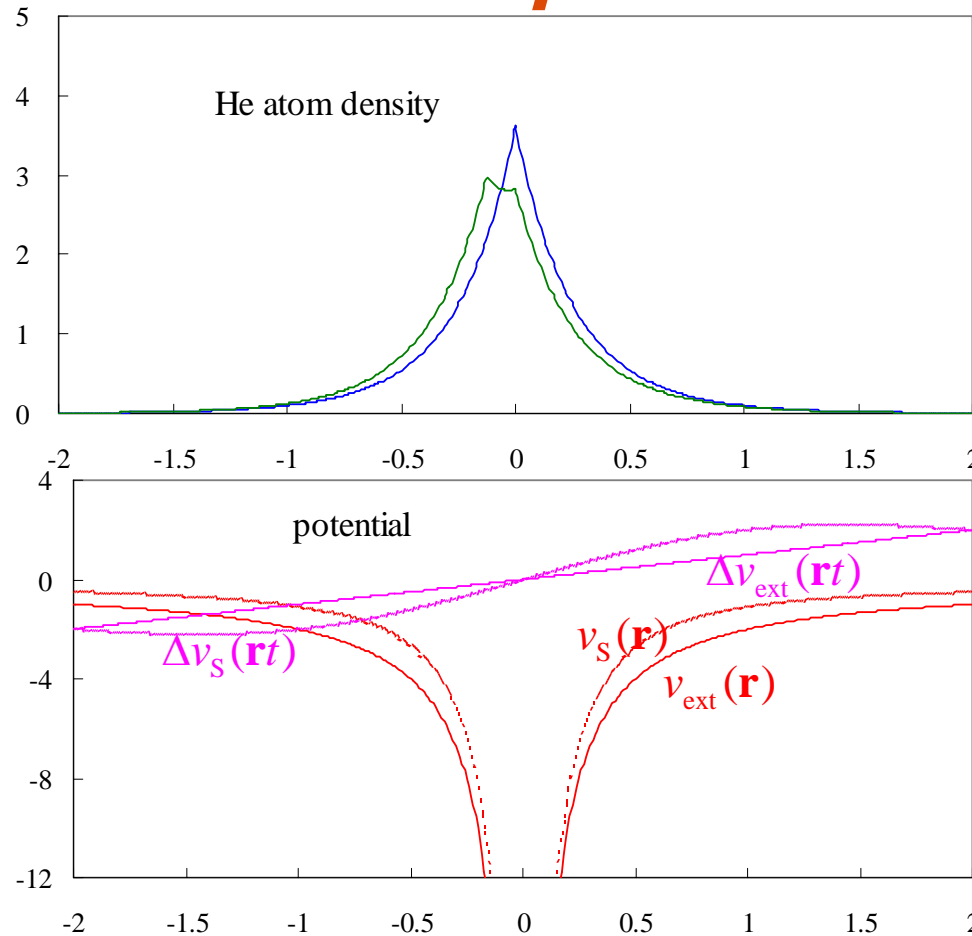


For a given interaction and statistics:

HK:  $v_{\text{ext}}[n](\mathbf{r})$

KS:  $v_S[n](\mathbf{r})$

# Exact ground-state DFT and now time-dependent DFT



In time-dependent external field

For a given interaction and statistics:

HS:  $v_{\text{ext}}[\rho](\mathbf{r})$

RG:  $v_{\text{ext}}[\rho(t), \Psi(0)](\mathbf{rt})$

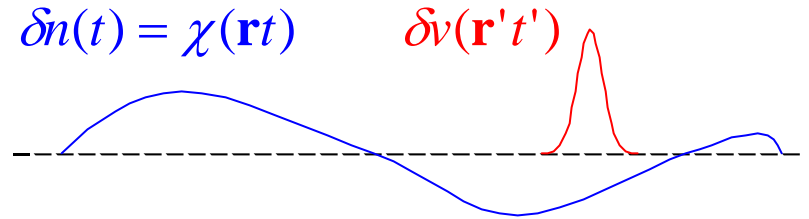
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KS:  $v_{\text{S}}[\rho(t), \Psi(0), \Phi(0)](\mathbf{rt})$

# Linear response in TDDFT

Key quantity is susceptibility

$$\chi(\mathbf{r}\mathbf{r}', t - t') = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')}$$



Dyson-like equation for a susceptibility:

$$\chi(\mathbf{r}\mathbf{r}', \omega) = \chi_s(\mathbf{r}\mathbf{r}', \omega) + \int d^3 r_1 \int d^3 r_2 \chi_s(\mathbf{r}\mathbf{r}_1, \omega) \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{\text{XC}}[\rho_0](\mathbf{r}_1 \mathbf{r}_2, \omega) \right\} \chi(\mathbf{r}_2 \mathbf{r}', \omega)$$

Two inputs: KS susceptibility

$$\chi_s(\mathbf{r}\mathbf{r}', \omega) = \sum_{jk} (f_k - f_j) \frac{\phi_j(\mathbf{r}) \phi_k^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i0_+}$$

and XC kernel

$$f_{\text{XC}}(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta v_{\text{XC}}(\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')}$$

# *TDDFT matrix equations (Casida, 1996)*

Eigenvalue equation for true excitations from KS transitions

$$\sum_{q'} \tilde{\Omega}_{qq'}(\omega) v_{q'} = \Omega v_q$$

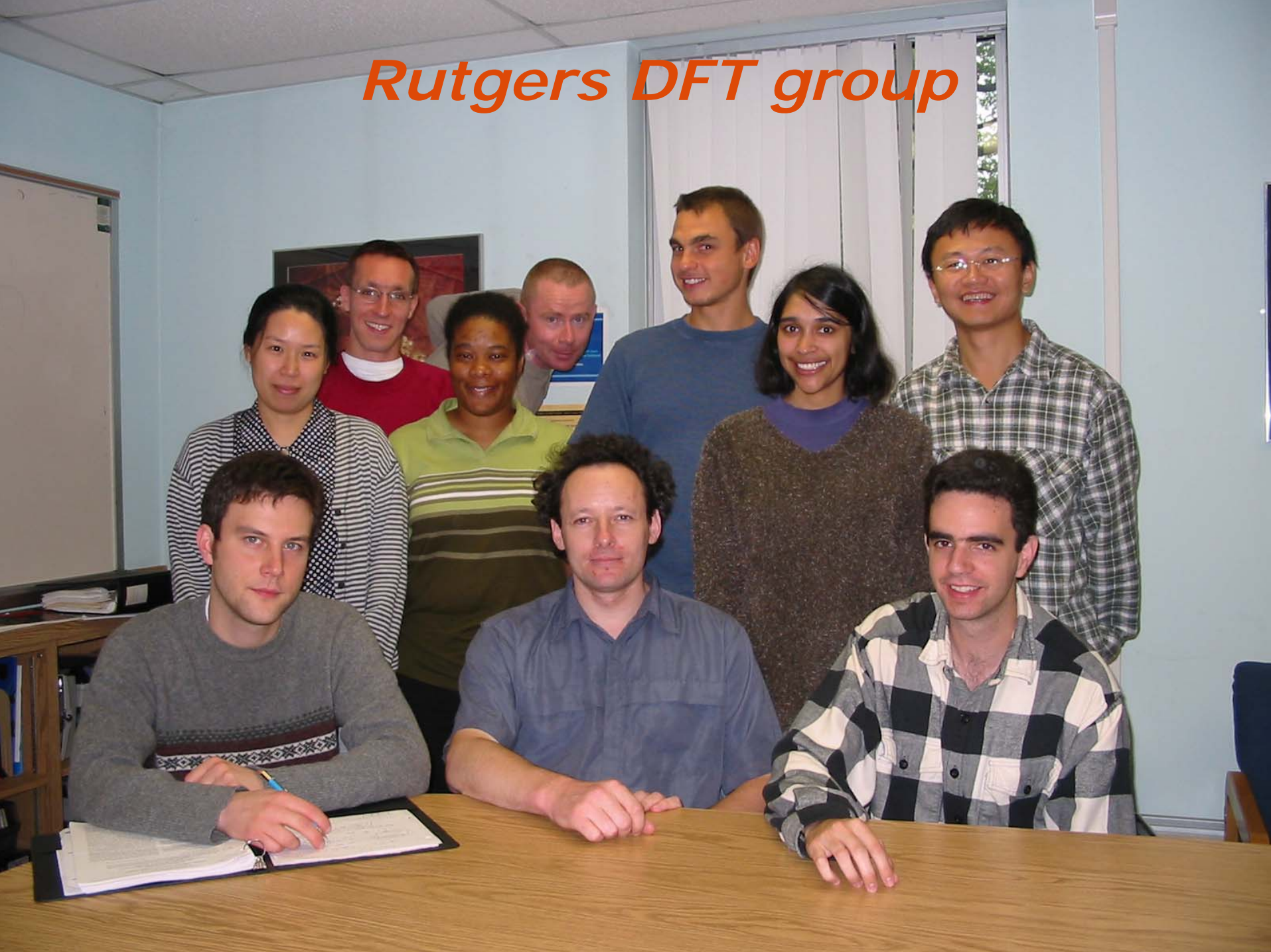
where  $q$  is a double index, representing a transition from occupied KS orbital  $i$  to unoccupied KS orbital  $a$ ,  $\omega_q = \varepsilon_a - \varepsilon_i$ ,  $\Omega = \omega^2$ , and  $\Phi_q(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_a(\mathbf{r})$ . The matrix is

$$\tilde{\Omega}_{qq'} = \delta_{qq'}\Omega_q + 2\sqrt{\omega_q\omega_{q'}}\langle q|f_{\text{HXC}}(\omega)|q'\rangle$$

where  $\langle q|f_{\text{HXC}}(\omega)|q'\rangle = \int d^3r \int d^3r' \Phi_q^*(\mathbf{r})f_{\text{HXC}}(\mathbf{r},\mathbf{r}',\omega)\Phi_{q'}(\mathbf{r}')$

**Single-pole approx:  $\omega = \omega_S + \langle q|f_{\text{HXC}}|q\rangle$**

# *Rutgers DFT group*



# *Overview of DFT projects*

- TDDFT for chemical systems
- Periodic boundary conditions
- Ground-state projects
- Offsite collaborations

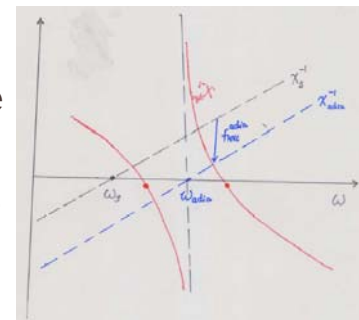


# Chemical systems

## • Double excitations from TDDFT

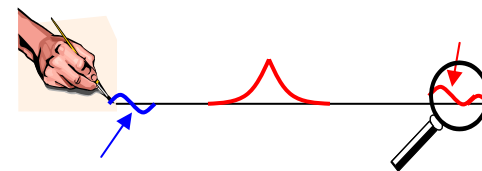
\* N. Maitra shows what becomes of double excitations in the linear response formalism (J. Chem. Phys. **120**, 5932 (2004).)

\* Bob Cave, using CI, has shown how to construct a system-specific  $\omega$ -dependent  $f_{XC}$  that incorporates double excitations – excellent results for butadiene (Chem. Phys. Lett. **389**, 39 (2004). )



## • Electron scattering via TDDFT

Adam Wasserman (with N. Maitra) has shown how, in principle, you can use TDDFT to calculate electron-molecule scattering cross sections (submitted).

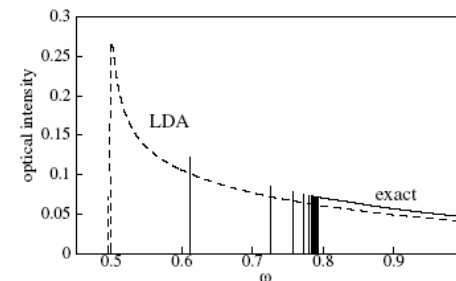


## • Accurate Rydberg excitations from LDA

Adam Wasserman, N. Maitra, KB, Phys Rev Letts **91** 263001 (2003).

\* Shows that many excitations, pushed into continuum by poor potentials, still produce correct oscillator strength

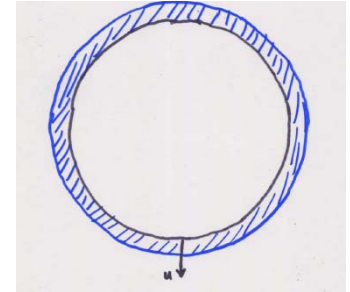
\* May even be able to produce correct excitation energies!



# Periodic boundary conditions

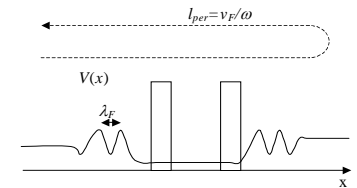
- **Optical response of solids.**

- \* In TDDFT, proved RG theorem for periodic systems; but must do finite  $q$  calculation, and take  $q \rightarrow 0$ .
- \* In TD current DFT, can perform  $q=0$  calculation.
- \* As  $\omega \rightarrow 0$ , recover GGG theorem.



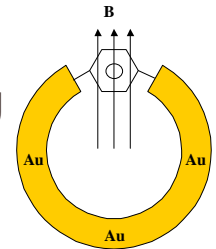
- **Weak bias limit of tunneling through wires**

KB, with Rene Gaudoin and Ferdinand Evers, show origin of XC corrections to Landauer formula for weak bias.



- **Density functional theory with Dissipation**

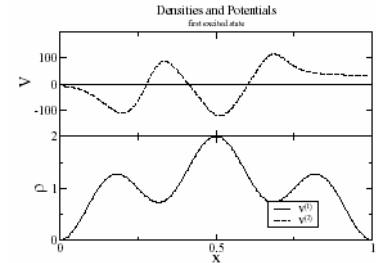
We show how to construct a dissipative Master equation using (generalized) time-dependent DFT. This allows correct first-principles treatment of tunneling through single molecules.



# Other Rutgers work (Sep 7, 04)

- **Energy-density relationship for excited states**

Rene Gaudoin has shown that, often, more than one potential can yield a given excited-state density, I.e., definitive examples of failure of HK for excited states, with a variety of serious consequences for DFT (accepted PRL, Aug 04).



- **Large Z atoms and the high-density limit**

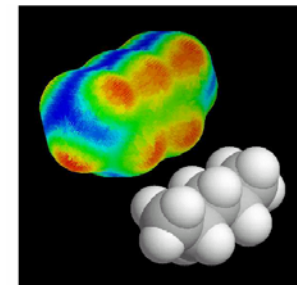
\*Takeyce Whittingham has shown that the highly accurate data of Davidson et al on large Z atoms can be related to the high-density expansion of DFT for hydrogenic densities, producing new and difficult tests for DFT (sub to JCP).

- **One-dimensional DFT with contact interaction**

Rudy Magyar (now at LANL) has constructed DFT for 1-d electrons with a contact interaction, and the corresponding LDA. This provides a simple model for testing formal properties of DFT and exploring difficult regimes(PRA 04).

- **Minimal Atomic Multipole Expansion for molecules**

Eugene Tsiper (now at NRL) has shown how to overcome redundancy and sampling problems to find chemically sensible partial charges for molecular modeling (JCP **120**, 1153 (2004)).

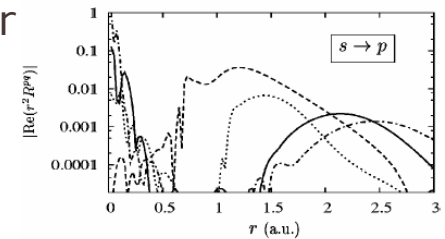


# Collaborations (Sep 7,04)

- **TDCDFT for atomic excitations**

- \* Carsten Ulrich developed single pole approximation for TDCDFT treatment of excitations (J. Chem. Phys. **120**, 5932 (2004).)

- \* Applied VK approx, found either small improvement over ALDA where it worked, and wild errors when ALDA not so good (Chem. Phys. Lett. **389**, 39 (2004).)



- **Bond-breaking via adiabatic connection**

- \* Martin Fuchs (and Gonze group) developed general formalism to get entire curve from adiabatic connection

- \* Long paper on how RPA yields correct dissociation energy and correct spin symmetry for dissociating H<sub>2</sub>.

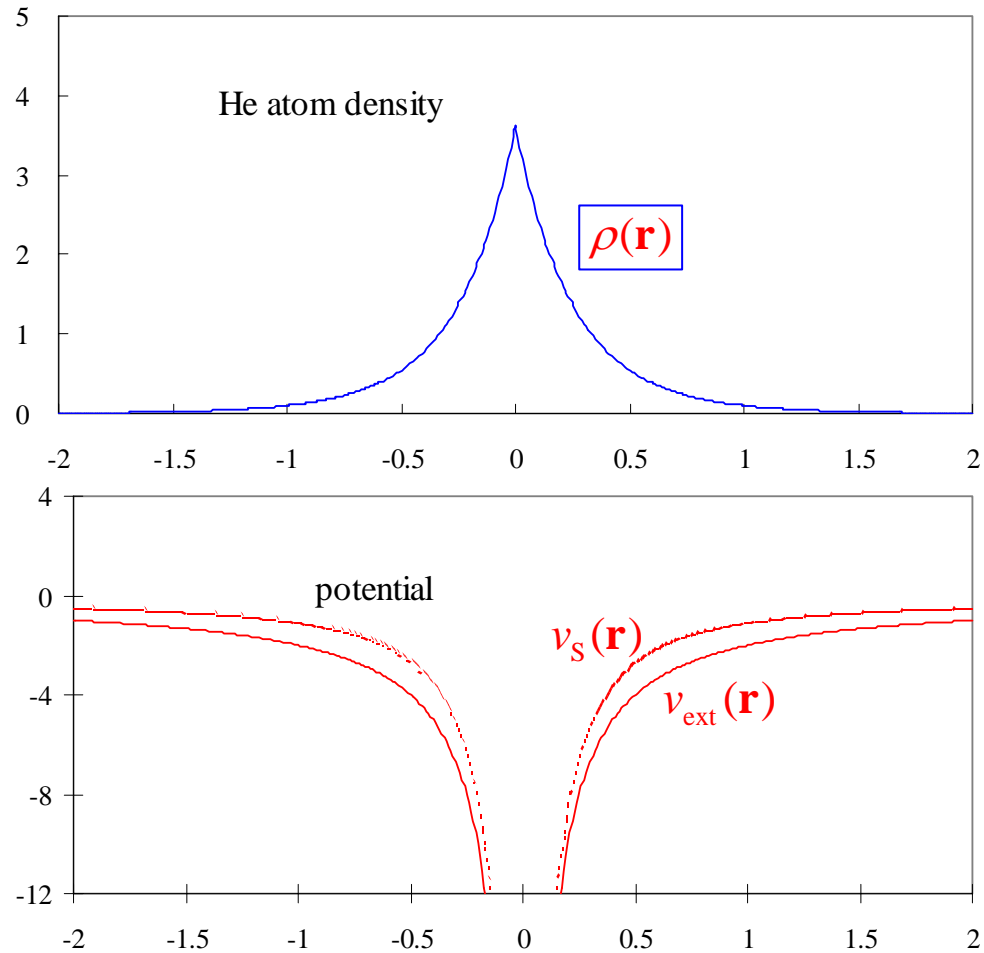
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- **A. Philosophy and aims**
- A. Review of DFT basics
- B. Problems with transport
- B. Linear response and Landauer
- C. Finite fields and Hamiltonian
- C. Kohn-Sham Master equation
- C. Results of model calculations

## *Philosophy and aims*

- To construct a **rigorous** DFT approach to single-molecule transport
- Avoid open boundary conditions
- Might not be most practical, but might be very important quantitatively (Evers)
- Should produce parameters for faster methods

# Exact ground-state DFT

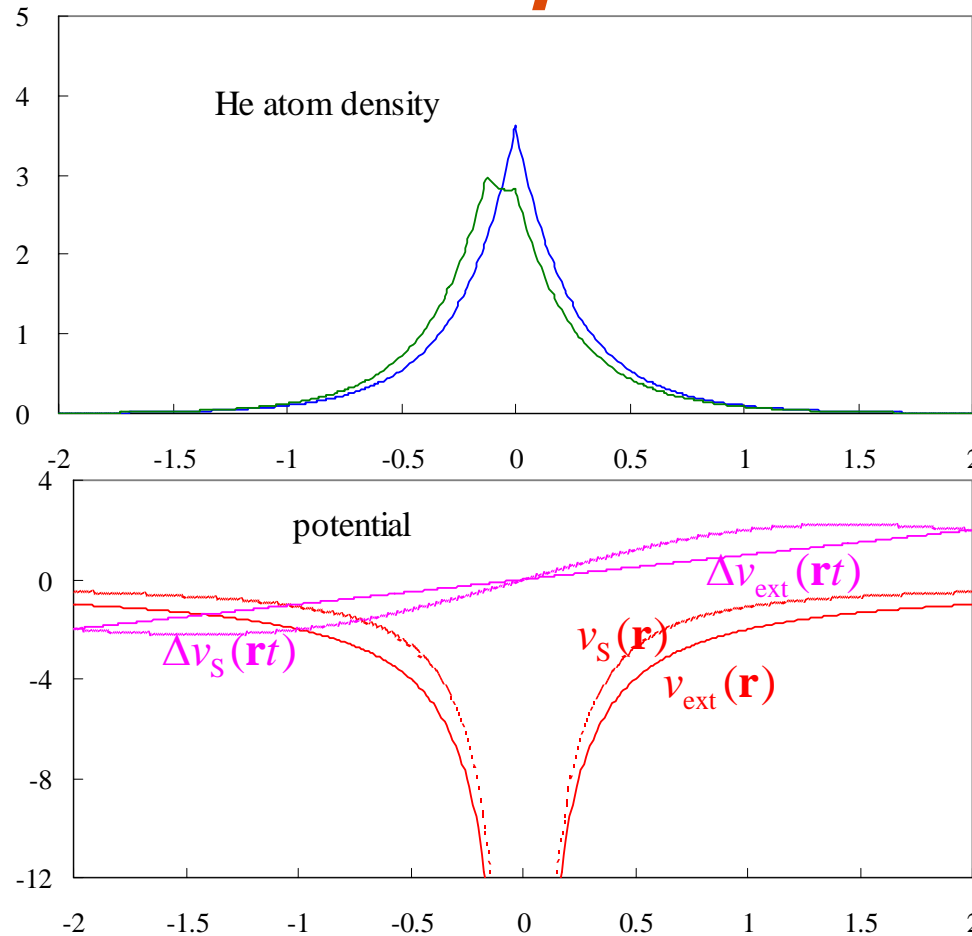


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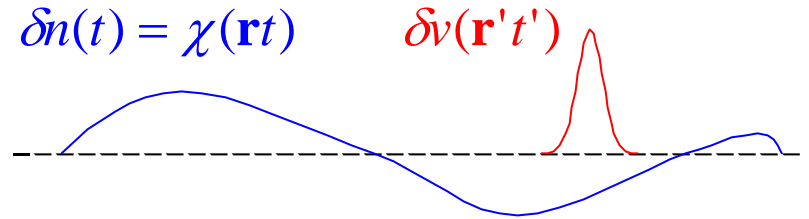
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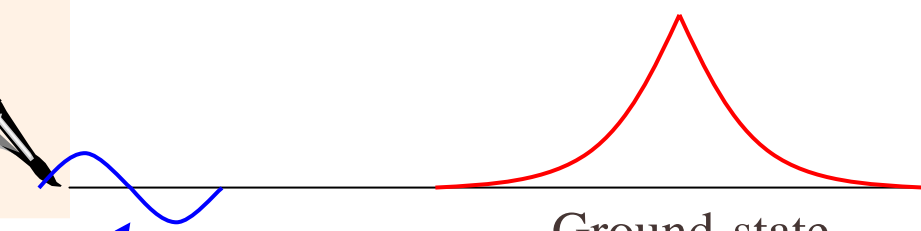
**Single-pole approx:  $\omega = \omega_S + \langle q|f_{\text{HXC}}|q\rangle$**

# Transmission amplitude from susceptibility (1d)

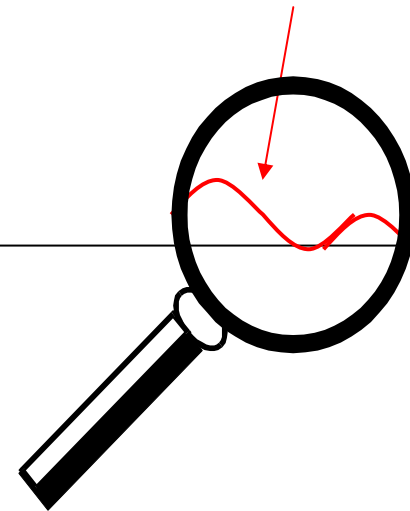
(Wasserman, Maitra, KB – submitted)

$$t(\varepsilon) = \lim_{x \rightarrow -\infty} \left[ \frac{i\sqrt{2\varepsilon}}{\sqrt{n(x)n(-x)}} \chi^{osc}(x, -x; \varepsilon + I) \right]$$

Density change



Perturbation  
( $\omega = I + \varepsilon$ )



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# *Xue and Ratner*

PHYSICAL REVIEW B 68, 115406 (2003)

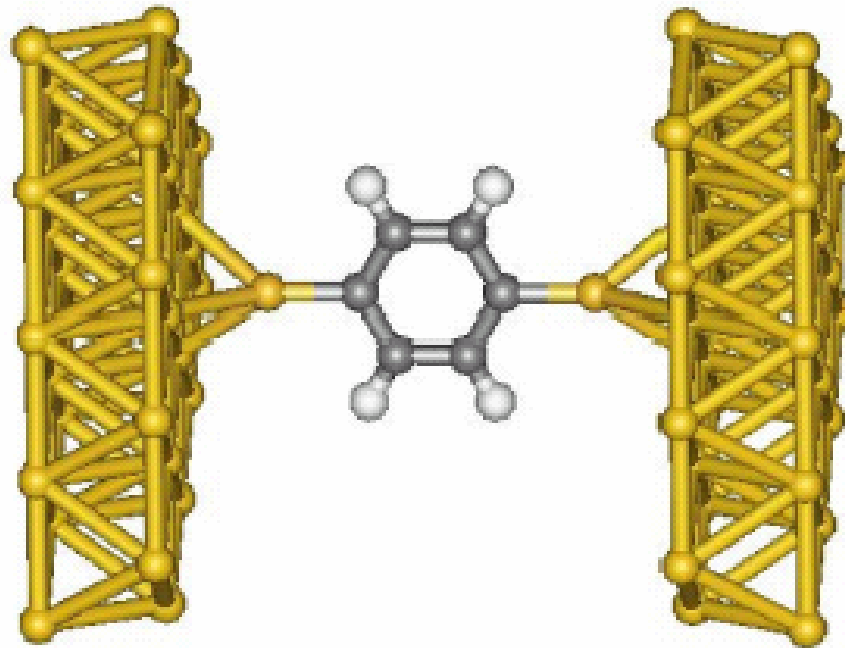
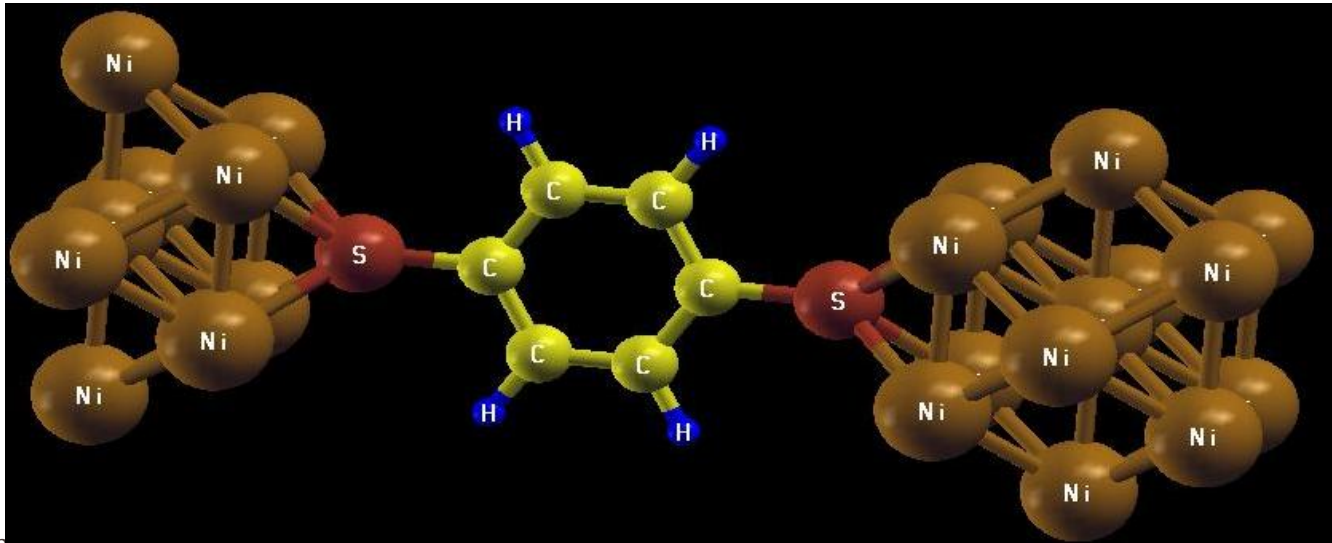


FIG. 1. (Color online) Atomic geometry of the gold-PDT-gold junction. Six gold atoms closest to the end sulfur atoms on each electrode are included into the “extended molecule.”

*Smeagol from TCD by Sanvito*

# Molecular Spin Valves



# Di Ventra, Pantelides, and Lang

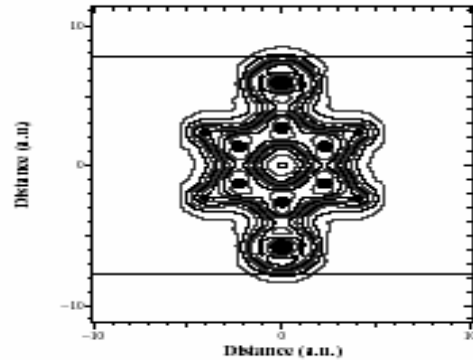


FIG. 1. Contour plot of the electron density of the molecule described in the text. The dots represent the positions of the atoms. The lines represent the position of the model metal surfaces.

assume that the molecule stands perpendicular to the metal surfaces. The molecule has  $\sigma$  bonding and  $\sigma^*$  antibonding orbitals formed by the carbon and sulfur  $p$  orbitals perpendicular to the ring plane and  $\sigma$  bonds due to the in-plane orbitals of the atoms.

We computed the  $I$ - $V$  characteristic using the method developed in Ref. [12]. The electron density of the jellium electrodes is taken equal to the value for metallic gold ( $\rho_s \approx 3$ ). The electron wave functions are computed by solving the Lippman-Schwinger equation iteratively to self-consistency in steady state. Exchange and correlation are included in the density-functional formalism within the local-density approximation [13]. All atomic positions are kept fixed at their equilibrium values in the free molecule. The current is computed from the wave functions of the electrode-molecule system. The differential conductance is then calculated as the derivative of the current with respect to the external bias. Small variations in the atomic positions (of the order of 0.1 Å) change the current by less than 1%.

The calculated  $I$ - $V$  characteristic is shown in the bottom panel of Fig. 2. The experimental curve is also shown for comparison in Fig. 2. It is clear that the shapes of the two curves are similar, but the absolute magnitude of the current and conductance is quite different. We will first discuss the origins of the shape and then address the question of absolute values.

We focus on three distinct regions in the calculated conductance curve: the initial rise (from zero bias to about 1 V), the first peak at 2.4 V, and the second peak at 4.4 V.

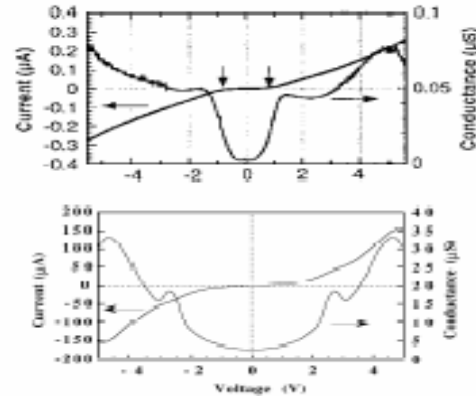


FIG. 2. Top: Experimental  $I$ - $V$  characteristic of a benzene-1,4-dithiolate molecule measured by Reed *et al.* [1]. Bottom: Conductance of the molecule of Fig. 1 as a function of the external bias applied to the metallic contacts.

In Fig. 3 we show the calculated density of states of the molecule for three different voltages, namely, 0.01, 2.4, and 4.4 V (the density of states shown is the difference between that of the molecule-electrode system and that of the electrodes without the molecule). The zero of energy is the left Fermi level so that the right Fermi level is equal

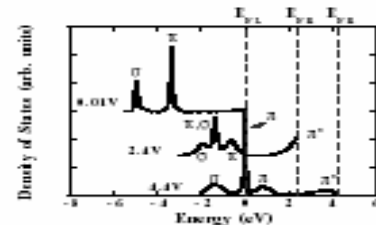


FIG. 3. Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule is between, for three different voltages. The left Fermi level ( $E_{FL}$ ) has been chosen as the zero of energy. The labels  $E_{FR}$  correspond to the energy position of the right Fermi levels. The three curves correspond to the bias voltages indicated.

## *Basic Problem*

- Conductance peaks occur at unocc. Kohn-Sham resonances
- TDDFT says true excitations differ.
- Many-body corrections not same as DFT
- At finite  $V$ , no true ground state
- Need formally rigorous DFT formulation of transport problem



## ***Simplest case: Weak Bias (with Ferdinand Evers and Rene Gaudoin)***

- Begin with ground-state DFT to get KS system
- Apply weak AC field across barrier
- Use Kubo response of electrons sloshing back and forth across barrier
- Take  $\omega \rightarrow 0$  very, very carefully.
- Need to use time-dependent *current* DFT, but still within framework of Runge-Gross theorem

# TDCDFT vs TDDFT

❖ Runge-Gross theorem proves 1-1 correspondence between time-dependent currents and vector potentials; Extra step needed for densities

Linear response: TDDFT

$$\delta\rho(z\omega) = \int dz' \chi(zz' \omega) \{ \delta v_{\text{ext}}(\omega) + \delta v_{\text{H}}(z' \omega) + \delta v_{xc}(z' \omega) \}$$

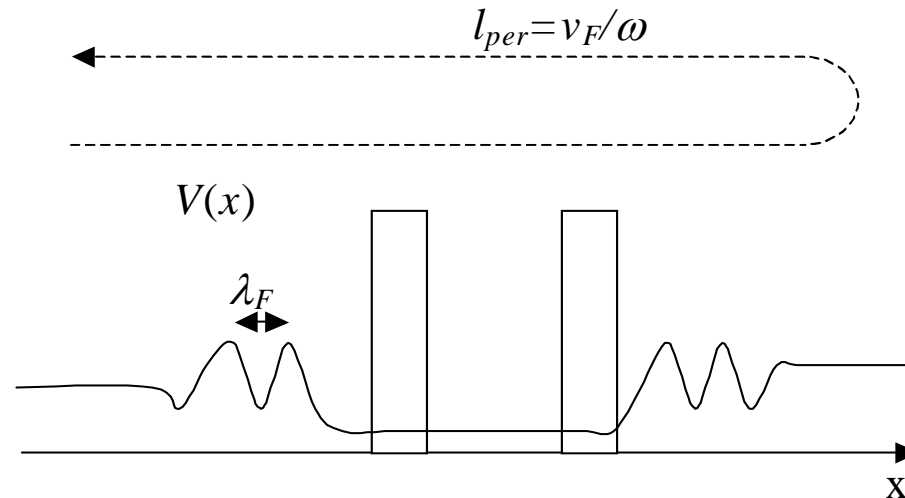
TDCDFT:

$$I(z\omega) = \int dz' \sigma_s(zz' \omega) \{ E_{\text{ext}}(\omega) + E_{\text{H}}(z' \omega) + E_{xc}(z' \omega) \}$$

Continuity and E from v:

$$\frac{d}{dz} \frac{d}{dz'} \sigma(zz' \omega) = -i\omega \chi(zz' \omega)$$

# Order of limits



- Take  $\omega \rightarrow 0$ , so that  $l_{per} \rightarrow \infty$
- Consider  $l_d \ll l_{per}$ , so only probe  $\sigma(\omega=0)$
- Write  $E_{ext} = V / l_d$ , where  $V = \text{potential drop}$ .

## *Results for weak bias limit*

- As  $\omega \rightarrow 0$ , find

$$I = \sigma_s(\omega = 0) \left( \int dz' [E_{ext} + E_H(z')] + V_{xc} \right)$$

- Can show  $\sigma_s(\omega = 0) = \frac{1}{\pi} \sum_i |t_i(\epsilon_F)|^2 = G_s$
- Here  $V_{xc} = \int dz' E_{xc}(z', \omega = 0)$
- If XC potential drop vanishes, get exactly same result as standard ground-state methodology!
- Need less local functionals than LDA or GGA (possibly VK) to get finite correction.

# *Resolution of Paradox*

- What happens to PARADOX: KS unocc levels not true excitations?
- In fact, only probing infinitesimal region around Fermi level.
- Only way to see unocc level is to scan Fermi level through it.
- But then, level becomes occ, so KS potential and  $G_s$  changes.

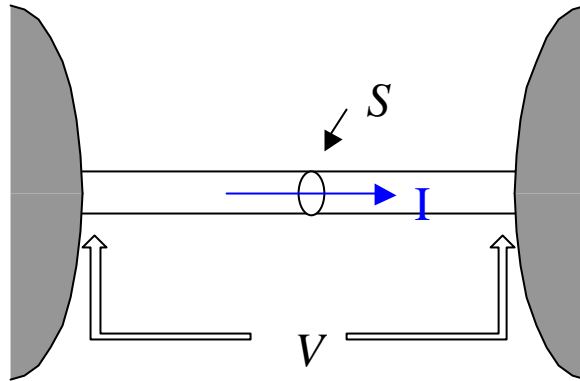
## *Appearance of Resonances*

- Suppose molecule is weakly coupled to leads. What happens as  $\mu$  touches LUMO?
- In LDA, start occupying, and get broad resonance spread over LUMO(N) and HOMO(N+1).
- In reality (and in OEP), should have sudden shift in molecular KS potential, to keep resonance sharp at A (electron affinity).

# *Summary of Weak Bias*

- When analyzed with TDCDFT, recover Landauer formula for weak bias using local approximations.
- Non-local functionals (eg VK) may yield corrections.
- Derivative discontinuity enforces sharp resonances. Origin of discrepancy with expt (theoretical conductance too large)?

# *DFT difficulties with open boundaries*

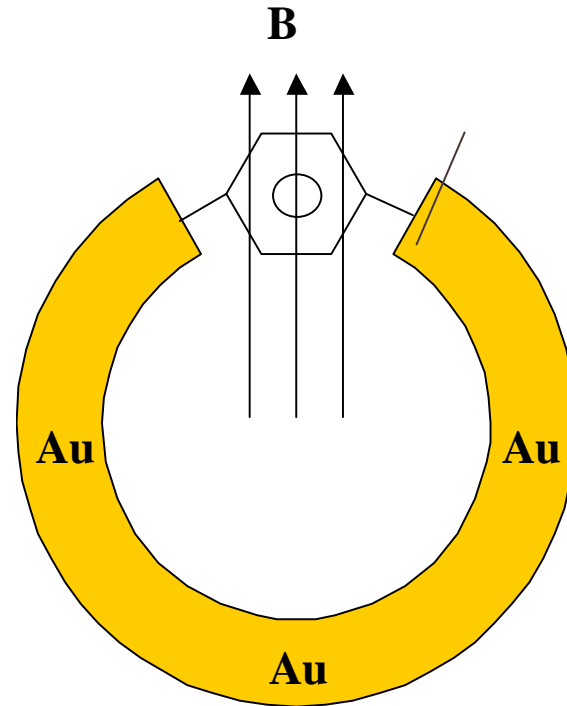


- In distant past, all three (L,R, mol) isolated
- Use Keldysh to adiabatically evolve into coupled system
- Means not starting from ground state, or have zero density regions (HK fails)



# *Finite Electric Fields WITHOUT open boundaries*

- Treats electric field in periodic potential correctly: no left and right chemical potentials
- No empirical parameters
- Leads chemically accurate (CP code)
- Entire problem becomes time-dependent, with no ground state, but only steady-state solutions
- So must have dissipation!



$$\mathbf{A} = -c \int_0^t dt' \mathbf{E}(t')$$

# *Master equation approach to dissipation (standard)*

- $H = H_{\text{el}} + H_{\text{ph}} + K_{\text{el-ph}}$
- Assume relaxation time much longer than time for transitions or phonon periods
- Coarse-grain over electronic transitions and average over bath fluctuations
- Master equation for system density matrix:

$$\frac{dS}{dt} = -i[H, S] + C(S(t))$$

## *Master equation continued*

- Operator  $C$  is from Fermi's golden rule applied to  $K_{\text{el-ph}}$
- Transition probabilities satisfy detailed balance
- Builds in irreversibility to evolution
- Allows off-diagonal density matrix elements, so not a pure state evolution
- Prototype: lifetime of two-level atom coupled to quantized photon field

# *Restoring continuity in Master equation*

- In t-dep Sch. Eqn:
- For  $A$ , define  $B=i[H,A]$ , so  $\langle B \rangle = d\langle A \rangle / dt$
- Eg  $B = \text{grad } j$  if  $A = \rho$
  
- In Master equation, find
- $d\langle A \rangle / dt = \langle B \rangle + \text{Tr } CA$
- Or  $d\langle A \rangle / dt = \langle B \rangle + \text{Tr } DB$
- Ralph and Roberto have explicit expression for operator  $D$

## *1-1 correspond. for Master eqn*

- Assume potential is Taylor-expandable about  $t=0$ .
- Consider two potentials that differ by more than  $c(t)$
- Show that current densities must then differ
- Use (restored) continuity to prove densities differ.

# *TDDFT of Master equation*

- For fixed  $S(0)$ ,  $C$ , e-e interaction, and statistics, can prove RG theorem: 1-1 correspondence between  $\rho(\mathbf{r},t)$  and  $V_{\text{ext}}(\mathbf{r},t)$
- Define a Kohn-Sham Master equation yielding same  $\rho(\mathbf{r},t)$  from  $v_s(\mathbf{r},t)$ , but choose  $C_s$  to equilibrate to the Mermin-Kohn-Sham  $S_s(0)$
- Requires  $v_{xc}[\rho, C, C_s](\mathbf{r},t)$ , but we neglect  $C$  dependence.
- Can recover Kubo linear response, so isothermal conductivity=adiabatic conductivity

# Summary

- TDDFT is alive and well in the state of New Jersey
- Can analyze molecular conductance in weak bias limit using linear response TDCDFT:  
Recovers Landauer for ground-state KS potential plus possible XC corrections
- For finite bias, we need dissipation, and now we have a new extension for doing it (Gebauer and Car calculations).
- Thanks to all friends and US DOE.

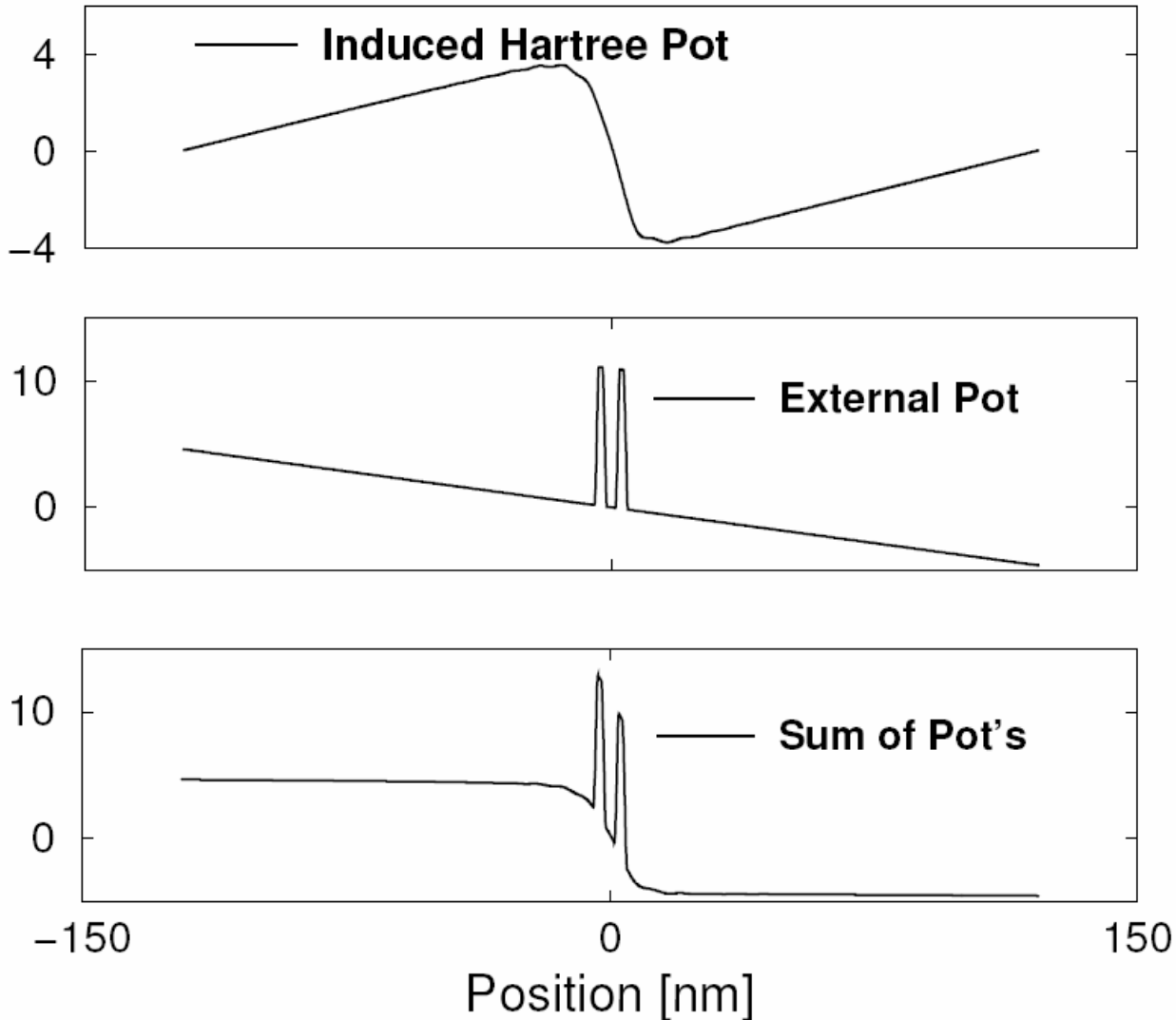
# *Calculations on a 1d model*

- All work of Ralph Gebauer with Roberto Car (no KB)
- 1d double barrier system in time-dependent Hartree
- Only find steady-state solution
- Simplified model of electron-phonon coupling, proportional to  $\gamma$

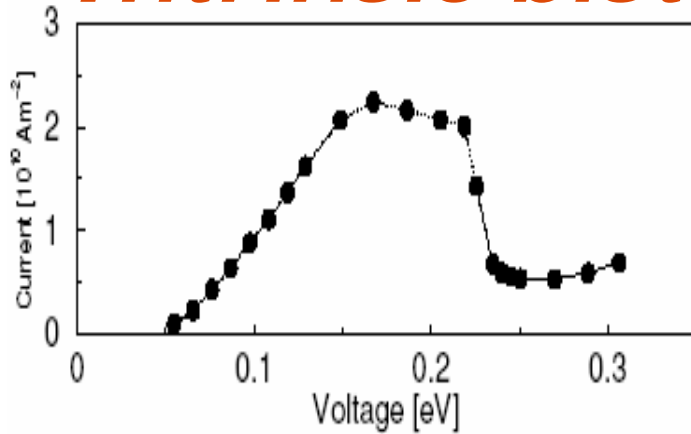


# Tunneling Barrier

## Potentials

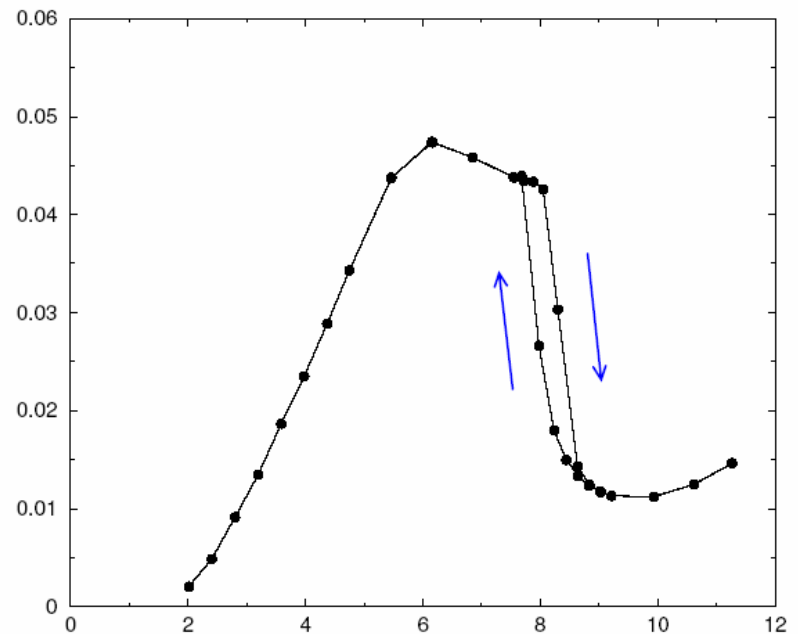


# *Intrinsic bistability at high fields*



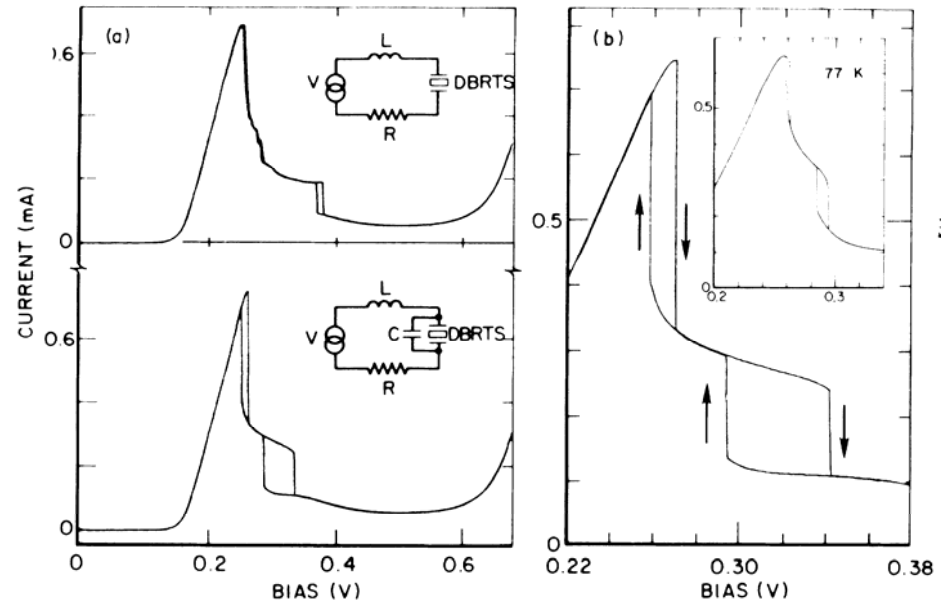
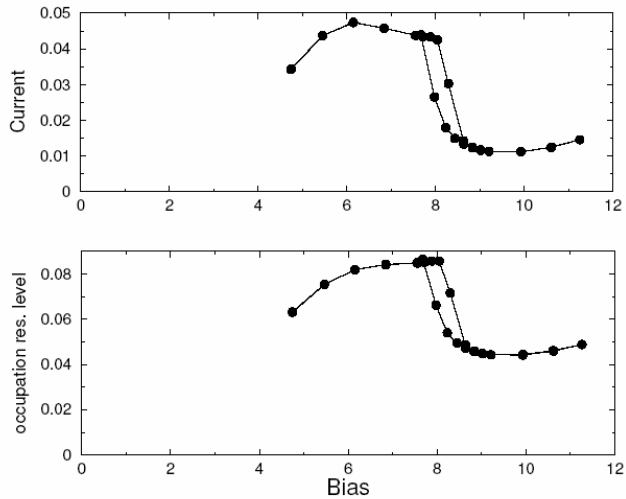
Self-consistent steady state calculation: each point is obtained by starting from scratch

A self-consistent steady state calculation which mimics an adiabatic sweep shows **intrinsic bistability**



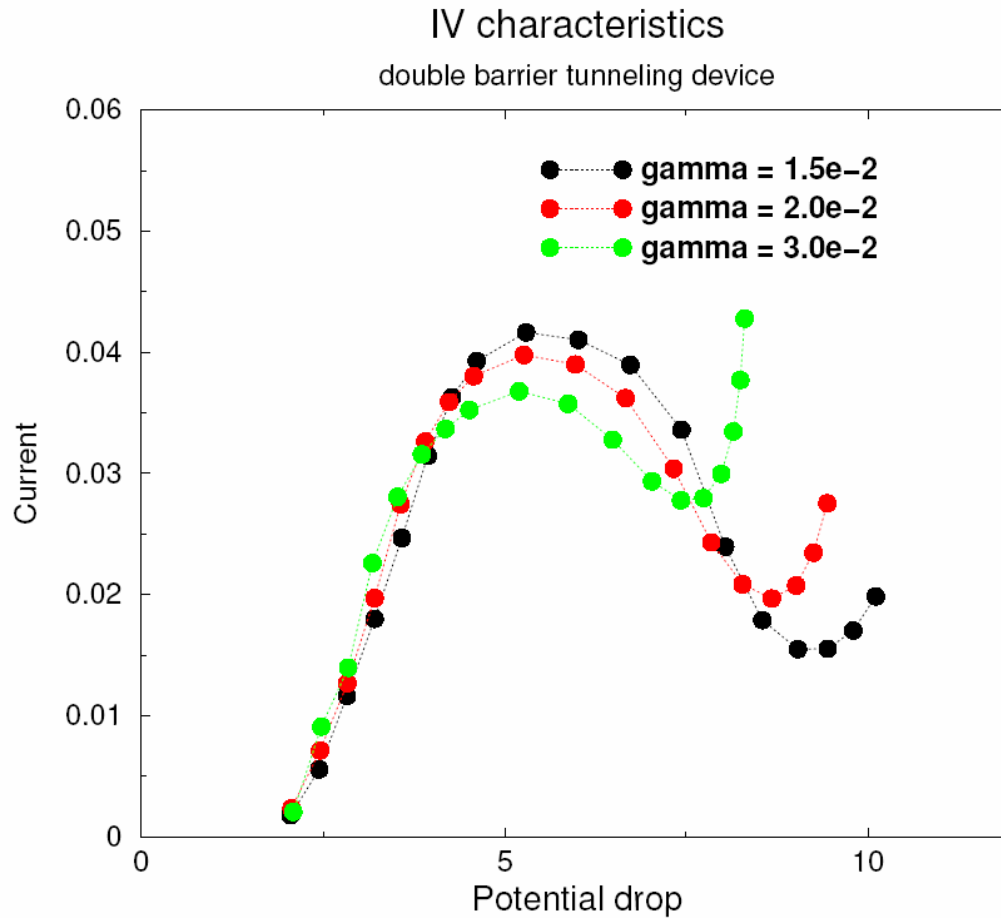
# Charging of resonant level

The origin of the intrinsic bistability is due to charging of the resonant level (as conjectured by Goldman, Tsui and Cunningham)

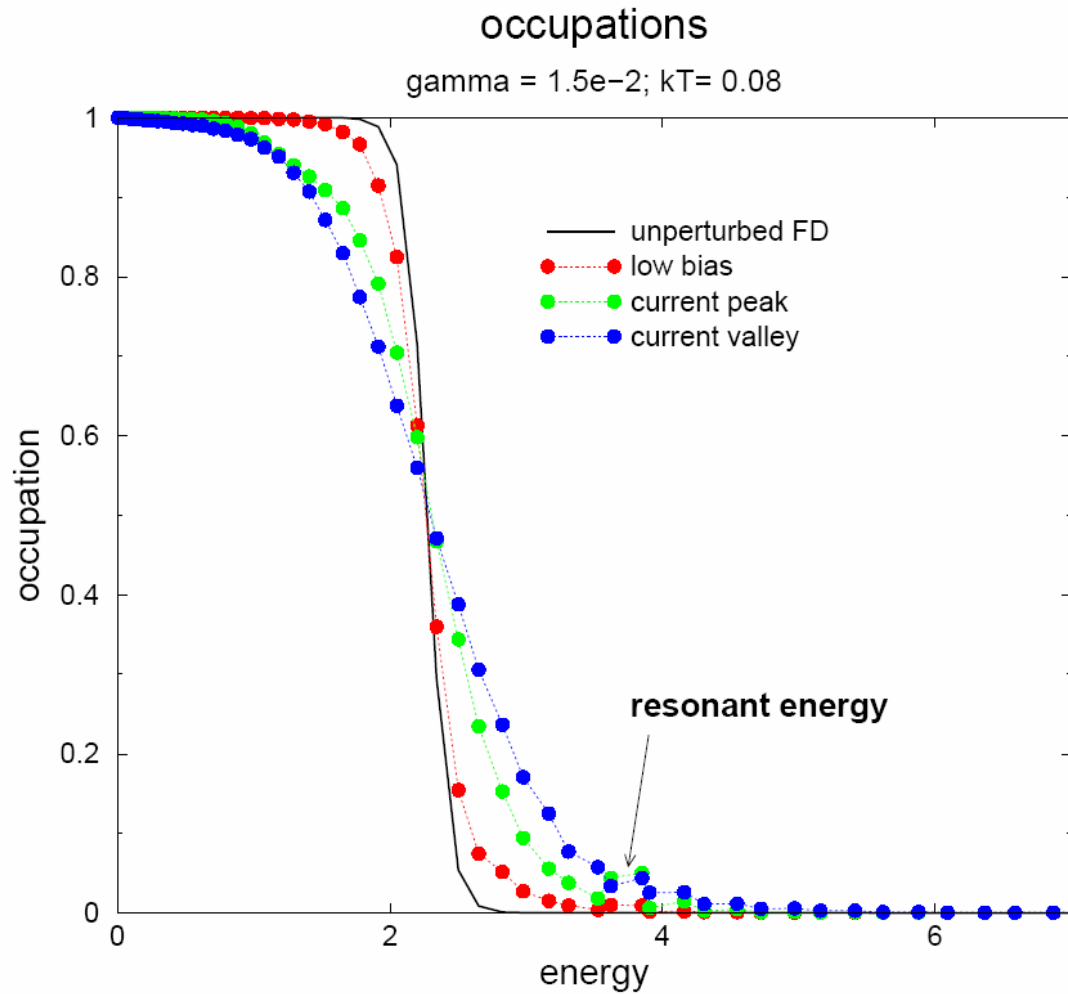


*hysteresis effects* (from Goldman, Tsui, Cunningham, *PRL* 58, 1256 (1987))

# *I-V characteristics for different couplings*



# *Deviation from equilibrium*



## *Work to be done*

- Building realistic CP simulation of this type (few weeks)
- Recover Landauer formula from this isothermal conductivity (linear response gives adiabatic conductivity)
- Run fully time-dependent simulations
- Coulomb blockade?

## *Discussion*

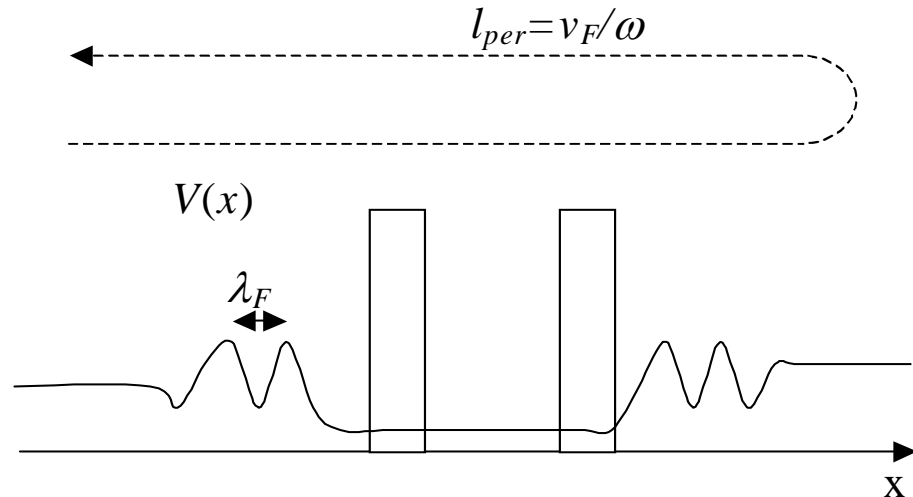
- The approach assumes an infinite bath (continuous spectrum) but the system is finite in numerical applications with PBC: finite  $T$  and electron-phonon coupling are required.
- Analogy with Non Equilibrium MD approaches for transport in the classical domain
- Non-linear effects are included but it is likely that the size and time scales that are accessible in numerical computations may require large electron-phonon couplings to achieve steady state conditions

## *Acknowledgements*

- This work is the result of a collaboration with Ralph Gebauer (currently at ICTP, Trieste)
- Ralph and I have benefited from stimulating discussions with many colleagues
- A realistic electronic structure implementation is under way (S. Piccinin and R. Gebauer)
  
- Funding has been provided by DOE



# Landauer in TDCDFT response



$$I(z\omega) = \int dz' \chi_{jjS}(zz'\omega) \{ E_{\text{ext}}(\omega) + E_H(z'\omega) + E_{\text{XC}}(z'\omega) \}$$

$$\chi_{jjS}(zz'\omega = 0) = \frac{1}{\pi} \sum_i |t_{iS}(\varepsilon_F)|^2 = G_S$$

Expect:

$$I = GV = (G_S + \Delta G_{\text{XC}}) V$$

just as in isolated molecule case

# *Back to basics: linear response*

- First, can we handle it at linear response level? Begin with ground-state DFT to get KS system.
- Following Kamenev and Kohn, apply weak AC field across barrier
- Use Kubo response of electrons sloshing back and forth across barrier
- Need to use time-dependent current

# Linear response in TD current DFT (TDCDFT)

Key quantity is tensor susceptibility:

$$\vec{\chi}(\mathbf{r}\mathbf{r}', t - t') = \frac{\delta \mathbf{j}(\mathbf{r}t)}{\delta \mathbf{a}(\mathbf{r}'t')}$$

where  $\mathbf{j}(\mathbf{r}t)$  is current-density, and  $\mathbf{a}(\mathbf{r}t)$  is vector potential,

$$\mathbf{E} = -\frac{\partial \mathbf{a}}{\partial t} \ .$$

KS linear response:

$$\mathbf{j}(\mathbf{r}\omega) = \int d\mathbf{r}' \vec{\chi}(\mathbf{r}\mathbf{r}'\omega) (a_{\text{ext}}(\mathbf{r}'\omega) + a_{\text{H}}(\mathbf{r}'\omega) + a_{\text{XC}}(\mathbf{r}'\omega))$$

## *Perspectives*

- Calculations on realistic models (real atoms, molecules and contacts) are possible by exploiting the flexibility of supercell geometries and of electronic structure codes based on DFT (we are already at an advanced stage of implementation)
- It would be feasible to use realistic phonon models and electron-phonon couplings
- The approach could be used to study dynamic phenomena within the limits of: (1) average density matrix dynamics, (2) Markov approximation.

## Linear response in TD current DFT

KS tensor susceptibility:

$$\vec{\chi}_s[n_0](\mathbf{r}\mathbf{r}'\omega) = \sum_{jk} (f_k - f_j) \frac{\phi_j(\mathbf{r})\vec{\nabla}\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\vec{\nabla}\phi_k(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i0_+}$$

where  $A\vec{\nabla}B = A\nabla B - B\nabla A$ , the Hartree potential is

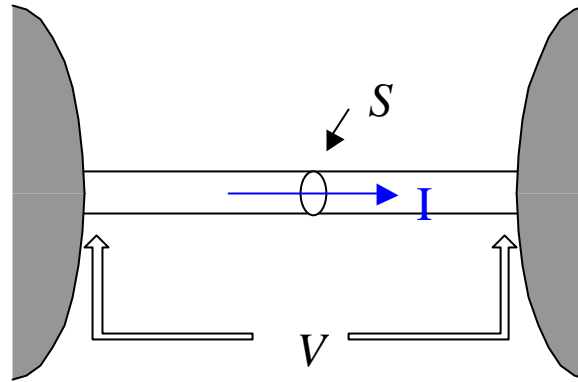
$$\mathbf{a}_H(\mathbf{r}\omega) = \frac{\nabla}{(i\omega)^2} \int d\mathbf{r}' \frac{\nabla' \cdot \mathbf{j}(\mathbf{r}'\omega)}{|\mathbf{r} - \mathbf{r}'|}$$

and

$$\mathbf{a}_{XC}^{ALDA}(\mathbf{r}\omega) = \frac{\nabla}{(i\omega)^2} \int d\mathbf{r}' \nabla' \cdot \mathbf{j}(\mathbf{r}'\omega) f_{XC}^{unif}(\mathbf{r}\mathbf{r}'\omega)$$

$$\Delta \mathbf{a}_{XC}^{VUC}(\mathbf{r}\omega) = -\nabla \vec{\sigma}_{XC}(\mathbf{r}\omega) / i\omega n_0(\mathbf{r})$$

where  $\vec{\sigma}_{XC}$  is a fictitious XC stress tensor for a slowly varying gas in an electric field.



For simplicity, assume only one channel, and take average over cross-section:

$$I(z\omega) = \int dz' g(zz'\omega) \{ E_{\text{ext}}(\omega) + E_{\text{H}}(z'\omega) + E_{\text{XC}}(z'\omega) \}$$

where  $I(z\omega) = \int dz' j_3(\mathbf{r}\omega)$  is total current,  $g(zz'\omega)$  is non-local conductance, the surface-averaged 3-component of tensor susceptibility (divided by  $i\omega$ ) and  $E(z\omega)$  is the surface-averaged 3-component of the electric field.

# *Outline*

- I. Background:
  - Philosophy and aims
  - Review of DFT and TDDFT
  - Problems with transport
- II. Weak bias:
  - DFT Derivation of Landauer
  - Corrections to KS Landauer
- III. Finite bias:
  - Avoiding open boundary conditions
  - Kohn-Sham Master eqn for dissipation
  - Results of model calculations
- Conclusions and perspectives
- Response in a wire (current)

## Response in a wire (conductance)

Continuity:

$$\partial I(z, \omega) / \partial z = i\omega n(z, \omega)$$

Hartree:

$$\partial E_H(z, \omega) / \partial z = 4\pi n(z, \omega) / S$$

which can be solved self-consistently. Then

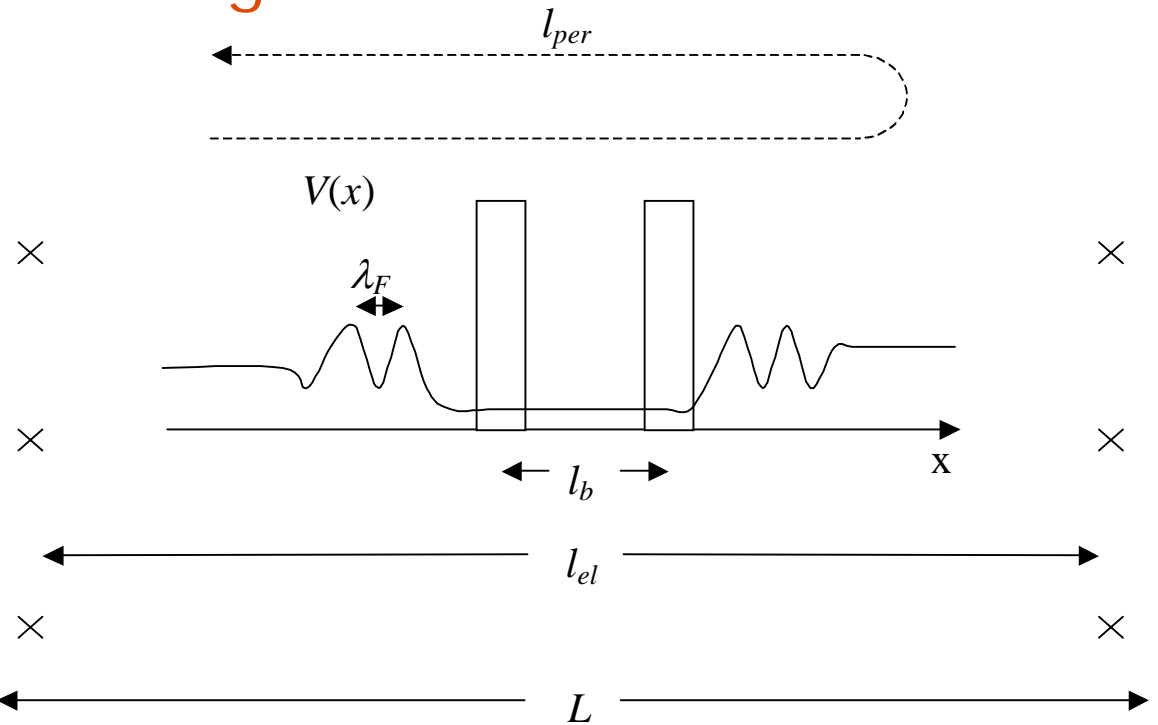
$$g_z = \frac{I_0}{V} = \frac{\int dz g_0(z, \omega) E_{\text{ext}}(\omega)}{\int dz E_H(z, \omega)}$$

where  $g_0$  is non-local conductance without barrier.



## Length scales

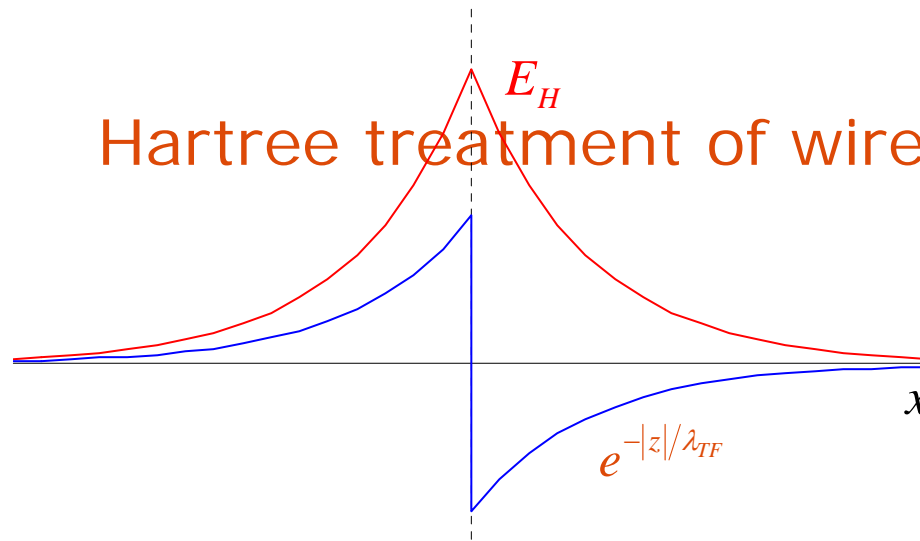
Model system:



- $L$  = length of leads
- $\lambda_F$  = Fermi wavelength
- $l_b$  = width of barrier
- $l_{el}$  = elastic scattering length
- $l_{per} = v_F/\omega =$  distance traveled by a Fermi electron during one period of external field, if free
- $\lambda_{TF}$  = Thomas-Fermi screening length  
 $= v_F/\omega_p$ , where  $\omega_p$  is the plasmon frequency.

Long clean leads:  $l_b, \lambda_{TF}, \lambda_F \ll l_{per} \ll L, l_{el}$ .

# Hartree treatment of wire



Find non-local conductance outside barrier:

$$g(zz'\omega) = \frac{e^2}{\pi\hbar} T e^{i(|z|+|z'|)/l_{per}}, \quad zz' < 0$$

$$= \frac{e^2}{\pi\hbar} \left\{ e^{i|z-z'|/l_{per}} - R e^{i(|z|+|z'|)/l_{per}} \right\}, \quad zz' > 0$$

Producing

$$\delta n(z\omega \rightarrow 0) = C \operatorname{sgn}(z) \exp(-|z|/\lambda_{TF})$$

$$E_H(z\omega) = -E_{\text{ext}} \frac{iRl_{per}}{T\lambda_{TF}} \exp(-|z|/\lambda_{TF})$$

Yields Landauer 4-terminal result:

$$\tilde{g} = \frac{e^2}{\pi\hbar} \frac{T}{R}$$

## XC corrections to Landauer?

- Include XC fields in response equations.

How does  $\tilde{g} = I_0 / V$  change?

- $I_0$  is uniform so can be taken far from barrier

$$I_0(-\infty) = \int dz' g(zz' \omega) \{E_{\text{ext}}(\omega) + E_{\text{XC}}(z' \omega)\}$$

\*  $I_0$  changes only if non-local response in XC fields

\* ALDA can only produce field where  $\delta n(z) \neq 0$ ,

\* Vignale-Kohn current gradient expansion yields corrections to ALDA, but only where  $\nabla \cdot \mathbf{j} \neq 0$ .

- $V = \int dz E_{\text{H}}[\delta\rho]$ , so only have XC corrections if XC effects significantly change density response.

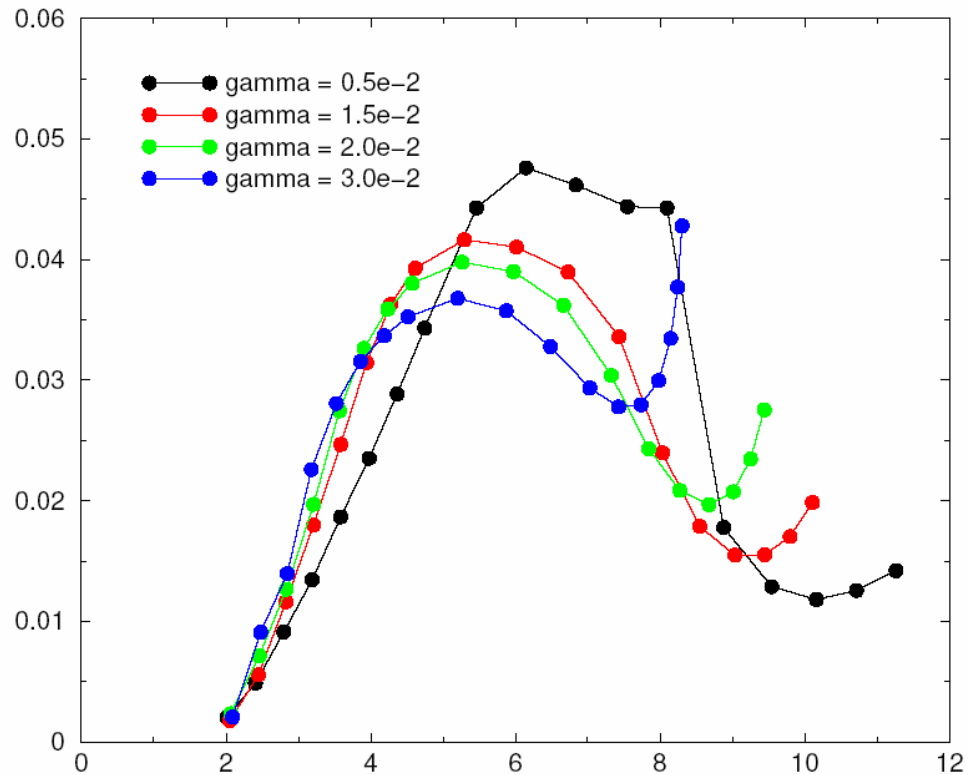
**This leaves two big questions:**

- Are XC corrections very small?

Calculations in progress on simple models (Eunji Sim, Rudy Magyar, Rene Gaudoin)

- Might they be zero? Its conceivable.

# *IV for different couplings*



# *Quantum Liouville Master equation*

- Gives evolution of system plus dissipative bath:

$$dS / dt = -i[H, S] + C(S(t))$$

- S = system density matrix, H=system Hamiltonian
- C contains coupling to bath, valid when weak so relaxation time is long
- BUT no longer unitary evolution via a Schrodinger equation, so even TDDFT does not apply!
- Entire problem becomes time-dependent, with no ground state, but only steady-state solutions
- **Not** accessible via TDDFT! (Need TDCDFT)
- **BUT must have DISSIPATION, or else no steady-state!**

## *Roberto's Bulk transport: the Boltzmann equation*

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

**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

## *Roberto's Master eqn*

At the nanoscale, when the dimensions of a device are comparable to the electron wavelength, the **semi-classical** Boltzmann equation should be replaced by a **quantum-mechanical** Liouville-Master equation for the reduced density operator describing a system coupled to a heat bath

$$f \rightarrow S$$

$$\frac{dS}{dt} = -i[H, S] + C[S]$$

**Steady State:**  $i[H, S] = C[S]$

# Electrons and Phonons

## Roberto's density matrix

$$H_T = H + R + V$$

$$R = \sum_{\alpha} \omega_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} = \int d\omega g(\omega) \omega a_{\omega}^{\dagger} a_{\omega}$$

$$V = \hat{\mathbf{a}}_i L_i F_i = \hat{\mathbf{a}}_{n,m,a} g_{n,m}^a c_n^{\dagger} c_m a_a^{\dagger} + c.c.$$

$$i \frac{\partial \mathbb{Z}}{\partial t} = [H_T, \mathbb{Z}]$$

Solve for the reduced density operator  $S(t) = \text{Tr}_R Z(t)$



# Roberto's derivation of Master

## Important approximations

- treat  $V$  to 2<sup>nd</sup> order in perturbation theory
- assume that the harmonic bath is in thermal equilibrium
- make Markov approximation, i.e. **coarse-graining in time** so that on the time scale of system damping electron-phonon scattering processes are treated as instantaneous processes via Fermi's golden rule

$$\tau_c \ll t \ll T_R$$

The resulting equation has the Lindblad form:

## Roberto's Lindblad

$$\frac{dS}{dt} = -i[H, S] - \sum_{n,m} G_{m,n} (L_{n,m} L_{m,n} S + S L_{n,m} L_{m,n} - 2L_{m,n} S L_{n,m})$$

$$L_{n,m} = c_n^\dagger c_m \quad G_{n,m} = \begin{cases} |g_{n,m}|^2 (\bar{n}_w + 1) g(w), & w = e_m - e_n \\ |g_{n,m}|^2 \bar{n}_w g(w), & w = e_n - e_m \end{cases}$$

The difference between emission and absorption processes ensures *detailed balance*:

$$\frac{G_{n,m}}{G_{m,n}} = e^{b(e_m - e_n)}$$

Notice:  $S$  is an  $N$ -particle density operator

The single particle density matrix is:  $f_{ij}(t) = \text{Tr} \left[ \hat{\rho} c_i^\dagger c_j \right]$

## Roberto's KS Master eqn

Then the Master Equation for  $f$  is:

$$\dot{f}_{n,m} = \frac{1}{2} (d_{n,m} - f_{n,m}) \sum_p (G_{n,p} + G_{m,p}) f_{p,p} - \frac{1}{2} f_{n,m} \sum_p (G_{p,n} + G_{p,m}) (1 - f_{p,p})$$

This has the **Fermi-Dirac** distribution as the equilibrium distribution ( $\dot{f}_{n,m} = 0$ )

For the diagonal elements this is:

$$\dot{f}_{n,n} = (1 - f_{n,n}) \sum_p G_{n,p} f_{p,p} - f_{n,n} \sum_p G_{p,n} (1 - f_{p,p}),$$

i.e. the familiar term for  $\left( \frac{\partial f}{\partial t} \right)_{\text{collisions}}$  in the Boltzmann equation

# *Periodic Supercell Approach*

A *ring geometry* allows current flow



...But a *static* uniform electric field breaks translational invariance

This difficulty is solved in a *dynamic* approach which uses a different *gauge* for the electric field

# *Roberto's gauge change*

Rather than

$$\mathbf{E} = -\nabla \varphi, \quad \varphi = -\mathbf{E} \cdot \mathbf{x}$$

Use

$$\mathbf{E} = -\frac{\partial A}{c \partial t}, \quad A = -c\mathbf{E}t$$

This corresponds to a *ring geometry* in which an electric current is induced by a magnetic flux

# Roberto's KS in new gauge

## Effective single-particle formulation:

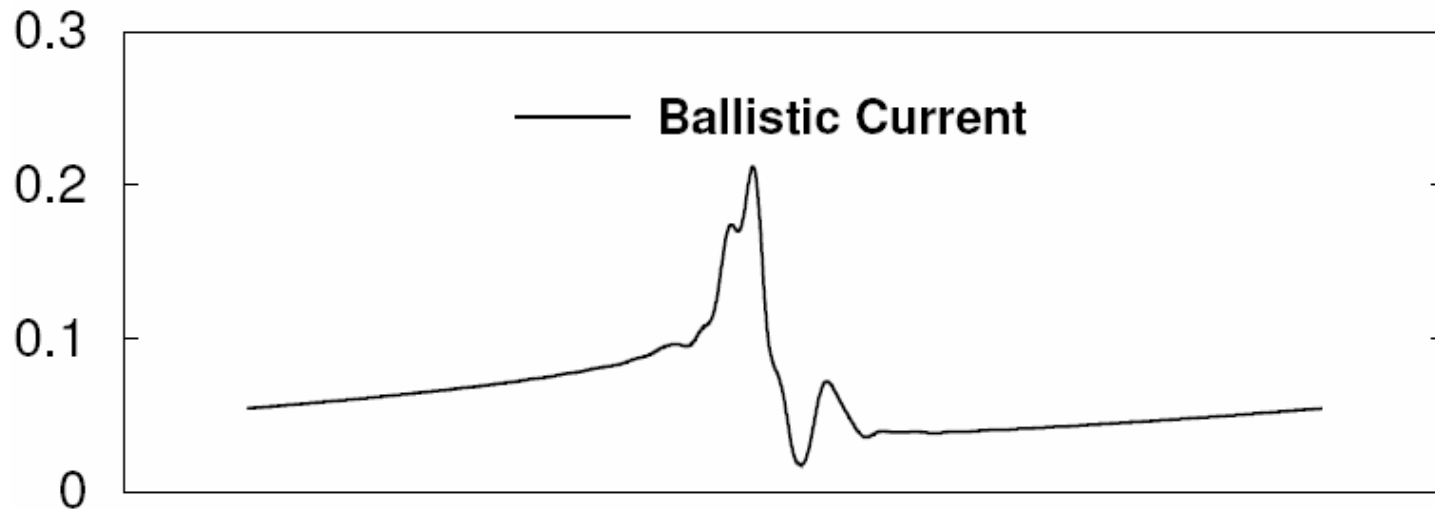
$$\dot{f}_{n,m} = -i \dot{\mathbf{a}}_p \left( H_{n,p}^E(t) f_{p,m} - f_{n,p} H_{p,m}^E(t) \right) \\ + (d_{n,m} - f_{n,m}) \dot{\mathbf{a}}_p \left( \mathbf{G}_{n,p} + \mathbf{G}_{m,p} \right) f_{p,p} - f_{n,m} \dot{\mathbf{a}}_p \left( \mathbf{G}_{p,n} + \mathbf{G}_{p,m} \right) (1 - f_{p,p})$$

Here:

$$H^E(t) = \frac{(p - Et)^2}{2} + U_0(x) + \int dx' \frac{\delta n(x';t)}{|x - x'|}$$

The electric field can be systematically “gauged” away from the kinetic energy to avoid indefinite “growth” of the Hamiltonian

# Roberto's current continuity problem



$$j(x;t) = \text{Tr} \left[ \hat{S}(t) \hat{J}(x) \hat{U} \right] \quad \hat{J}(x) = \frac{1}{2} [\hat{p}d(x-\hat{x}) + d(x-\hat{x})\hat{p}]$$

**Why is continuity violated ?**  $\partial_t \rho(x;t) = - \tilde{\mathbf{N}} \times j(x;t)$

## *Roberto's Current continuity soln*

$$\frac{dS}{dt} = -i[H, S] \Rightarrow \langle x | \frac{dS}{dt} | x \rangle = \frac{dn(x; t)}{dt} = -\nabla \cdot j(x; t)$$

$$\frac{dS}{dt} = -i[H, S] + C[S] \Rightarrow \langle x | \frac{dS}{dt} | x \rangle = \frac{dn(x; t)}{dt} = -\nabla \cdot j(x; t) - \nabla \cdot j_C(x; t)$$

Omission of a contribution due to the bath must account for the apparent violation of continuity

Only when the bath does not cause charge density rearrangement:

$$\nabla \cdot j_C(x; t) = 0 \quad \text{and the standard definition is valid}$$



Although the coupling of the system to the bath is *local*, a contribution to the current due to the bath is present because of the *coarse graining* in time implicit in the Markov approximation.

The bath contribution has the form of a “coarse grained” average:

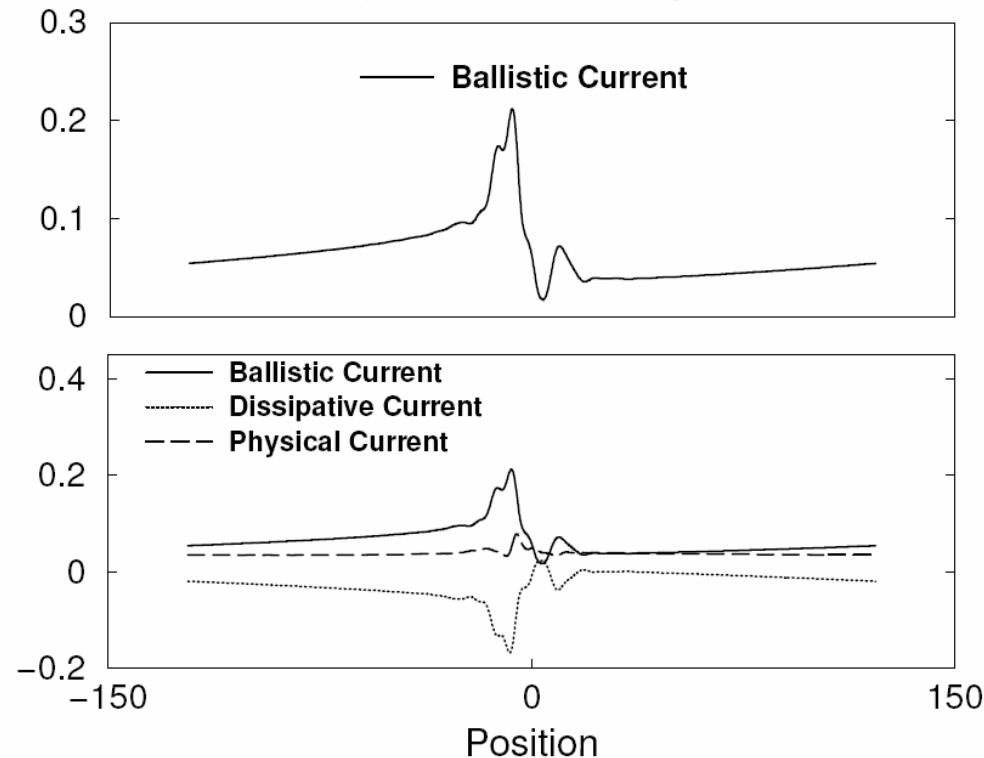
$$j_C(x, t) = \frac{\text{Tr} \int_{t_0}^t dt \rho(S(t) - S_H(t)) \hat{J}(x)}{t - t_0}$$

This can be calculated by perturbation theory by taking the limit  $t - t_0 \rightarrow \infty$  as done to derive Fermi's golden rule.

The dependence on  $t_0$  disappears and we can prove that

$$\left( \frac{dn(x; t)}{dt} \right)_{\text{collisions}} = -\nabla \cdot j_C(x; t)$$

# Roberto's results for fixing Tunneling Barrier currents



On the coarse grained time scale of Markovian dynamics the physical current is  $j_T(x;t) \equiv j(x;t) + j_C(x;t)$

# *A seemingly trivial application*

A 1D wire (flat potential) in contact with a double barrier resonant tunneling structure in a ring geometry

Use a simplified model for electron-phonon collisions

$$G_{n,m} = \begin{cases} |g|^2 (\bar{n}_w + 1) w^2, & w = e_m - e_n \\ |g|^2 \bar{n}_w w^2, & w = e_n - e_m \end{cases}$$

Look for steady state:  $\frac{df_{n,m}}{dt} = 0$