Electron Transport at the Molecular Scale: A Biased Overview

Kieron Burke

(instead of Roberto Car)

http://dft.uci.edu

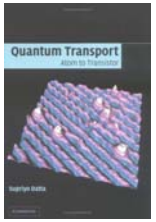
Cast of characters

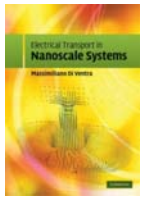
- Roberto Car 
- Rex Godby 
- E.K.U. Gross 
- Max di Ventra 
- Latha Venkataraman 
- Giovanni Vignale 

Cast of characters

- Roberto 
- Rex 
- Hardy 
- Max 
- Latha 
- Giovanni 

References





- Technology: Supriyo Datta's nanohub website
- Overview at atomic level: Max di Ventra's book
- Fundamentals: Many-body and TDDFT: TDDFT book, ed Marques et al.
- Summary of work with Roberto: Max Koentopp et al, J Phys: Cond Mat review (2008), plus monster paper to follow.

Prediction: Aviram and Ratner

Volume 29, number 2 CHEMICAL PHYSICS LETTERS 15 November 1974

MOLECULAR RECTIFIERS

Arieh AVIRAM
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and

Mark A. RATNER*
Department of Chemistry, New York University, New York, New York 10003, USA

Received 10 June 1974

The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor pi system and an acceptor pi system, separated by a sigma-bonded (methylene) tunnelling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.

Experiment: Reed and Tour

Conductance of a Molecular Junction

M. A. Reed,* C. Zhou, C. J. Muller, T. P. Burgin,
J. M. Tour*

Molecules of benzene-1,4-dithiol were self-assembled onto the two facing gold electrodes of a mechanically controllable break junction to form a statically stable gold-sulfur-aryl-sulfur-gold system, allowing for direct observation of charge transport through the molecules. Current-voltage measurements at room temperature demonstrated a highly reproducible apparent gap at about 0.7 volt, and the conductance-voltage curve showed two steps in both bias directions. This study provides a quantative measure of the conductance of a junction containing a single molecule, which is a fundamental step in the emerging area of molecular-scale electronics.

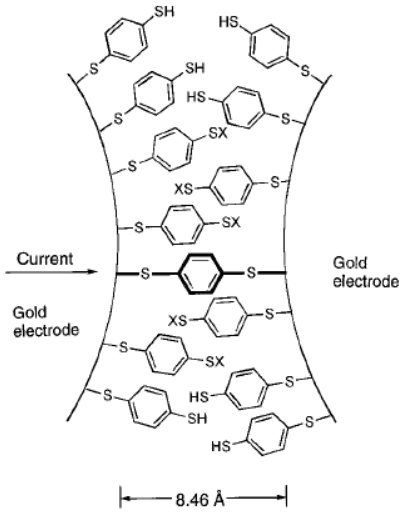
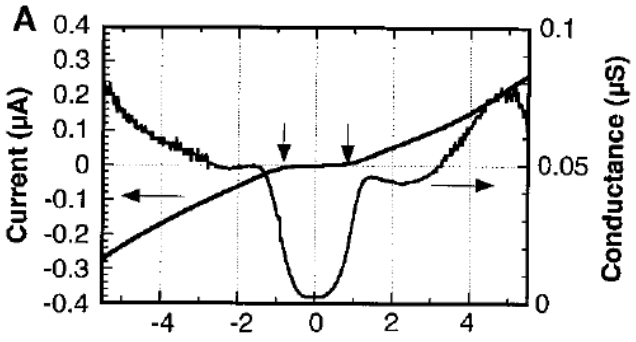


Fig. 3. A schematic of a benzene-1,4-dithiolate SAM between proximal gold electrodes formed in an MCB. The thiolate is normally H-terminated after deposition; end groups denoted as X can be either H or Au, with the Au potentially arising from a previous contact/retraction event. These molecules remain nearly perpendicular to the Au surface, making other molecular orientations unlikely (*21*).



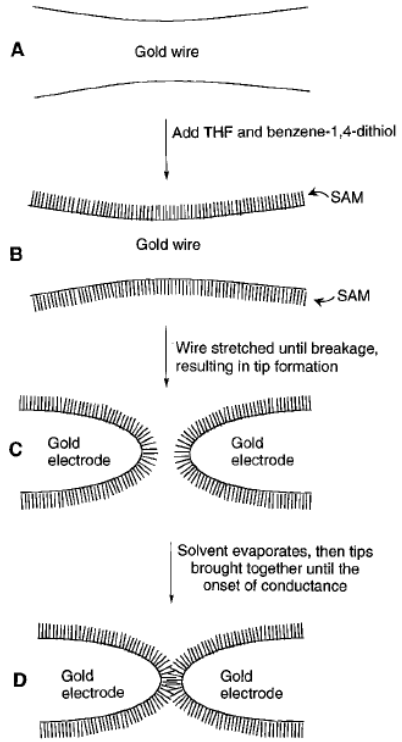
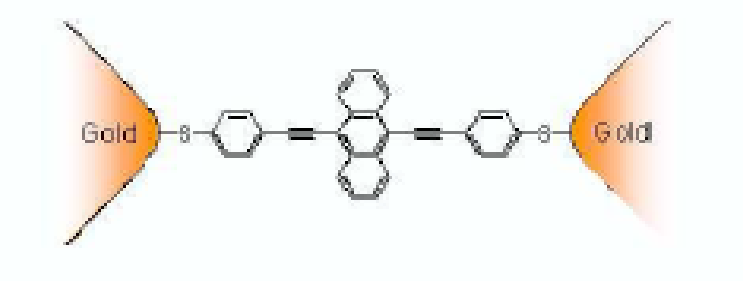
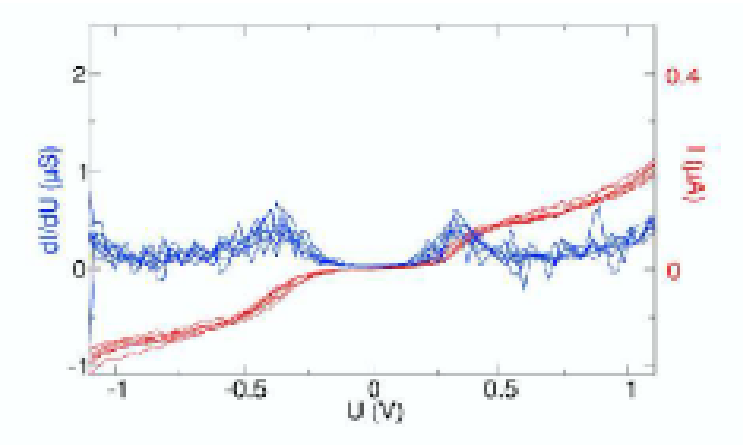


Fig. 2. Schematic of the measurement process. (**A**) The gold wire of the break junction before breaking and tip formation. (**B**) After addition of benzene-1,4-dithiol, SAMs form on the gold wire surfaces. (**C**) Mechanical breakage of the wire in solution produces two opposing gold contacts that are SAM-covered. (**D**) After the solvent is evaporated, the gold contacts are slowly moved together until the onset of conductance is achieved. Steps (C) and (D) (without solution) can be repeated numerous times to test for reprodicibility.

SCIENCE • VOL. 278 • 10 OCTOBER 1997 • www.sciencemag.org

Better break junction expts





Experiments:

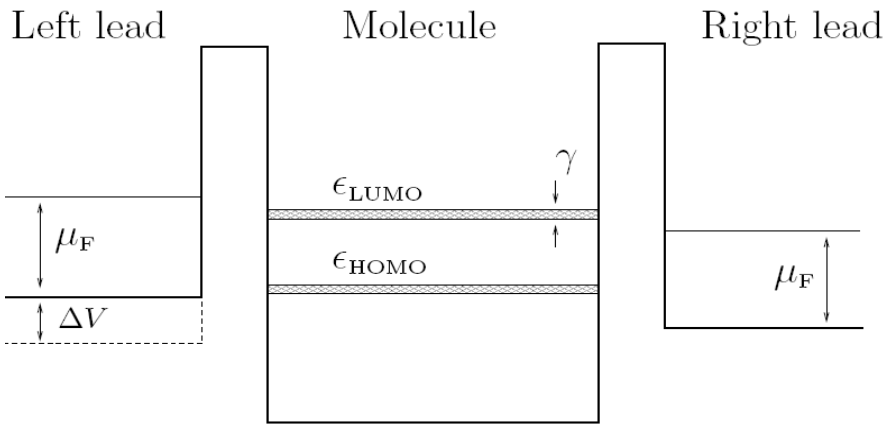
H. Weber, R. Ochs, J. Reichert,

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

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

See Latha's talk NEXT for why amide linkages are better for comparison.

Simple view: Non-interacting particles



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

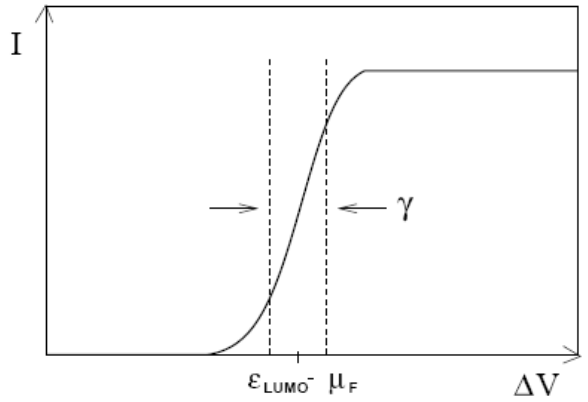


FIG. 2: Schematic current-voltage characteristic of the resonant tunneling device displayed in Fig. 1. The onset of the current occurs around $\epsilon_{\mathrm{LUMO}} - \mu_{\mathrm{F}}$. The step is broadened by the coupling γ.

Interaction: Landauer-Buttiker

R. Landauer

Spatial Variation of Currents and Fields Due to Localized Scatterers in Metallic Conduction

Abstract: Localized scatterers can be expected to give rise to spatial variations in the electric field and in the current distribution. The transport equation allowing for spatial variations is solved by first considering the homogeneous transport equation which omits electric fields. The homogeneous solution gives the purely diffusive motion of current carriers and involves large space charges. The electric field is then found, and approximate space charge neutrality is restored, by adding a particular solution of the transport equation in which the electric field is associated only with space charge but not with a current. The presence of point scatterers leads to a dipole field about each scatterer. The spatial average of a number of these dipole fields is the same as that obtained by the usual approach which does not explicitly consider the spatial variation. Infinite plane obstacles with a reflection coefficient r are also considered. These produce a resistance proportional to $r/(1-r)$.

IBM JOURNAL • JULY 1957

Mesoscopic physics: Quantum dots

INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology 18 (2007) 044029 (5pp) doi:10.1088/0957-4484/18/4/044029

Mesoscopic capacitance oscillations

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Abstract
We examine oscillations as a function of Fermi energy in the capacitance of a mesoscopic cavity connected via a single quantum channel to a metallic contact and capacitively coupled to a gate. The oscillations depend on the distribution of single levels in the cavity, the interaction strength and the transmission probability through the quantum channel. We use a Hartree–Fock approach to exclude self-interaction. The sample specific capacitance oscillations are in marked contrast to the charge relaxation resistance, which together with the capacitance defines the RC-time, and which for spin polarized electrons is quantized at half a resistance quantum. Both the capacitance oscillations and the quantized charge relaxation resistance are seen in a strikingly clear manner in a recent experiment.

(Some figures in this article are in colour only in the electronic version)

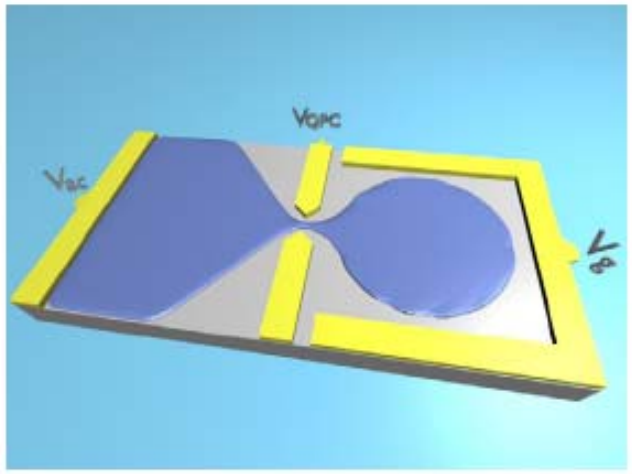


Figure 1. Mesoscopic capacitor: a cavity is connected via one lead to an electron reservoir at voltage V_{ac} and capacitively coupled to a gate with voltage V_g. Only one contact formed by a quantum point contact permits carrier exchange. The voltage V_{qpc} controls the transmission through the quantum point contact.

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 DFT 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

Basic agreement?

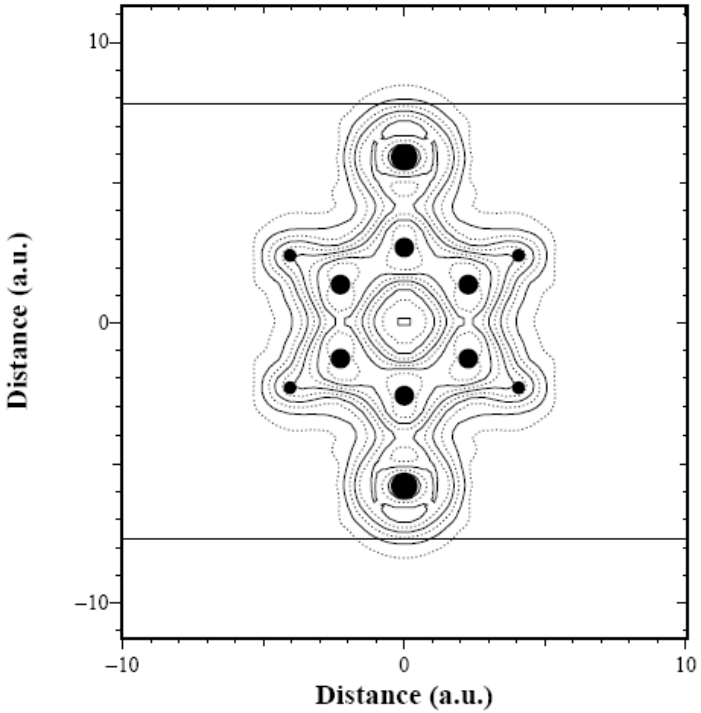


FIG. 1. Contour plot of the electron density of the molecule described in the text. The dots represent the positions of the atoms. The lines represent the position of the model metal surfaces.

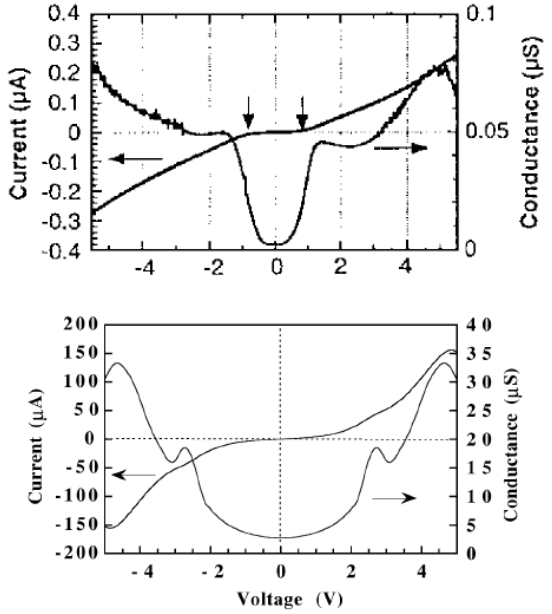


FIG. 2. Top: Experimental *I-V* characteristic of a benzene-1,4-dithiolate molecule measured by Reed *et al.* [1]. Bottom: Conductance of the molecule of Fig. 1 as a function of the external bias applied to the metallic contacts.

Di Ventra, Pantelides, Lang, PRL 2000

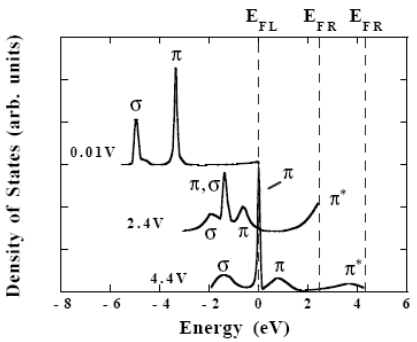


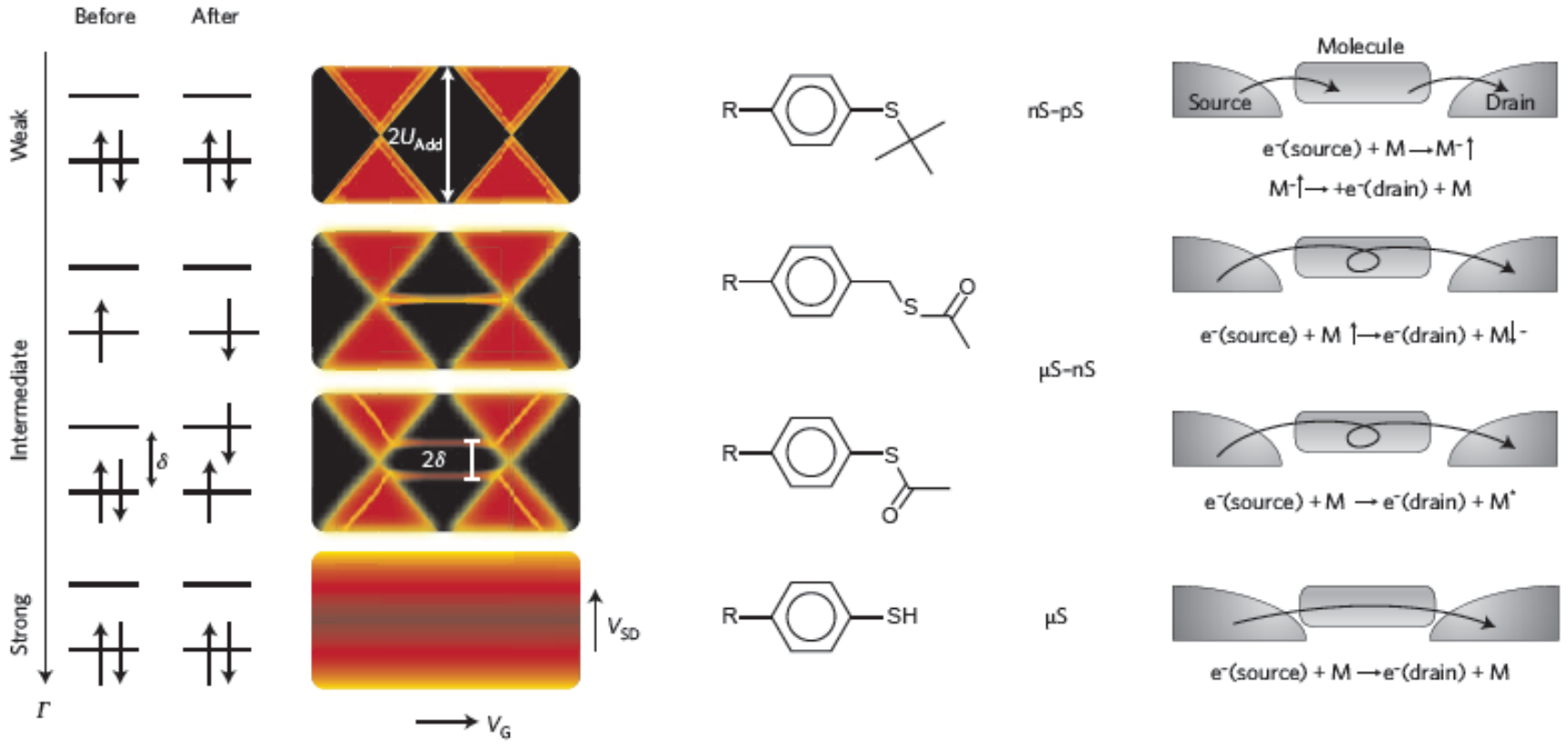
FIG. 3. Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule in between, for three different voltages. The left Fermi level (E_{FL}) has been chosen as the zero of energy. The labels E_{FR} correspond to the energy position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

But…Coulomb blockade

- Electron hops on to molecule
- Reduces current because charging stops a second electron until potential can overcome charging
- Move levels on molecule by applying gate voltage
- Get CB `diamonds'

Strong and weak coupling

Box 1 | Electron transport at different coupling strengths.



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Molecular electronics with single molecules in solid-state devices

Kasper Moth-Poulsen and Thomas Bjørnholm*

The ultimate aim of molecular electronics is to understand and master single-molecule devices. Based on the latest results on electron transport in single molecules in solid-state devices, we focus here on new insights into the influence of metal electrodes on the energy spectrum of the molecule, and on how the electron transport properties of the molecule depend on the strength of the electronic coupling between it and the electrodes. A variety of phenomena are observed depending on whether this coupling is weak, intermediate or strong.

Why is it difficult?

- Need chemical-type accuracy
- Hundreds of atoms needed to get details right
- Poorly characterized experiments (now improving)
- Lots of difficulties for theory, all combined in one problem:
  - Not a ground state
  - Not a finite system, but not bulk either
  - Can have both strong and weak correlation.

Basic questions I'll address

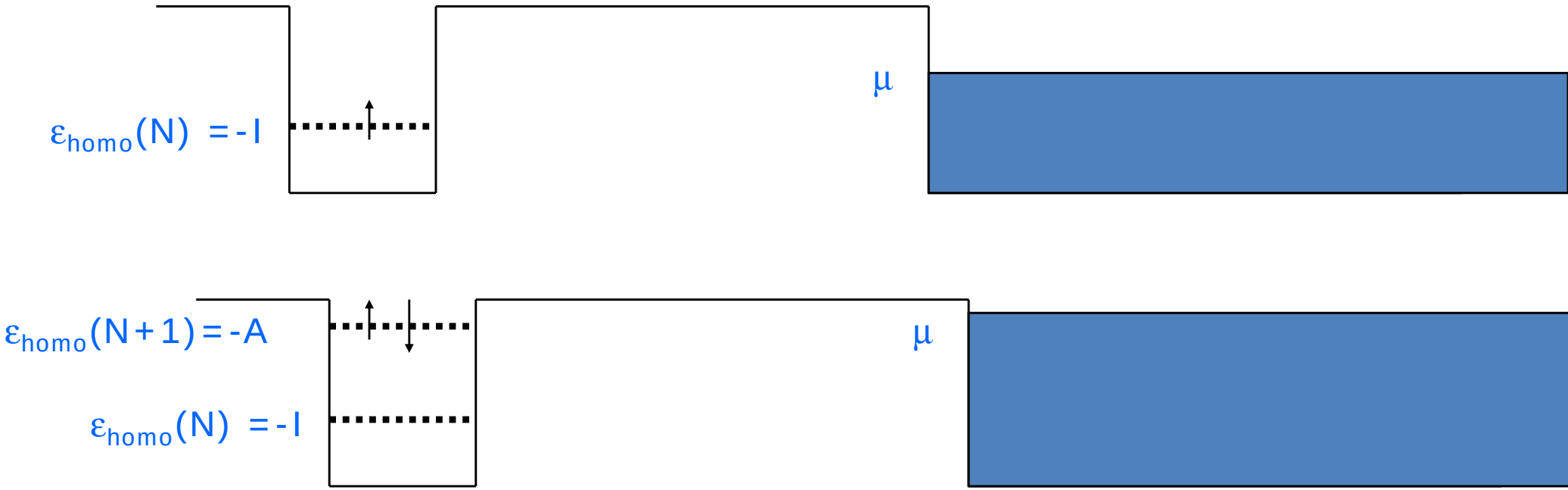
- If standard DFT approach is OK, are functionals good enough for accurate results?
- Is Landauer formula correct in weak-bias limit?
- How do you do finite bias?

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

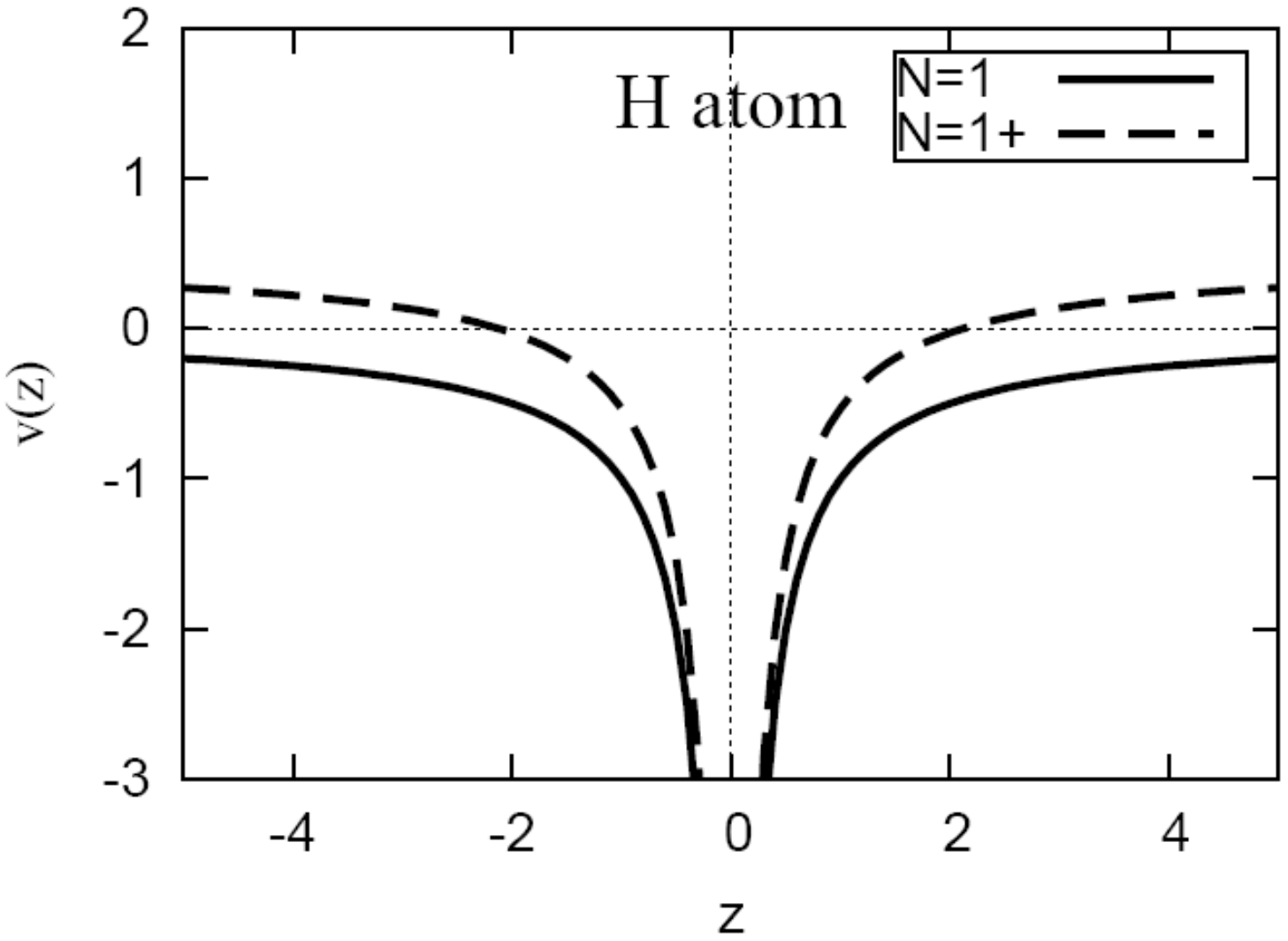
- Can see answer is NO in weakly-coupled limit, because of derivative discontinuity.
- LDA/GGA/hybrids have self-interaction and put levels (HOMO) in wrong place.
- They also smear out resonance peaks due to lack of derivative discontinuity

Derivative discontinuity

Perdew,Parr,Levy and Balduz, PRL 82



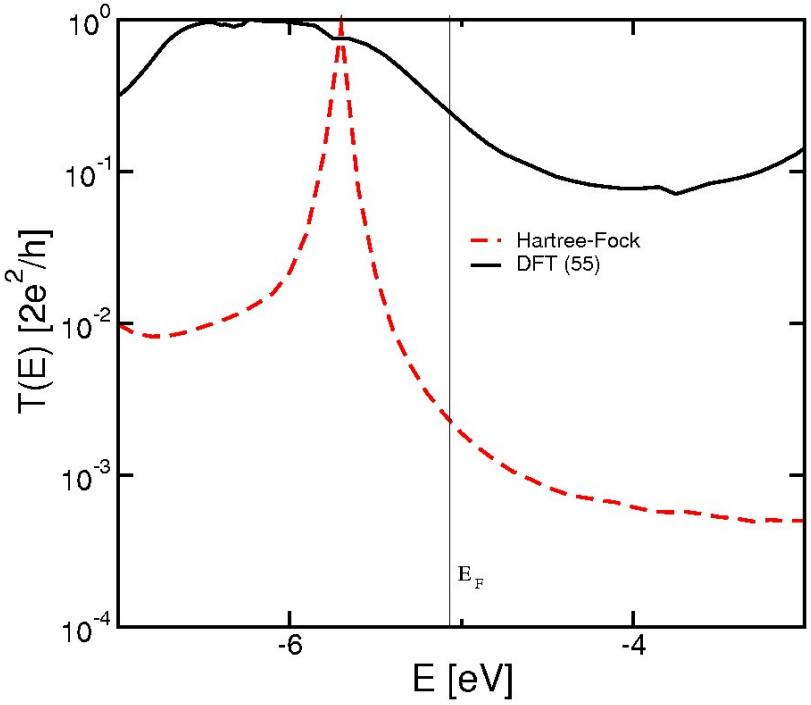
KS potential of H atom



Effect on resonant tunneling

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

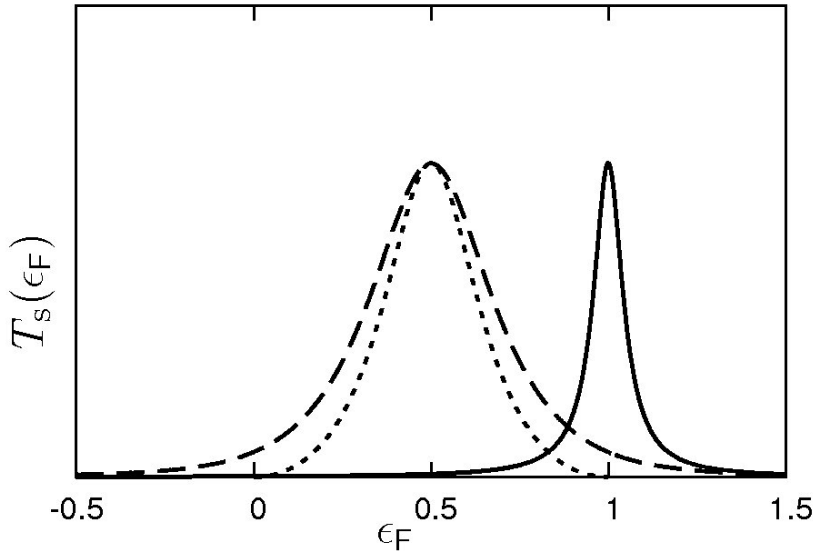
• conductance of benzenedithiol: HF instead of DFT/GGA



→ T reduced by 100

• double barrier: resonance shape and position

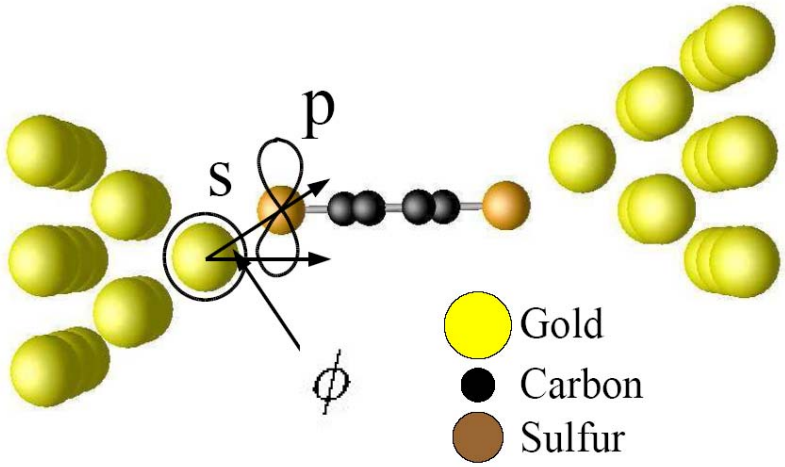
• compare smooth functional with exact result:

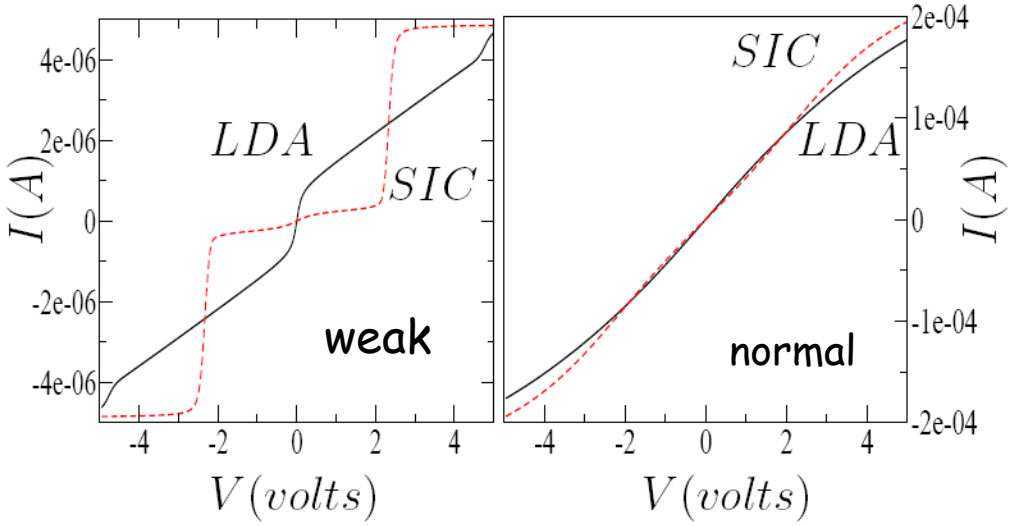


→ Peaks too broad, wrong postion

Molecule weakly coupled to leads

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





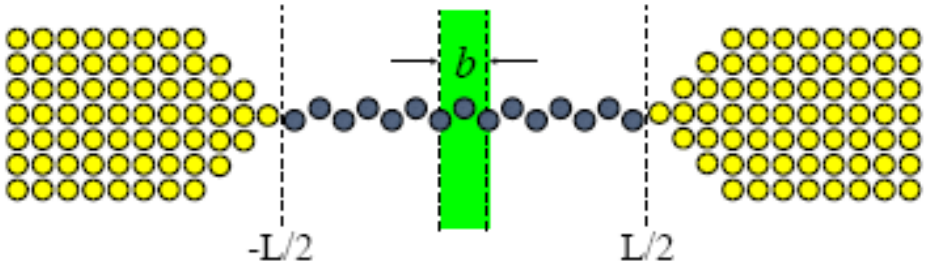
- For weak coupling, see much lower conductance when SIC turned on.
- No effect for normal (chemical) bonding.

Jeff Neaton with Columbians

- Over last several years, Latha 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%

- Rex will discuss doing full GW for transport

Complex band structure for length dependence

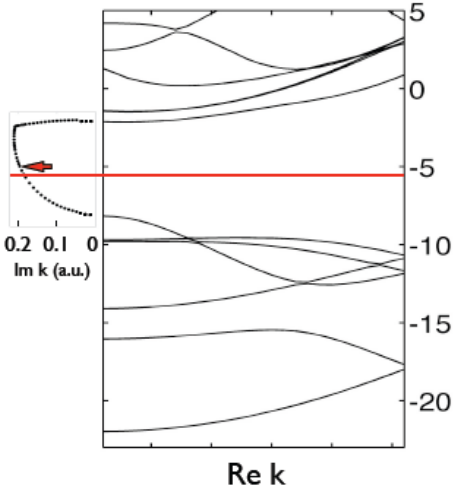


$$H = -\nabla^2 + V_0(\mathbf{r}) + \Delta V(\mathbf{r}) \equiv H_0 + \Delta V(\mathbf{r})$$

$$\Delta V = \Delta V_{\mathrm{L}} + \Delta V_{\mathrm{R}}$$

$$G_\epsilon = G^0_\epsilon + G^0_\epsilon T_\epsilon G^0_\epsilon \qquad T_\epsilon = \Delta V + \Delta V G_\epsilon \Delta V$$

$$T_{\mathrm{LR}} = [1 + o(e^{-2\beta_{\min} L})] T_{\mathrm{L}} G^0_\epsilon T_{\mathrm{R}}$$



It is convenient to model the system as a strictly periodic molecular chain (an infinite polymer) *strongly* perturbed by the metallic leads (Car and Prodan, PRB 07).

Basic questions I'll address

- If standard DFT approach is OK, are functionals good enough for accurate results?
- Is Landauer formula correct in weak-bias limit?
- How do you do finite bias?

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.

TDCDFT response eqns

- Three different ways to calculate δj:
- Full non-local conductivity in response to external E-field:

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

- Proper cond. in response to total field:

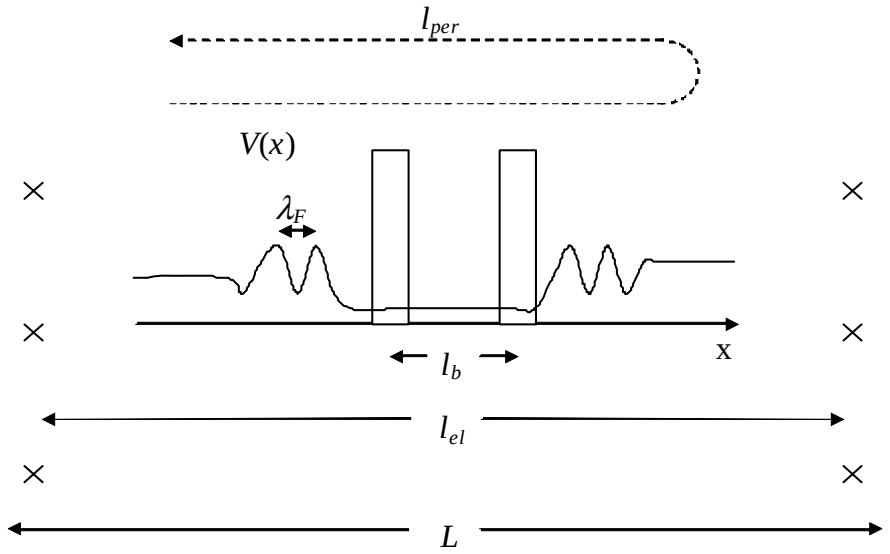
$$\delta j(\mathbf{r}\omega) = \int d^3 r' \sigma_{prop}(\mathbf{r}\mathbf{r}'\omega) \bullet (\mathrm{E}_{ext}(\omega) + \mathrm{E}_H(\mathbf{r}'\omega))$$

- KS conductivity in response to KS pot:

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

Treatment of length scales as $\omega -> 0$

- L = length of leads
- λ_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
- λ_{TF} = Thomas-Fermi screening length
  $= v_F/\omega_p$, where ω_p is the plasmon frequency.



Long clean leads:

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

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

Extreme simplicity at ω=0

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

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

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

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

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

Low frequency limit

- As ω->0, σ_s indep of **r**,**r'** and equals $T_s(\varepsilon_F)/\pi$.

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

Becomes

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

But integral of field is just potential drop:

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

Compare with Landauer:

$$I = \frac{1}{\pi}\int_{\mu}^{\mu+V} d\varepsilon\ T_s(\varepsilon,V)\left(f_L(\varepsilon)-f_R(\varepsilon)\right)\rightarrow\frac{T_s(\varepsilon_F)}{\pi}V$$

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 ω->0 limit of TDCDFT).
- Adiabatic: No contribution from LDA or GGA

$$E_{XC} = -\partial_z v_{XC} \quad \int dz\, E_{XC}(z) = -v^r_{XC} + v^l_{XC} = 0$$

- 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 ω, doesn't apply here.
  - Missed some other terms (see comments by Bokes et al in PRL).
  - Recent Max+Giovanni work (PRB 09) suggests only dynamic corrections

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?

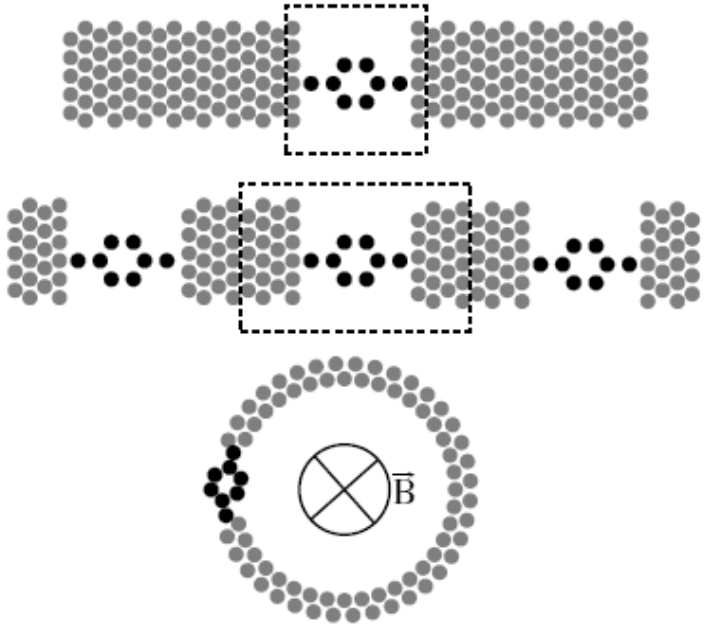
Basic questions I'll address

- If standard DFT approach is OK, are functionals good enough for accurate results?
- Is Landauer formula correct in weak-bias limit?
- How do you do finite bias?

Finite bias

- How to approach basic problem:
  - Euro: Real-time non-equilibrium Green's functions: *Kurth, Rubio, Gross, Almbladh, Stefanucci, van Leeuwen*
  - US: TD(C)DFT for open quantum systems *Car, Gebauer, Burke, di Ventra,…*

A kinetic approach (beyond linear response) which also includes dissipation



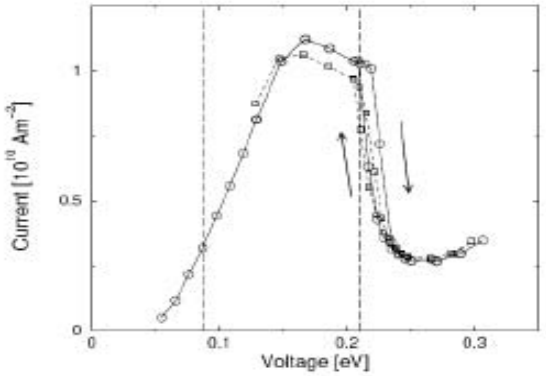
$$\frac{dS}{dt} = -i[H,S] + \mathrm{C}[S]$$

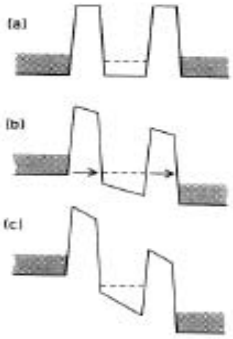
From Piccinin, Gebauer, Burke, Car, in preparation (2009?), Burke, Car, Gebauer, *PRL* (2005), Gebauer, Car, *PRB* (2004)

Optical bistability

I-V characteristics

From R Gebauer and RC, *PRB* (2004)

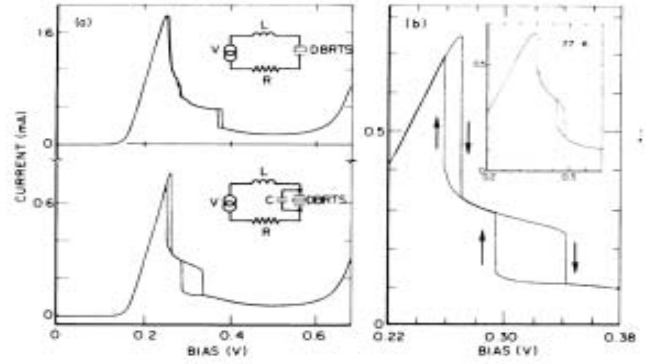




Intrinsic bistability results from charging the resonant level

The effect is more pronounced at small dissipative coupling

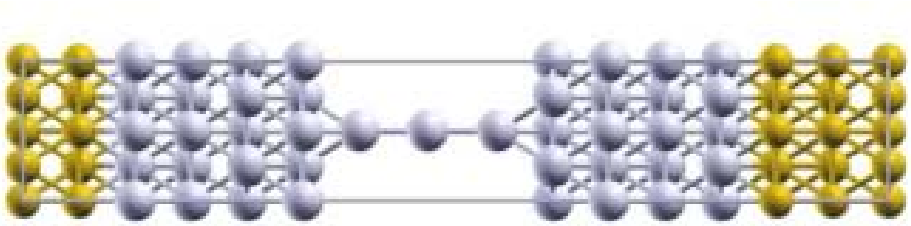
hysteresis effects were first observed in DBRTS made by GaAs-AlAs heterostructures by Goldman, Tsui, and Cunningham, *PRL* (1987)

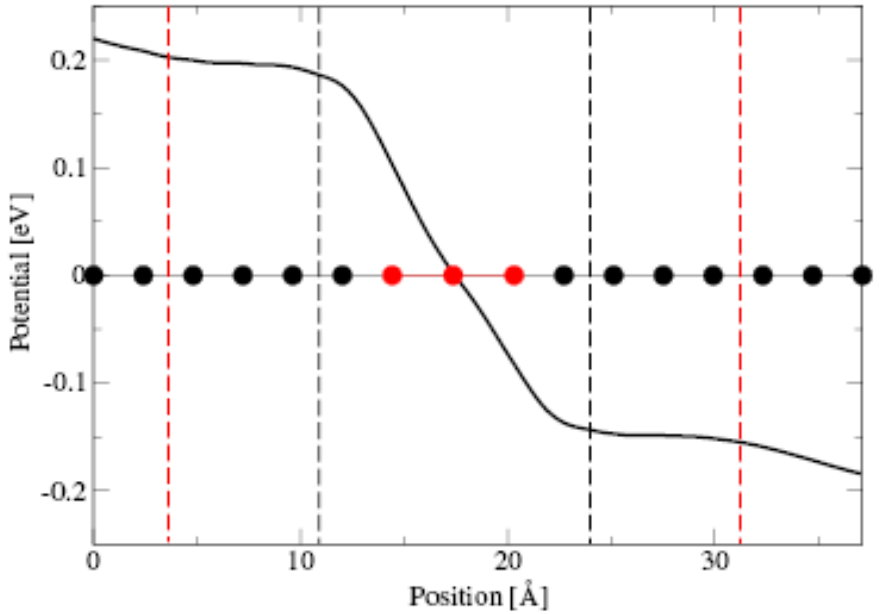


See Kurth's talk online and Hardy's talk this afternoon.

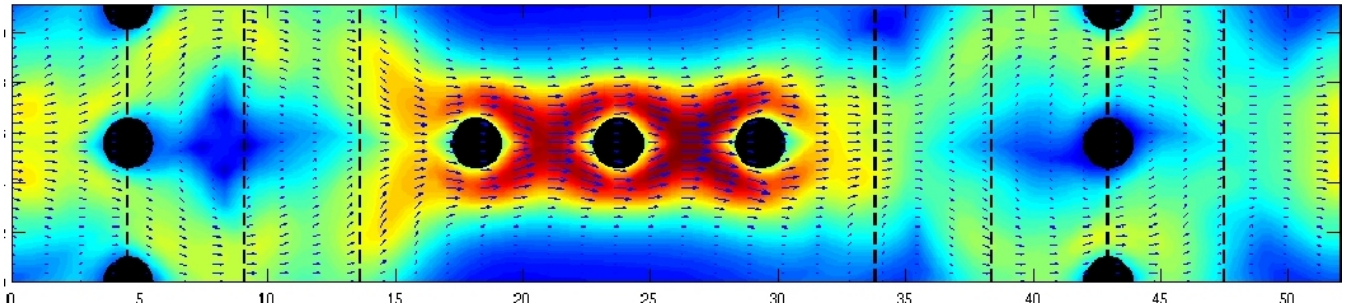
A 3-atom gold wire

Calculations using pseudopotentials and plane waves in a supercell geometry





Potential drop in the position gauge



Spatial dependence of current density containing wire

Periodic cell in x,y direction

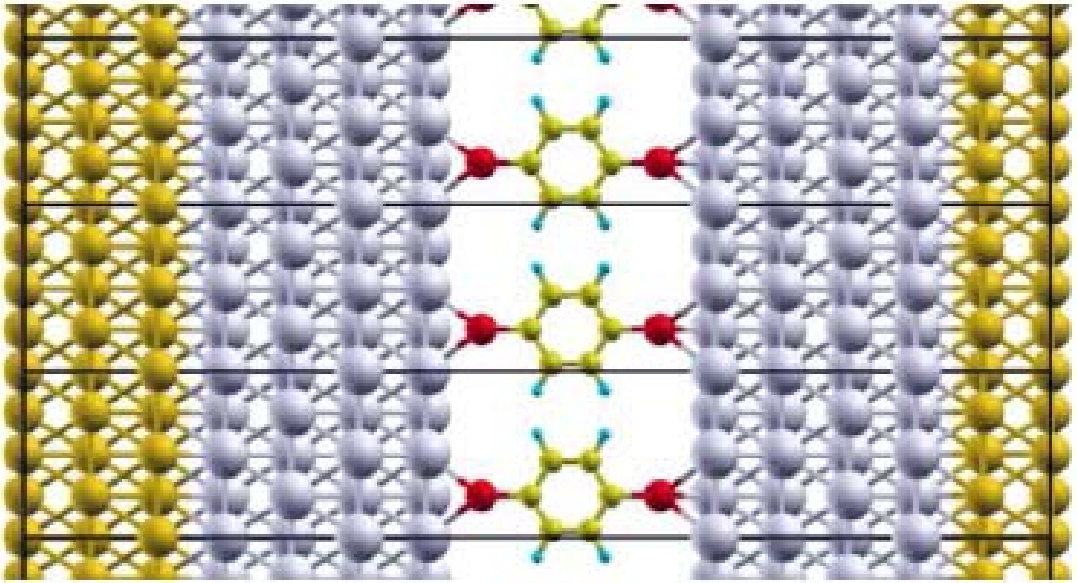


FIG. 16: Unit cell used for the study of the electronic structure of the Au(111)-BDT-Au(111) system. The molecule is adsorbed as a thiolate diradical on the FCC hollow site of the Au surface. The atomic positions have been relaxed.

Master equation for dissipation

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

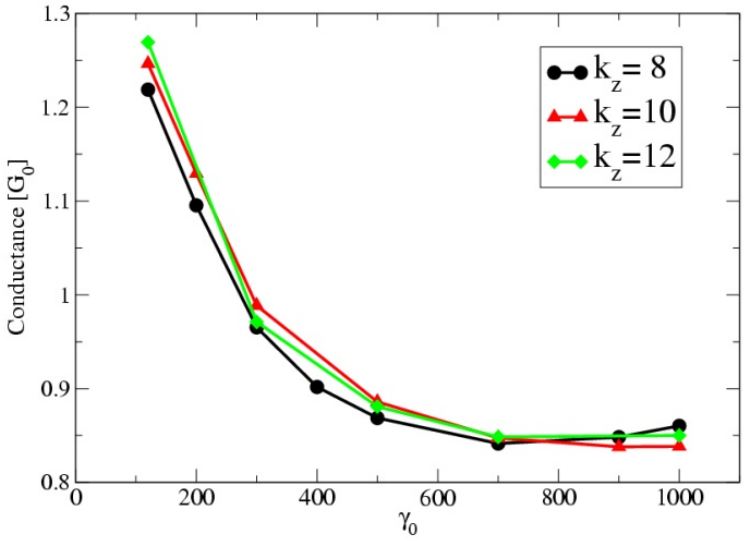
$$\frac{dS}{dt} = -i[H, S] + C(S(t))$$

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 $S_s(0)$

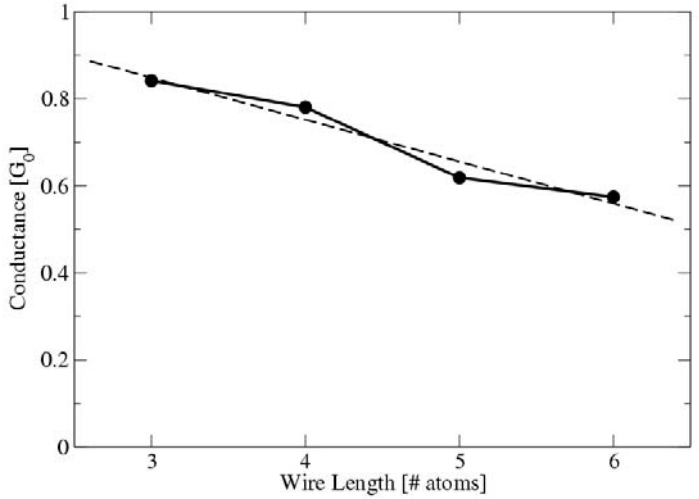
$$\frac{dS_s}{dt} = -i[H, S_s] + C_s(S_s(t))$$

Effect of dissipation on current



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



Comparison with standard

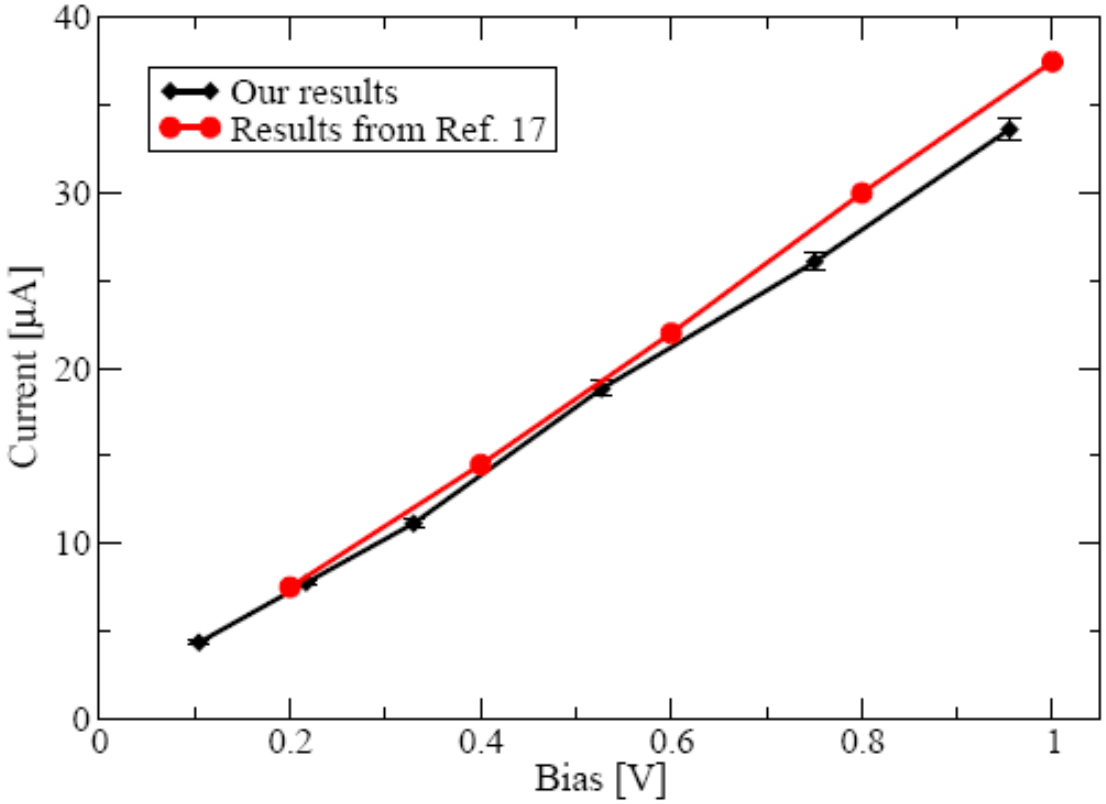


FIG. 19: Comparison between our results and the ones obtained using the NEGF approach[7] . A linear fit of our results gives a low bias conductance of 0.45 G_0.

Return to weak bias

- Usual Kubo calculation yields *adiabatic* conductivity
- Our approach produces true *isothermal* conductivity
- Can show, as C_s->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.
- See Max's talk later this morning.

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

Outlook

- Do we know how steady current arises?
  - Kurth et al 
- What is the exact Landauer formula for interacting system in steady state? **???**
  - Meir-Wingreen is very special case.
- If standard model were true, are standard functionals good enough?
  - Sanvito et al. **NO!, but help is almost here**
- 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)