

# DFT for molecular transport: A tutorial

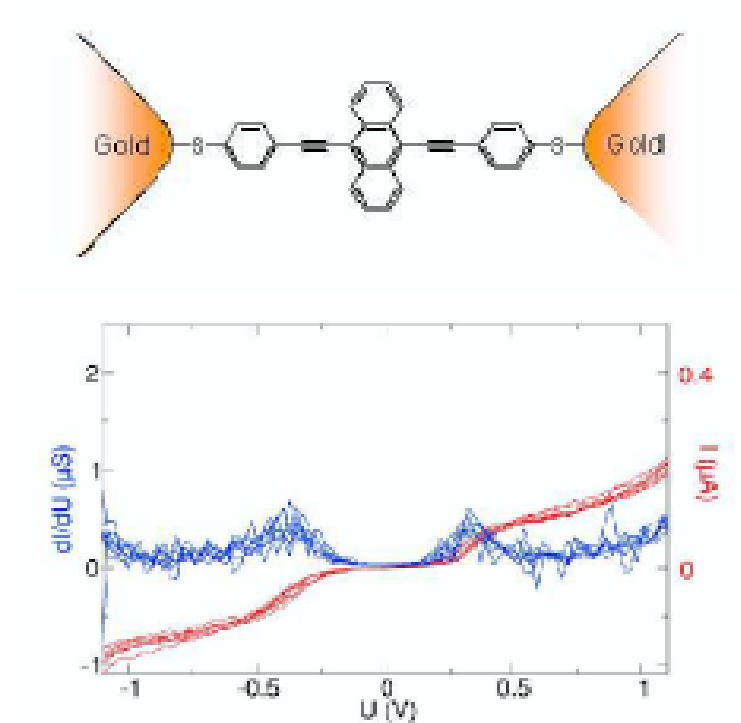
Kieron Burke

<http://dft.uci.edu>

# What we'll cover

- Only electronic degrees of freedom (but see Galli on weds, KITP)
- Not metal chains or CNT's
- Just molecular electronics with organics

# Break junction expts



Experiments:

H. Weber, R. Ochs, J. Reichert,

M. DiLeo, J. Würfel, INT Research Center Karlsruhe

PRL 88, 176804 (2002); PNAS 102, 8815 (2005)

# Why is it difficult?

- Need chemical-type accuracy
- Hundreds of atoms needed to get details right
- Poorly characterized experiments (now improving)
- Lots of difficulties with theories all combined in one problem:
  - Not a ground state
  - Not a finite system, but not bulk either

# Difficult regime (for DFT)

- Strong correlation:
  - Developed over decades in mesoscopic physics, especially by Landauer and Buttiker
  - Imagine molecule weakly coupled to leads
  - Get Coulomb blockade effects: One electron on molecule stops a second electron getting through
  - Supriyo Datta (great website – the nanohub) uses rate equations and MBT to describe.
  - Can study effect with model Hamiltonians (e.g., Kristian Thygesen).

# Standard approach: History

- Late 90's, after Reed-Tour experiment
- Hong Guo et al – used Green's functions
- diVentra, Pantelides, and Lang – scattering state approach
- Now many groups with variety of codes
- Sanvito et al – Spintronics code (Blugel, tomorrow at KITP, Ullrich – Friday, KITP).

# Standard approach

- Apply Landauer formula to ground-state KS potential
- Calculate transmission as a function of energy
- Not really non-equilibrium Greens functions
- Just ground-state DFT for KS potential and transmission through that.

# Standard approach: NEGF

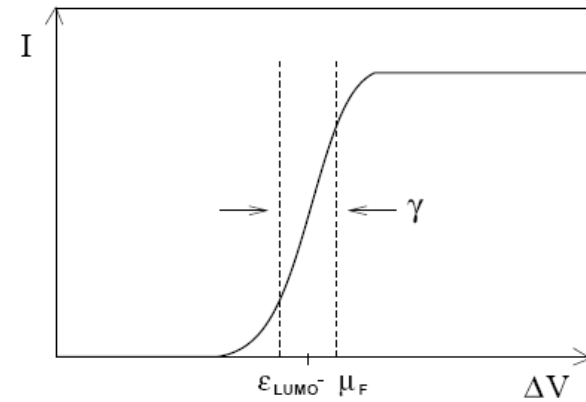
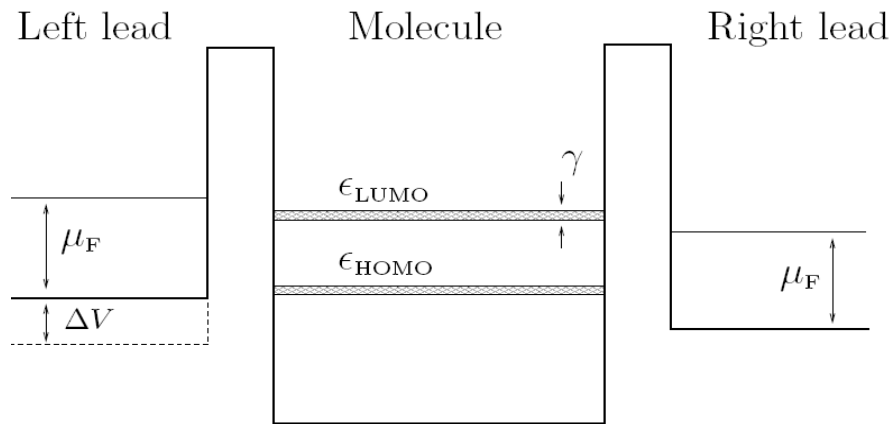


FIG. 2: Schematic current-voltage characteristic of the resonant tunneling device displayed in Fig. 1. The onset of the current occurs around  $\epsilon_{\text{LUMO}} - \mu_F$ . The step is broadened by the coupling  $\gamma$ .

$$I = \frac{1}{\pi} \int_{-\infty}^{\infty} d\epsilon T_s(\epsilon, V) (f_L(\epsilon) - f_R(\epsilon))$$



# Basic agreement?

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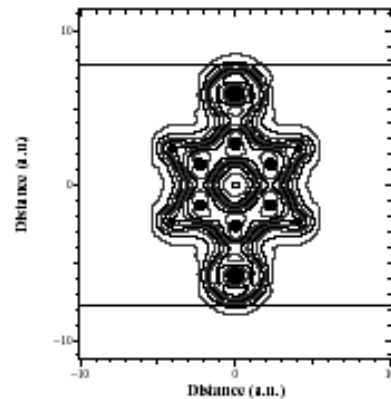


FIG. 1. Contour plot of the electron density of the molecule described in the text. The dots represent the positions of the atoms. The lines represent the position of the metal surfaces.

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.

980

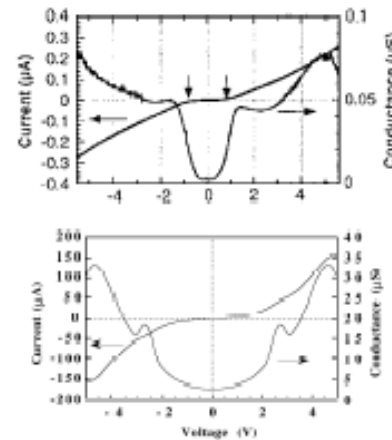


FIG. 2. Top: Experimental  $I$ - $V$  characteristic of a benzene-1,4-dithiolate molecule measured by Reed *et al.* [1]. Bottom: Conductance of the molecule of Fig. 1 as a function of the external bias applied to the metallic contacts.

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

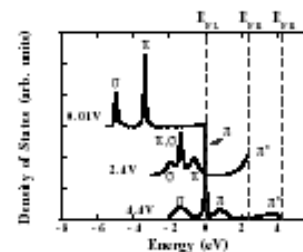


FIG. 3. Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule is shown, for three different voltages. The left Fermi level ( $E_{FL}$ ) has been chosen as the zero of energy. The labels  $E_{FR}$  correspond to the energy position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

Di Ventra,  
Pantelides,  
Lang

# Basic questions we'll address

- Do we know how steady current arises?
  - Kurth et al
- What is the exact Landauer formula for interacting system?
  - Meir-Wingreen is very special case.
- If standard model were true, are standard functionals good enough?
  - Sanvito et al., Neaton et al.

# Advanced questions we'll address

- In the limit of weak bias, is the standard model correct? Koentopp et al, diVentra et al.
- Where do TDDFT and TD current DFT come in?
- What is best approach to general problem?
  - Full time-dependent electronic approach (Euro)
  - Master equation approach to steady state (US)

# How does steady current arise?

- If reservoirs are finite, and potential step is applied and then held constant, there's no more time-dependence
- But you're not in an eigenstate, so get transitions between states forever, so no steady state.
- Need infinite reservoirs so electrons can pass through and never reflect.
- Von Alnbladh and Stefanucci proved for non-interacting electrons, and gave conditions (PRB 03)
- Kurth et al showed time-propagation for infinite leads produces steady solution = Landauer for non-interacting particles (PRB 05)

# What is exact Landauer formula?

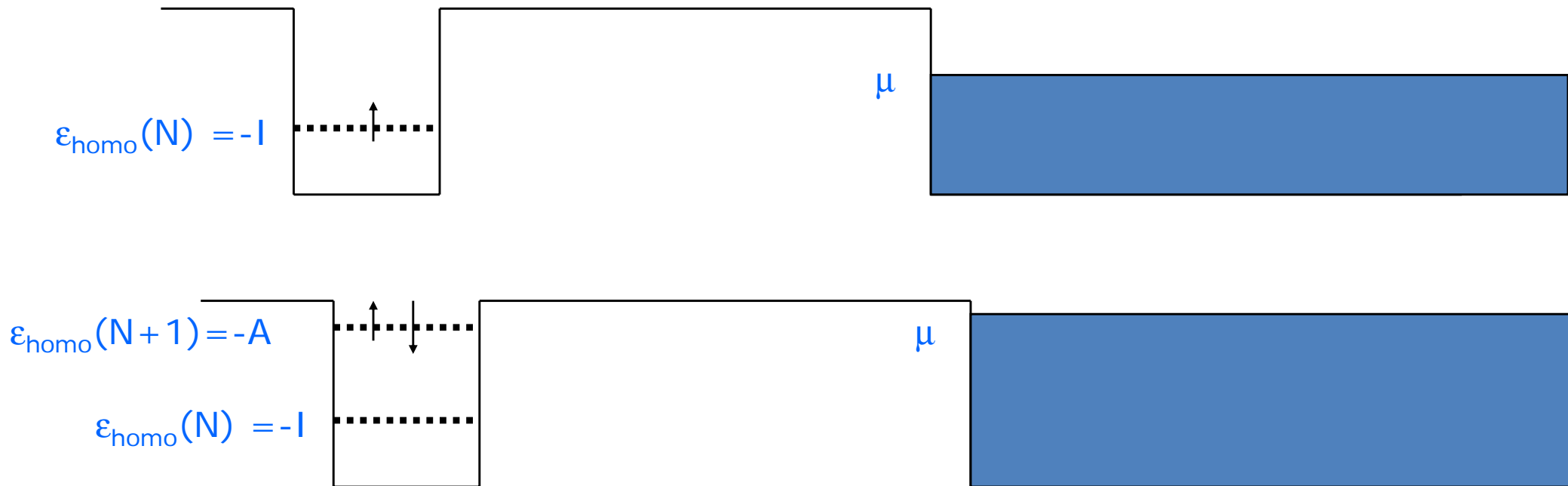
- Can show Landauer correct for non-interacting problems, and bias.
- For zero-bias limit, Landauer gets Hartree corrections right, but not XC.
- Meir-Wingreen (PRL89) limited by one-site molecule plus non-interacting leads
- Euros (esp Robert van Leeuwen) produce exact interacting formula for time-dependent non-equilibrium Green's functions.

# If standard model were correct, do popular functionals give right answer?

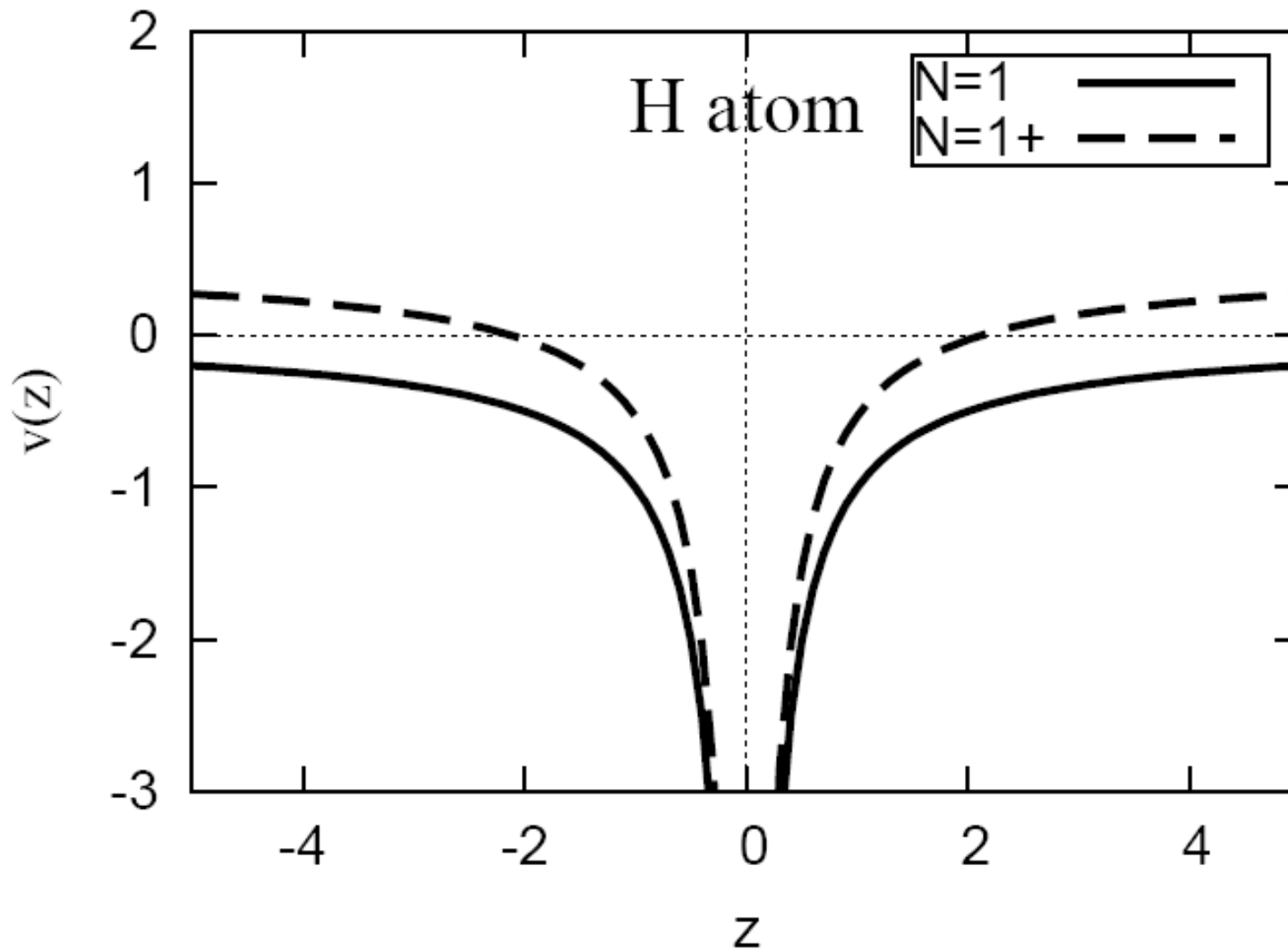
- Can see answer is NO in weakly-coupled limit, because of derivative discontinuity.
- LDA/GGA/hybrids have self-interaction and put levels (HOMO) in wrong place.
- They also smear out resonance peaks due to lack of derivative discontinuity

# Derivative discontinuity

Perdew, Parr, Levy and Balduz, PRL 82



# KS potential of H atom

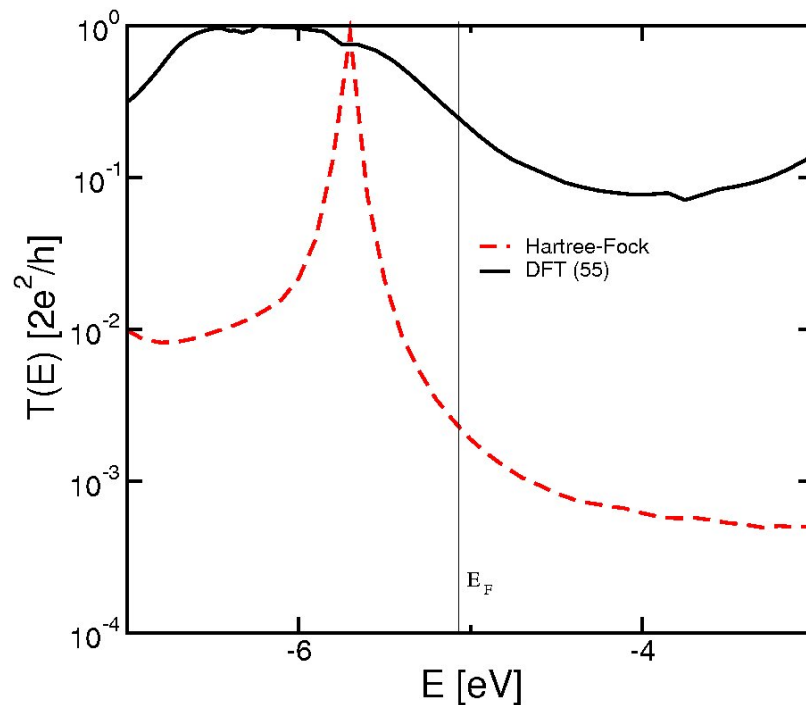




# Effect on resonant tunneling

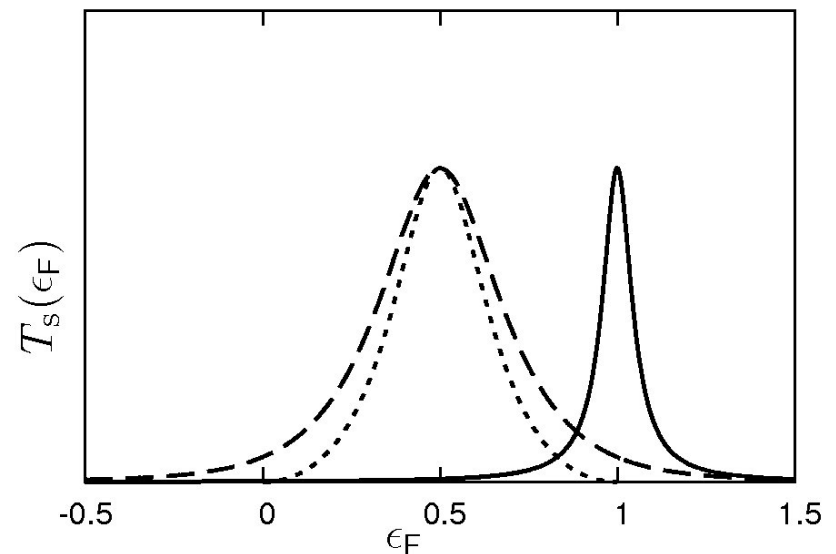
(Koentopp, Evers, and KB. PRB 05).

- conductance of benzenedithiol:  
HF instead of DFT/GGA



➔ T reduced by 100

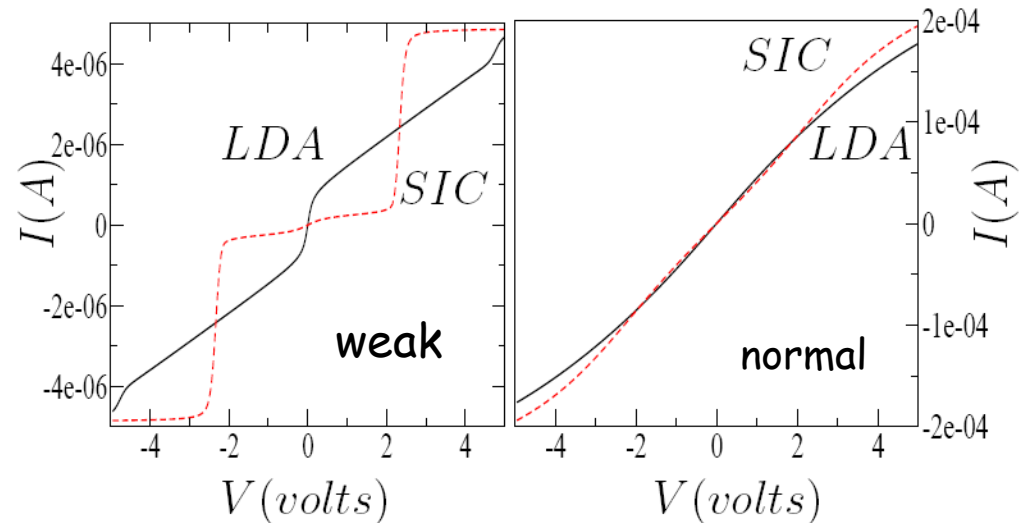
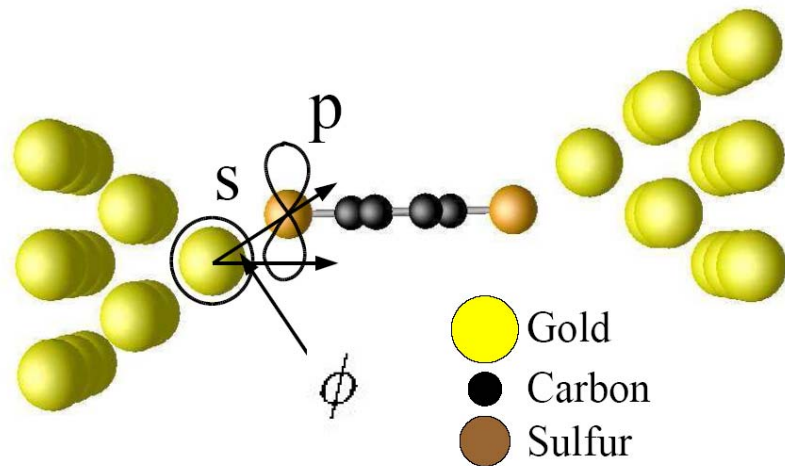
- double barrier: resonance shape and position
- compare smooth functional with exact result:



➔ Peaks too broad, -2, wrong position

# Molecule weakly coupled to leads

Tohar, Filipetti, Sanvito, and KB (PRL, 2005).



- For weak coupling, see much lower conductance when SIC turned on.
- No effect for normal (chemical) bonding.

# Jeff Neaton with Columbians

- Over last several years, Lanthan Venkataraman has done amide linkages instead of thiol, and gotten much better characterized results.
- Jeff combines applies two shifts from GW calculations to his standard-model calcs:
  - Gas-phase shift of HOMO
  - Image shift of molecule on surface
  - General agreement to within 50%



# Static density response eqns

- Three different ways to calculate  $\delta\rho$ :
- Full non-local susceptibility in response to external field:

$$\delta\rho(\mathbf{r}, \omega) = \int d^3r' \chi(\mathbf{r}\mathbf{r}', \omega) v_{ext}(\mathbf{r}', \omega)$$

- Proper susceptibility in response to total potential:

$$\delta\rho(\mathbf{r}, \omega) = \int d^3r' \chi_{prop}(\mathbf{r}\mathbf{r}', \omega) (v_{ext}(\mathbf{r}', \omega) + v_H(\mathbf{r}', \omega))$$

- KS susceptibility in response to KS pot:

$$\delta\rho(\mathbf{r}, \omega) = \int d^3r' \chi_s(\mathbf{r}\mathbf{r}', \omega) (v_{ext}(\mathbf{r}', \omega) + v_H(\mathbf{r}', \omega) + v_{XC}(\mathbf{r}', \omega))$$

# TDCDFT response eqns

- Three different ways to calculate  $\delta j$ :
- Full non-local conductivity in response to external E-field:

$$\delta j(\mathbf{r}\omega) = \int d^3 r' \sigma(\mathbf{r}\mathbf{r}'\omega) \bullet \mathbf{E}_{ext}(\omega)$$

- Proper cond. in response to total field:

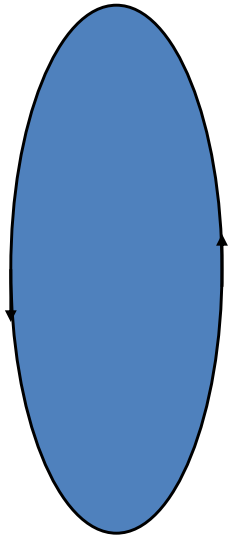
$$\delta j(\mathbf{r}\omega) = \int d^3 r' \sigma_{prop}(\mathbf{r}\mathbf{r}'\omega) \bullet (\mathbf{E}_{ext}(\omega) + \mathbf{E}_H(\mathbf{r}'\omega))$$

- KS conductivity in response to KS pot:

$$\delta j(\mathbf{r}\omega) = \int d^3 r' \sigma_s(\mathbf{r}\mathbf{r}'\omega) \bullet (\mathbf{E}_{ext}(\omega) + \mathbf{E}_H(\mathbf{r}'\omega) + \mathbf{E}_{xc}(\mathbf{r}'\omega))$$

## TDCDFT derivation of KS-Landauer at weak bias

- Express conductivity as integral over Green's functions times spectral density



$$\hat{\sigma}_s(\mathbf{r}\mathbf{r}'\omega) = \left( n_0(\mathbf{r}) \delta^{(3)}(\mathbf{r} - \mathbf{r}') \mathbb{1} + \hat{R}(\mathbf{r}\mathbf{r}'\omega) \right) / i\omega \quad (5)$$

where

$$\hat{R}(\mathbf{r}\mathbf{r}'\omega) = \frac{1}{2} \sum_{ij} \frac{f_i - f_j}{\omega + (\epsilon_i - \epsilon_j) + i0_+} \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \vec{\nabla} \otimes \vec{\nabla}' \phi_j(\mathbf{r}) \phi_i(\mathbf{r}') \quad (6)$$

$$a(\mathbf{r}) \vec{\nabla} b(\mathbf{r}) = a(\mathbf{r}) \nabla b(\mathbf{r}) - b(\mathbf{r}) \nabla a(\mathbf{r})$$

# KS conductivity from Green's function

- Contribution to the KS conductivity from paramagnetic current

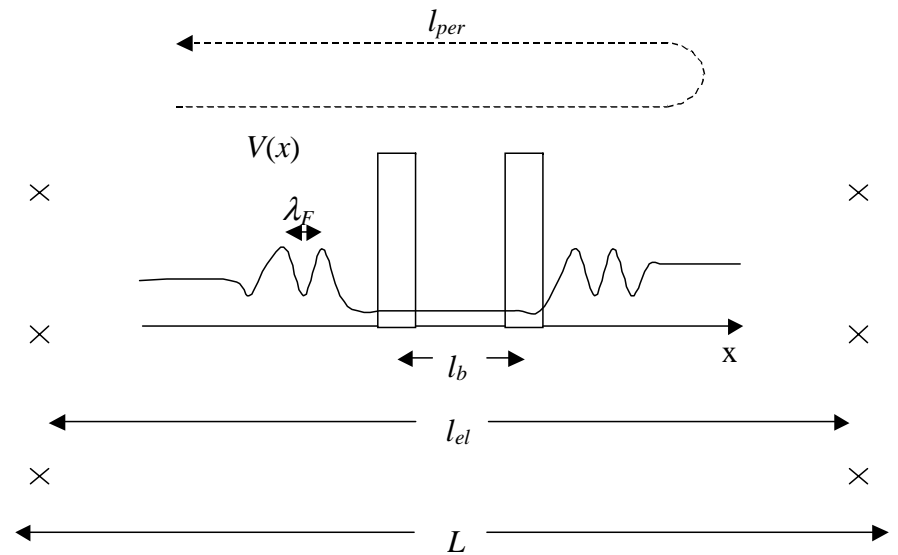
$$R(\mathbf{r}\mathbf{r}', \omega) = -\frac{1}{2} \int d\epsilon f(\epsilon) \{-G^r(\mathbf{r}\mathbf{r}', \epsilon + \omega) + (G^r)^*(\mathbf{r}\mathbf{r}', \epsilon - \omega)\} \overleftrightarrow{\partial\partial'} A_S(\mathbf{r}\mathbf{r}', \epsilon)$$

- Where G is the KS Green's function and A is the KS spectral density, and

$$a(\mathbf{r}) \overleftrightarrow{\nabla} b(\mathbf{r}) = a(\mathbf{r}) \nabla b(\mathbf{r}) - b(\mathbf{r}) \nabla a(\mathbf{r})$$

# Treatment of length scales as $\omega \rightarrow 0$

- $L$  = 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:

$$l_b, \lambda_{TF}, \lambda_F \ll l_{per} \ll L, l_{el}.$$

Godby and Bokes discuss this limit extensively, to extract response from finite box



# Simplification for small $\omega$

For small  $\omega$ , the real parts of both KS Green's functions  $G^{(r,a)}$  (for  $\omega, -\omega$ ) are the same, as the real part is parabolic in  $\omega$ . Thus, the real part drops out and only the imaginary components contribute to  $R_{\mu\nu}$ .

We then have

$$R_{\mu\nu}(\mathbf{r}\mathbf{r}', \omega \rightarrow 0) = -\frac{1}{2} \int d\epsilon f(\epsilon) \{i\Im(G(\mathbf{r}\mathbf{r}', \epsilon + \omega) - i\Im(G^*(\mathbf{r}\mathbf{r}', \epsilon - \omega))\} \overleftrightarrow{\partial}_\mu \overleftrightarrow{\partial}'_\nu A(\mathbf{r}\mathbf{r}', \epsilon) \quad (9)$$

Plugging in A,

$$R_{\mu\nu}(\mathbf{r}\mathbf{r}', \omega \rightarrow 0) = \frac{1}{2} \int d\epsilon \pi i \{A(\mathbf{r}\mathbf{r}', \epsilon + \omega) - A(\mathbf{r}\mathbf{r}', \epsilon - \omega)\} \overleftrightarrow{\partial}_\mu \overleftrightarrow{\partial}'_\nu A(\mathbf{r}\mathbf{r}', \epsilon) \quad (10)$$

which is just the derivative

$$R_{\mu\nu}(\mathbf{r}\mathbf{r}', \omega \rightarrow 0) = \frac{i\pi}{2} \int d\epsilon f(\epsilon) 2\omega \frac{\partial A(\mathbf{r}\mathbf{r}', \epsilon)}{\partial \epsilon} \overleftrightarrow{\partial}_\mu \overleftrightarrow{\partial}'_\nu A(\mathbf{r}\mathbf{r}', \epsilon) \quad (11)$$

$$= \frac{i\pi\omega}{2} \int d\epsilon f(\epsilon) \frac{\partial}{\partial \epsilon} \left\{ A(\mathbf{r}\mathbf{r}', \epsilon) \overleftrightarrow{\partial}_\mu \overleftrightarrow{\partial}'_\nu A(\mathbf{r}\mathbf{r}', \epsilon) \right\} \quad (12)$$

Integration by parts yields

$$R_{\mu\nu}(\mathbf{r}\mathbf{r}', \omega \rightarrow 0) = \frac{i\omega\pi}{2} \int d\epsilon \frac{\partial f}{\partial \epsilon} \left\{ A(\mathbf{r}\mathbf{r}', \epsilon) \overleftrightarrow{\partial}_\mu \overleftrightarrow{\partial}'_\nu A(\mathbf{r}\mathbf{r}', \epsilon) \right\} \quad (13)$$

Integrating, we thus obtain the expression for the response:

$$R_{\mu\nu}(\mathbf{r}\mathbf{r}', \omega \rightarrow 0) = \frac{i\omega\pi}{2} A(\mathbf{r}\mathbf{r}', \epsilon_F) \overleftrightarrow{\partial}_\mu \overleftrightarrow{\partial}'_\nu A(\mathbf{r}\mathbf{r}', \epsilon_F) \quad (14)$$

# Extreme simplicity at $\omega=0$

- For one dimensional case (complications in 3D):

$$A(zz'\epsilon) = \frac{1}{\pi k} \Re \{ t \phi_L(z_{<}) \phi_R(z_{>}) \}$$

- And inserting in  $R_s$  yields  $\sigma_s$  yields independent of positions, and depending only on transmission thru barrier at  $E_F$ :

$$\sigma_s(\mathbf{r}\mathbf{r}'\omega) \rightarrow \frac{T_s(\epsilon_F)}{\pi}, \quad \omega \rightarrow 0$$

- Generalization to 3d by Prodan and Car (PRB 08).

# Low frequency limit

- As  $\omega \rightarrow 0$ ,  $\sigma_s$  indep of  $\mathbf{r}, \mathbf{r}'$  and equals  $T_s(\epsilon_F)/\pi$ .

$$\delta j(\mathbf{r}\omega) = \int d^3 r' \sigma_s(\mathbf{r}\mathbf{r}'\omega) \bullet (\mathbf{E}_{ext}(\omega) + \mathbf{E}_H(\mathbf{r}'\omega) + \mathbf{E}_{xc}(\mathbf{r}'\omega))$$

Becomes

$$\delta I(\omega = 0) = \frac{T_s(\epsilon_F)}{\pi} \int d^3 r' (\mathbf{E}_{ext}(\omega) + \mathbf{E}_H(\mathbf{r}'\omega) + \mathbf{E}_{xc}(\mathbf{r}'\omega))$$

But integral of field is just potential drop:

$$\delta I(\omega = 0) = \frac{T_s(\epsilon_F)}{\pi} (V + V_{xc})$$

Compare with Landauer:

$$I = \frac{1}{\pi} \int_{\mu}^{\mu+V} d\epsilon T_s(\epsilon, V) (f_L(\epsilon) - f_R(\epsilon)) \rightarrow \frac{T_s(\epsilon_F)}{\pi} V$$

# Consequences: good

- If  $V_{xc} \neq 0$ , there are XC corrections to Landauer!

- Two types:

- Adiabatic (show up in static DFT calculation)
- Dynamic (show up as  $\omega \rightarrow 0$  limit of TDCDFT).

- Adiabatic: No contribution from LDA or GGA

$$E_{XC} = -\partial_z v_{XC} \int dz E_{XC}(z) = -v_{XC}^r + v_{XC}^l = 0$$

- Thus, present calculations with standard functionals, don't need to account for this.
- Even in TD(C)DFT within eg ALDA, get no corrections.

# Likely corrections

- Adiabatic
  - Do EXX static orbital-dependent calculation
  - No reason why there won't be an overall drop in  $V_x$  across molecule
- Dynamic
  - Use VK to estimate (Na Sai et al, PRL 05)
  - Find small but finite corrections
  - But VK is for high  $\omega$ , doesn't apply here.
  - Missed some other terms (see comments by Bokes et al in PRL).

# Role of TD(C)DFT

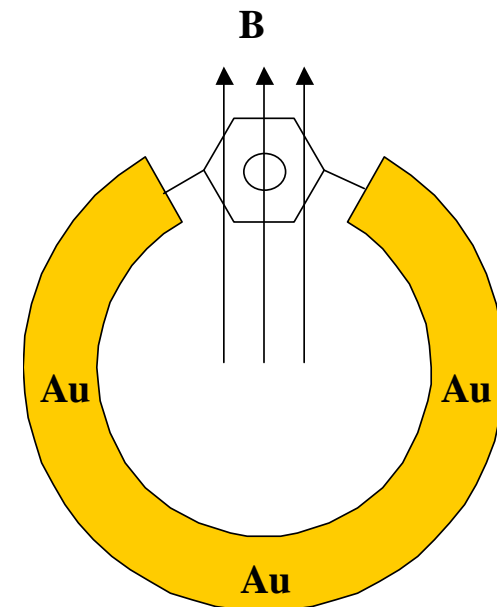
- TDDFT does not strictly apply, because system is infinite.
- Even not worrying about that, need zero-frequency, long-wavelength response, so have all problems due to locality.
- Only approximation we have beyond ALDA is VK, but no reason for it to be accurate.
- Nanoquanta kernel?

# Finite bias

- How to approach basic problem:
  - Euro: Real-time non-equilibrium Green's functions: *Kurth, Rubio, Gross, Almbladh, Stefanucci, van Leeuwen*
  - US: TDDFT for open quantum systems *Car, Gebauer, Burke, di Ventura,...*

# TDDFT for Open Systems

- Put electrons on finite ring in solenoidal field:
- Prove TDDFT theorems about Lindblad form of Master equation for N electrons coupled to a bath of phonons.
- In principle, can get coupling from phonons, in practice, must be much stronger to dissipate energy, but can then extrapolate to zero coupling.
- Two contributions to current: Hamiltonian and dissipative

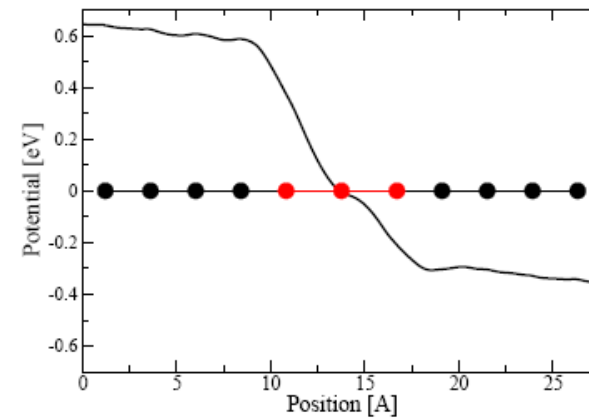
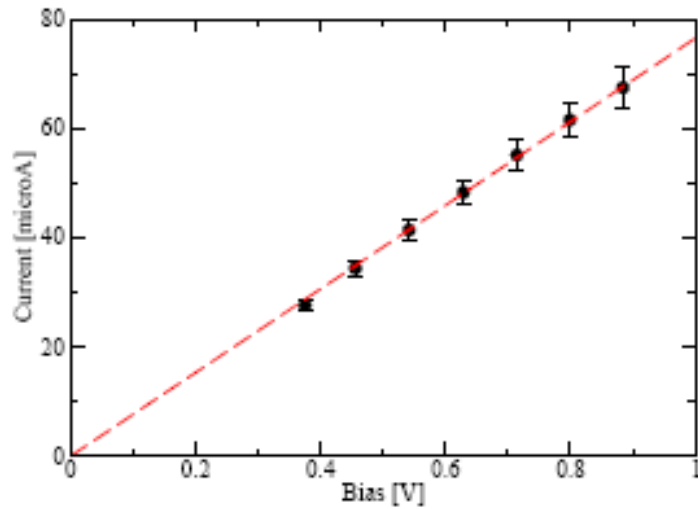
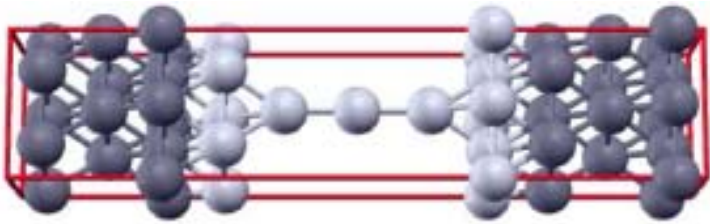


$$\mathbf{A} = -c \int_0^t dt' \mathbf{E}(t')$$

Burke, Car, Gebauer, PRL 05



# Recent calculations



*(Picinnin thesis with Car)*

# Master equation for dissipation

- $H = H_{\text{el}} + H_{\text{ph}} + K_{\text{el-ph}}$
- 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:

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

# Kohn-Sham Master equation

- 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  $S_s(0)$

$$\frac{dS_s}{dt} = -i[H, S_s] + C_s(S_s(t))$$

## Return to weak bias

- Usual Kubo calculation yields *adiabatic* conductivity
- Our approach produces true *isothermal* conductivity
- Can show, as  $C_s \rightarrow 0$ , it becomes  $i\eta$  in Kubo formula

# Variation on open systems TDDFT: Stochastic TDDFT

- Stochastic Schrodinger equation yields realizations whose average follows Master equation
- Di Ventra and d'Agosta suggested applying KS treatment to that directly, not Master equation.
- Leads to alternative approximations.

# Comparison of Electronic vs Open


## Euro

- steady state via continuum; purely electronic
- finite system with sinks and sources
- density as basic variable
- allows non steady processes
- no dissipation at present.
- no new functionals needed

## US

- dissipation.
- periodic boundary conditions
- current density as basic variable
- allows non-steady processes
- shows Joule heating to phonons
- slightly new functionals needed

# Summary

- Do we know how steady current arises?
  - Kurth et al 
- What is the exact Landauer formula for interacting system? **???**
  - Meir-Wingreen is very special case.
- If standard model were true, are standard functionals good enough?
  - Sanvito et al. **NO!**
- In the limit of weak bias, is the standard model correct? Koentopp et al, diVentra et al. **NO!**
- Where do TDDFT and TD current DFT come in?
  - Need corrections, but non-local **???**
- What is best approach to general problem? **???**
  - Full time-dependent electronic approach (Euro)
  - Master equation approach to steady state (US)