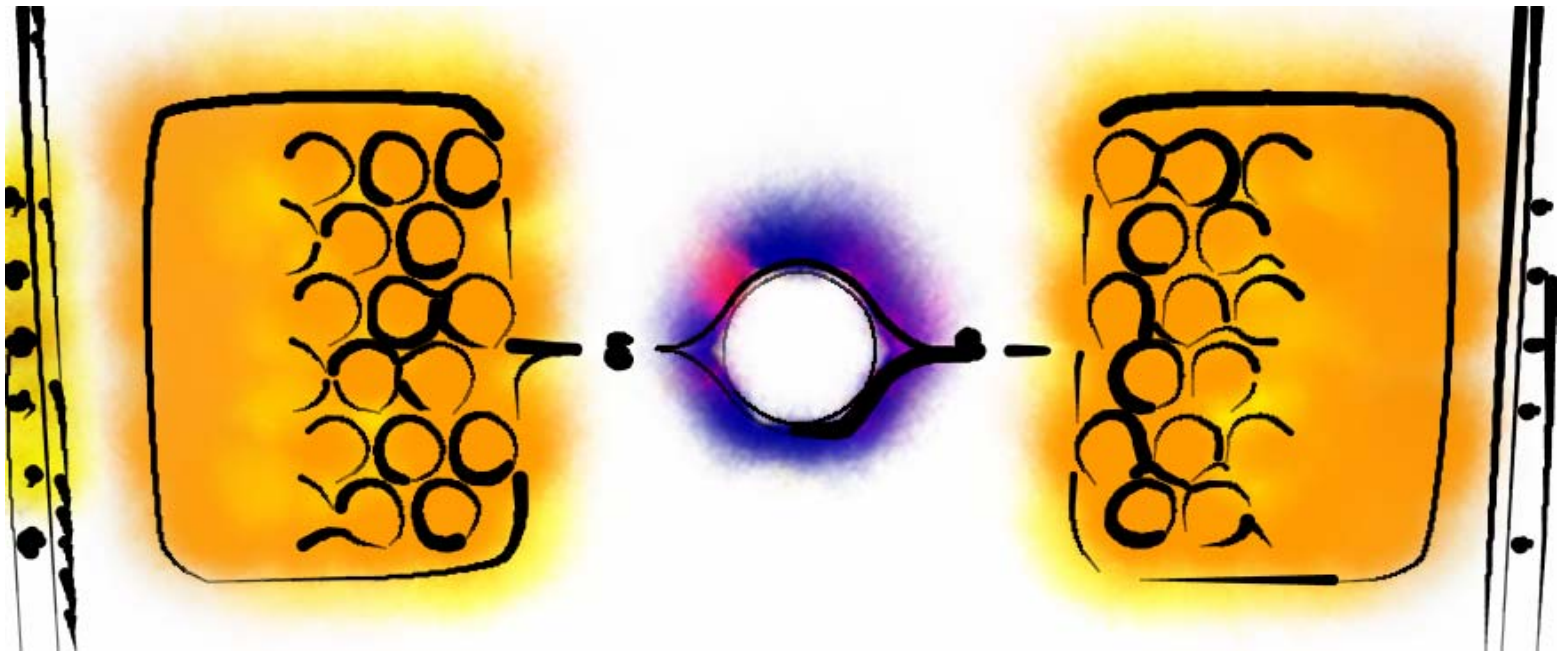# Ab initio impedance of a molecular junction
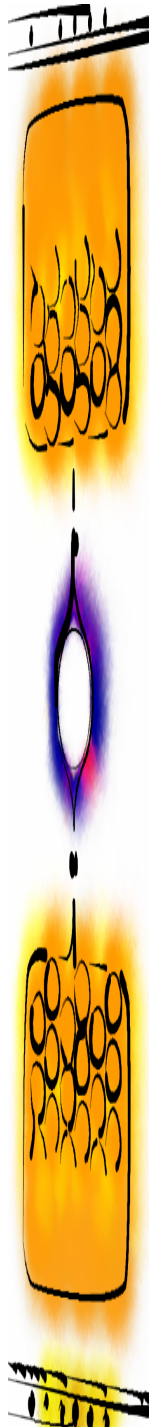
Roi Baer

Institute of Chemistry and the Lise Meitner Center,

The Hebrew University of Jerusalem,
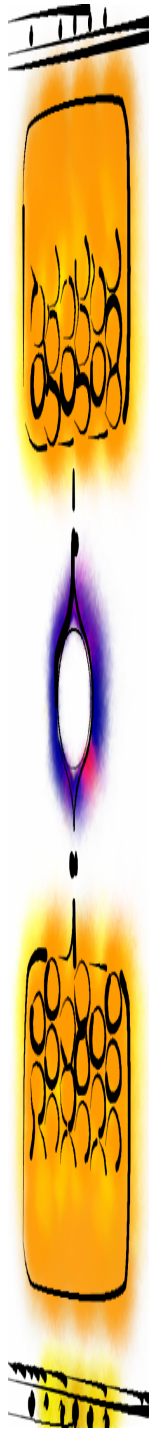
Jerusalem, Israel

Helsinki, December 2003

Overview

- Introduction:
    - Molecular electronics
    - Short course in LRC electronics: Impedance
    - Definition of DC conductance in molecules (zero temp., small bias)
- Simplified Theory, DFT based
    - Method of calculation (Monte Carlo(!))
    - Nice intuitive understanding
- Rigorous Method: simulation of a real measurement
- TDLDA approximation within of the rigorous method
    - Time dependent LDA in real time
    - Calculating and seeing the response
    - Averaging and calculating DC conductance
    - Not averaging and calculating impedance
- Summary and conclusions

Acknowledgments

- Work done in collaboration with:
  - Prof. Daniel Neuhauser (UCLA)
  - Prof. Tamar Seideman (Northwestern)
  - Shahal Ilani (Weizmann Inst.) soon a postdoc in Cornell at P. McEuen's

- Funding:

  Israel Science Foundation
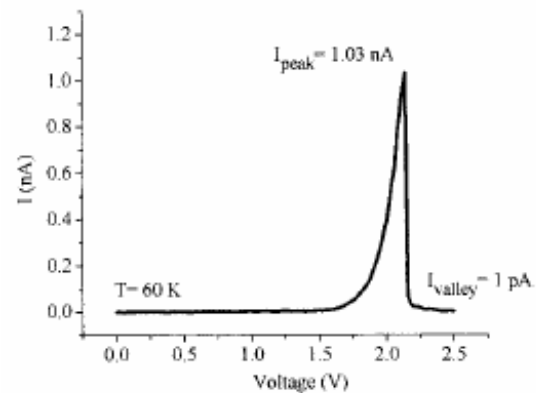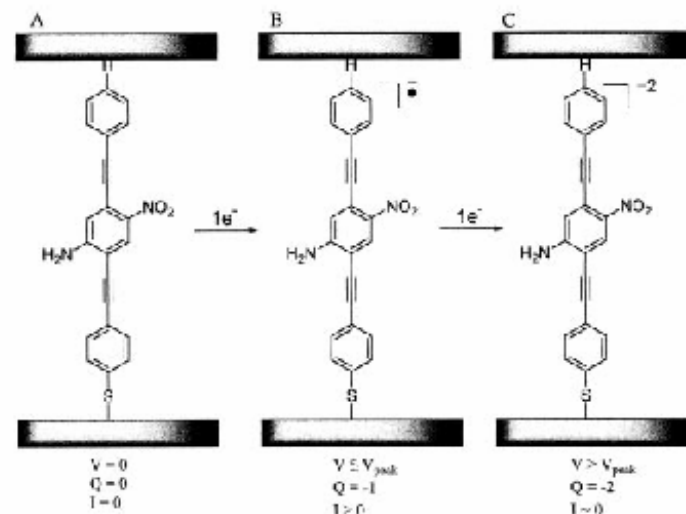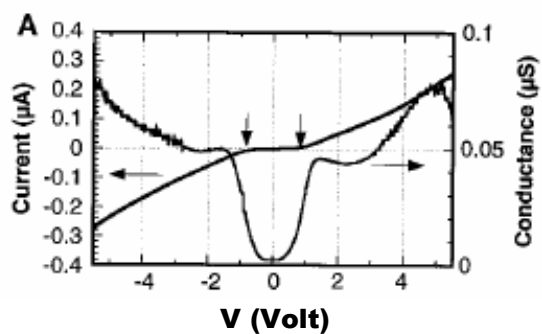
Chapter 1: Introduction

- Molecular electronics

- Short course in LRC electronics: Impedance

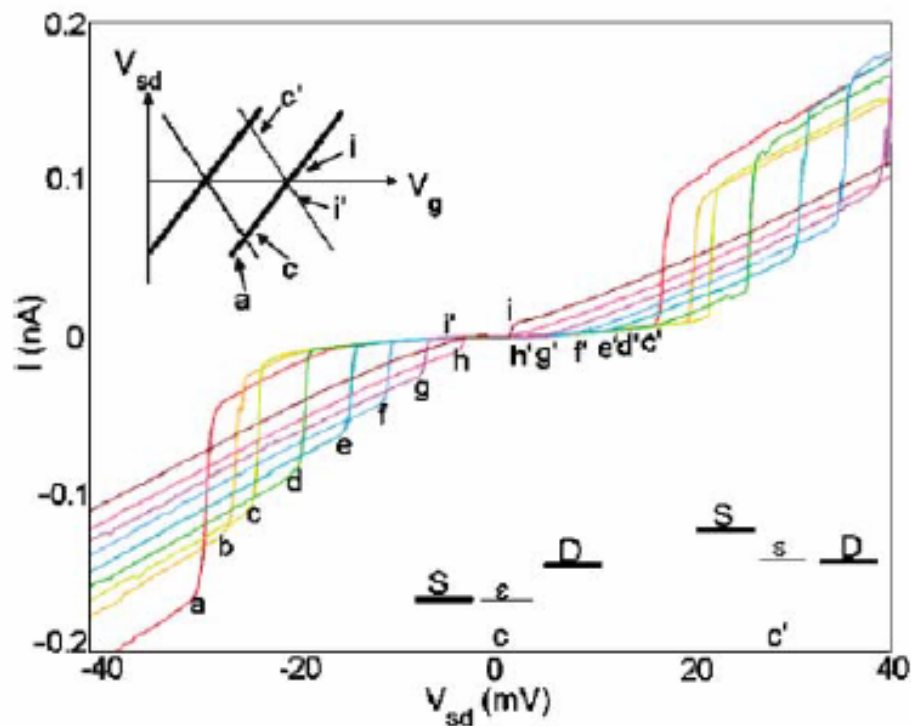- Definition of DC conductance in molecules

Synthetic methods do it!

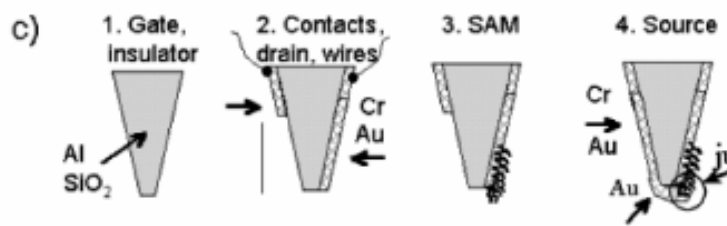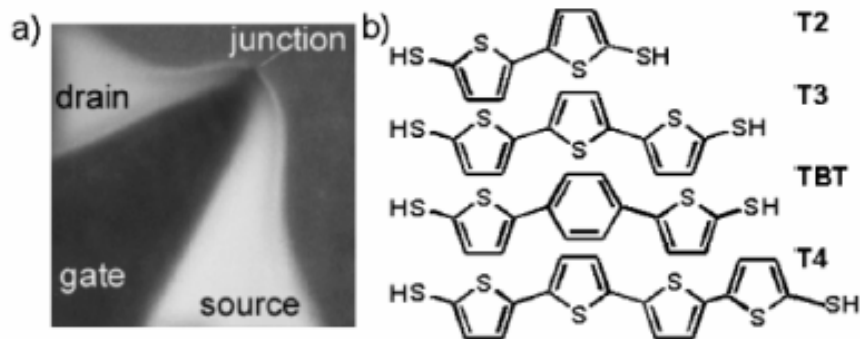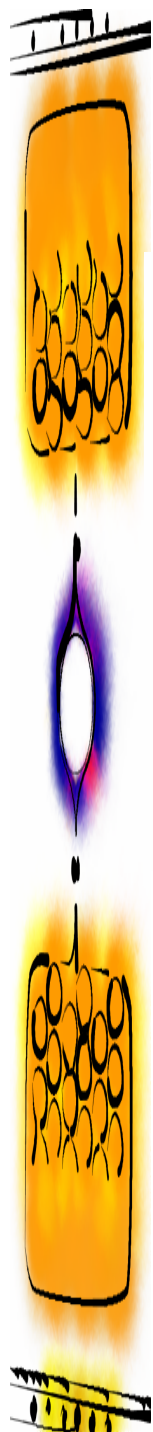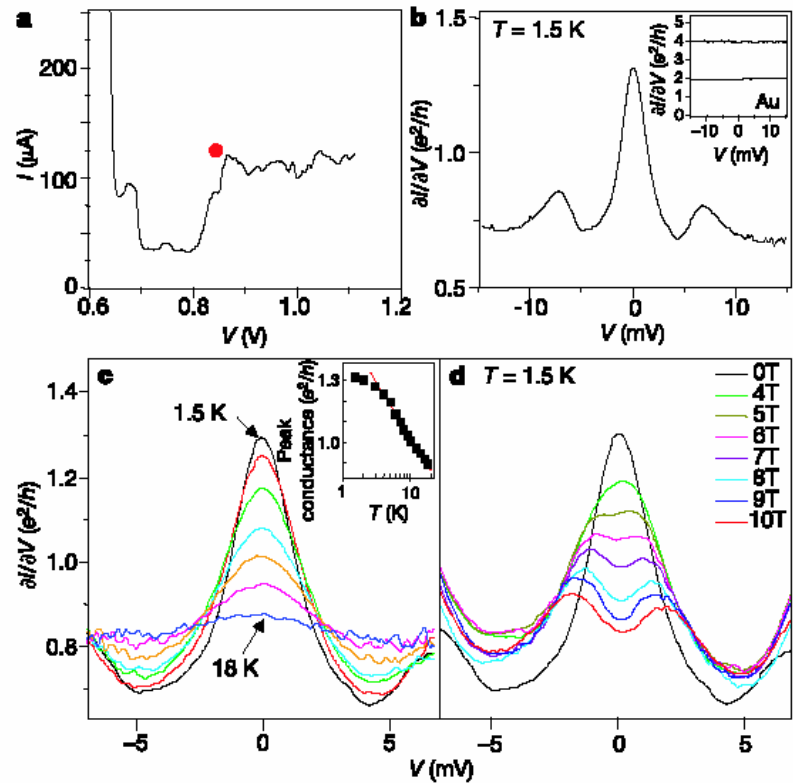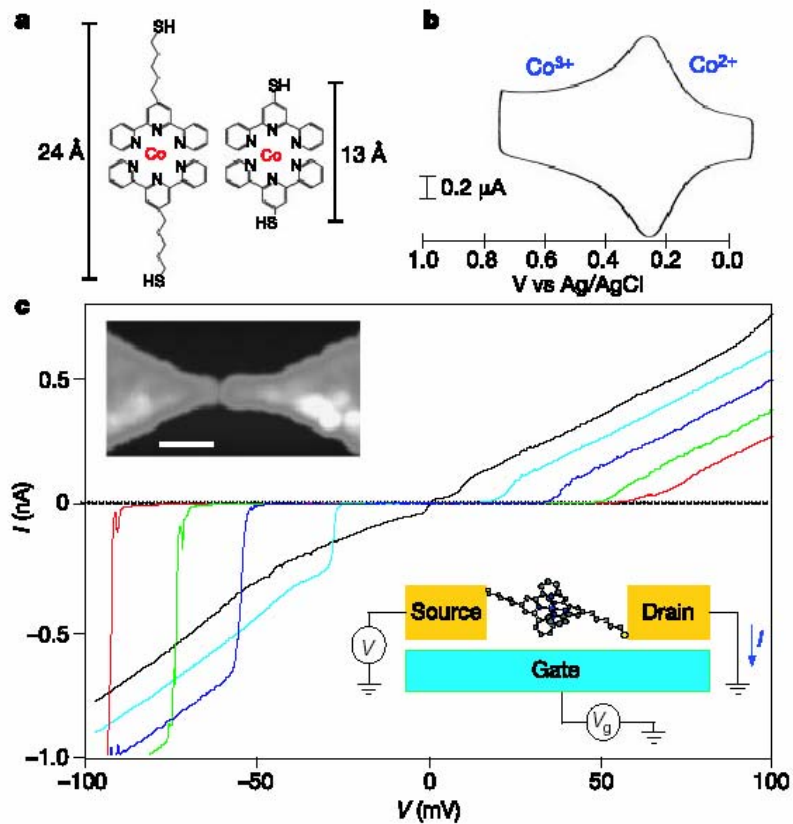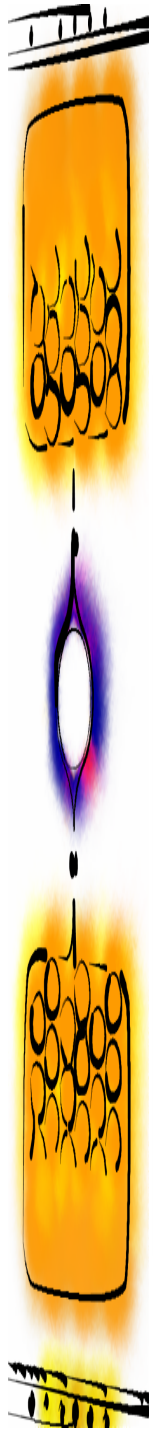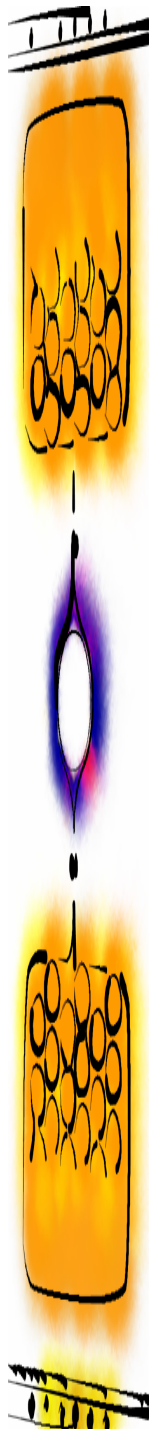Reed et al,
Science 278,252 (1997)
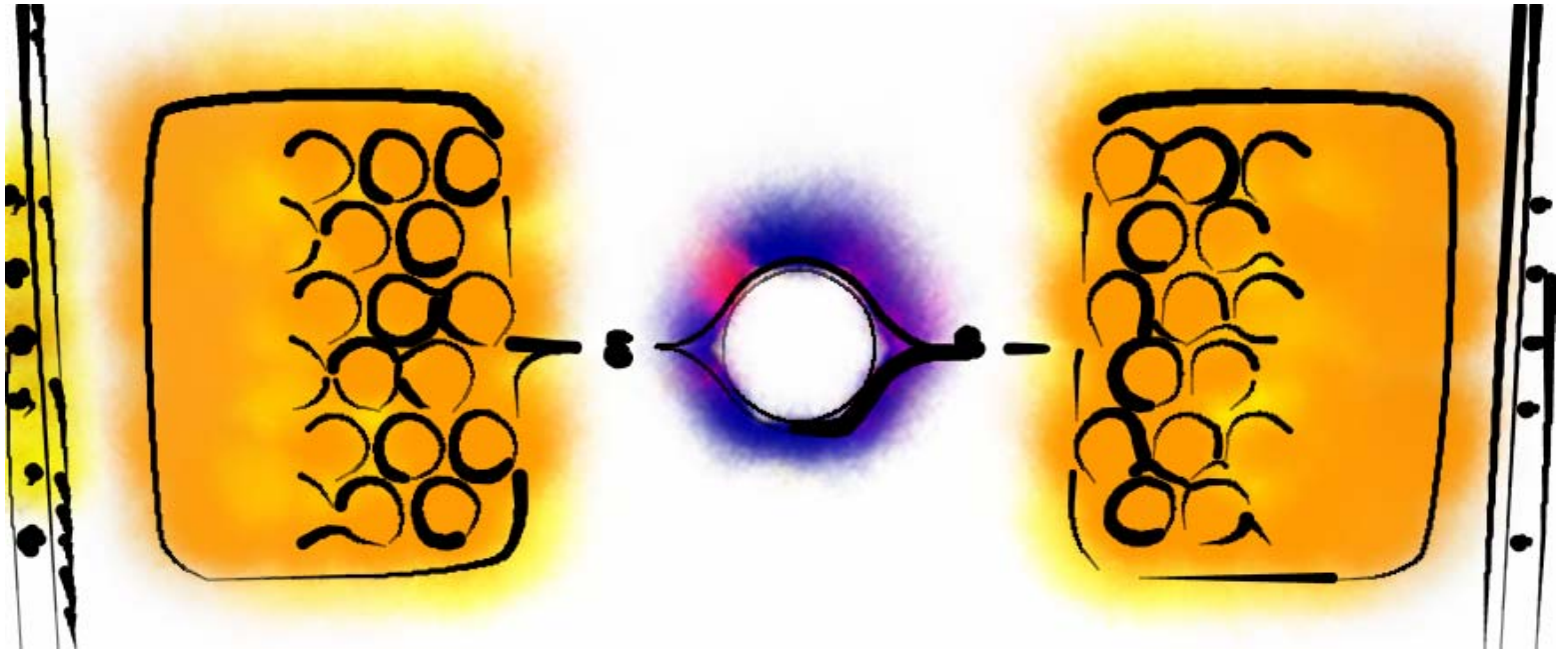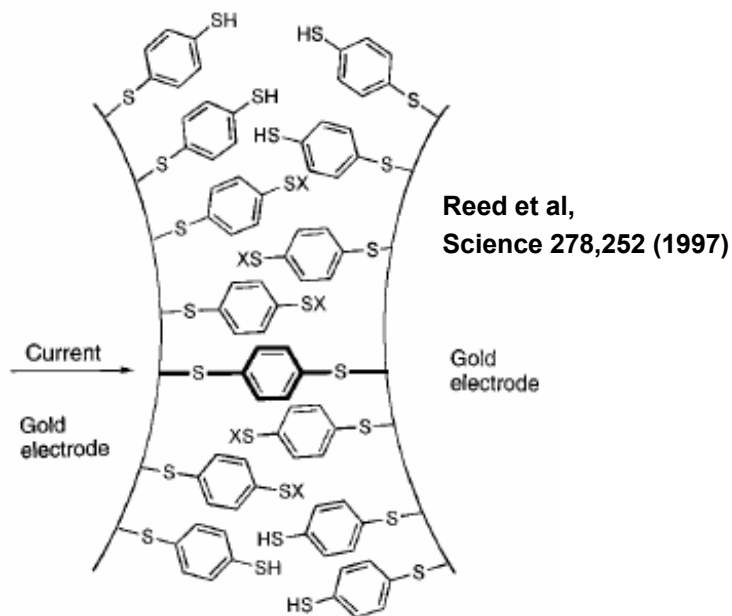
Chen et al,
Science 286,1550 (1998)

Molecular transistor

Coulomb blockade and Kondo effect

Computing conductance (I)

$$\mu_L = \varepsilon_F + \frac{e\Delta V}{2}$$

$$\mu_R = \varepsilon_F - \frac{e\Delta V}{2}$$

- Leads are electron reservoirs
- Each lead in chemical equilibrium μ_L, μ_R, β
- Current from left to right $\qquad I_{L\to R} = \frac{2e}{h}\int_{-\infty}^{\infty} F_L(E)T(E)\,dE$

- Current from right to left $\qquad I_{R\to L} = \frac{2e}{h}\int_{-\infty}^{\infty} F_R(E)T(E)\,dE$
- Total current (Landauer picture):

$$I = I_R - I_L = \frac{2e}{h}\int_{-\infty}^{\infty}\Big(F_R(E) - F_L(E)\Big)T(E)\,dE$$

$$\text{At zero temp:} \quad G = \frac{I}{\Delta V} = \frac{2e^2}{h}T(\varepsilon_F)$$

Calculating T(E)
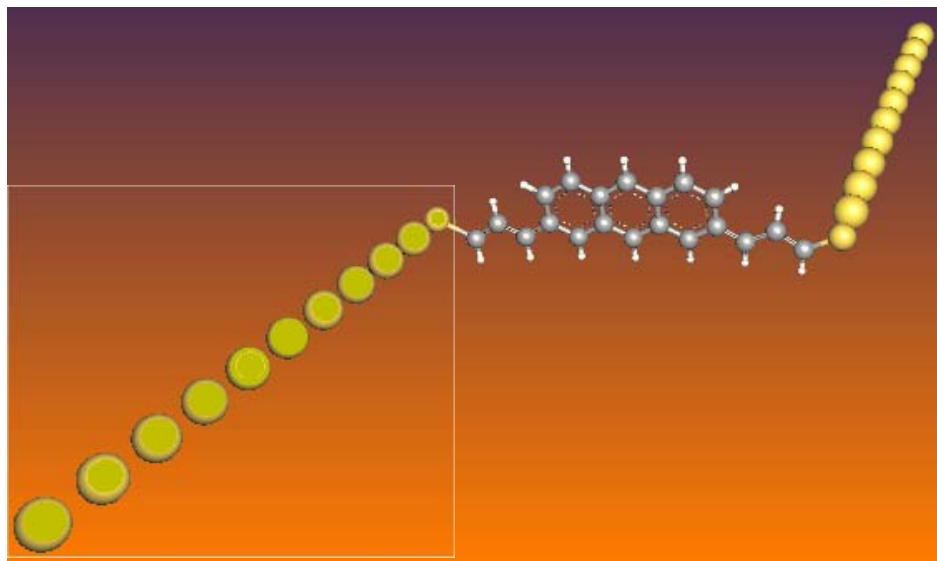
$$T\left(E\right) = 4Tr\left[G^{\dagger}\left(E\right)\Gamma^{L}G\left(E\right)\Gamma^{R}\right]$$

T. Seideman and W. H. Miller, J. Chem .Phys. 97, 2499 (1992).
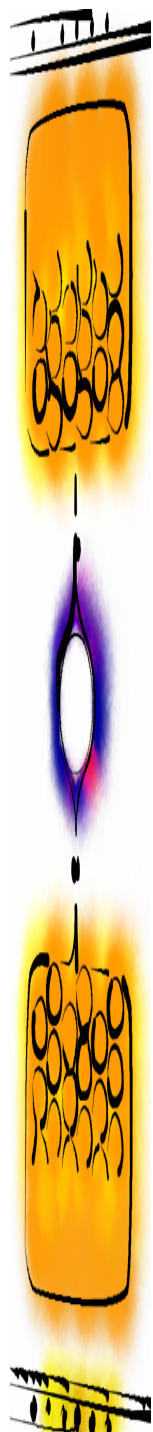
Possibility of interference
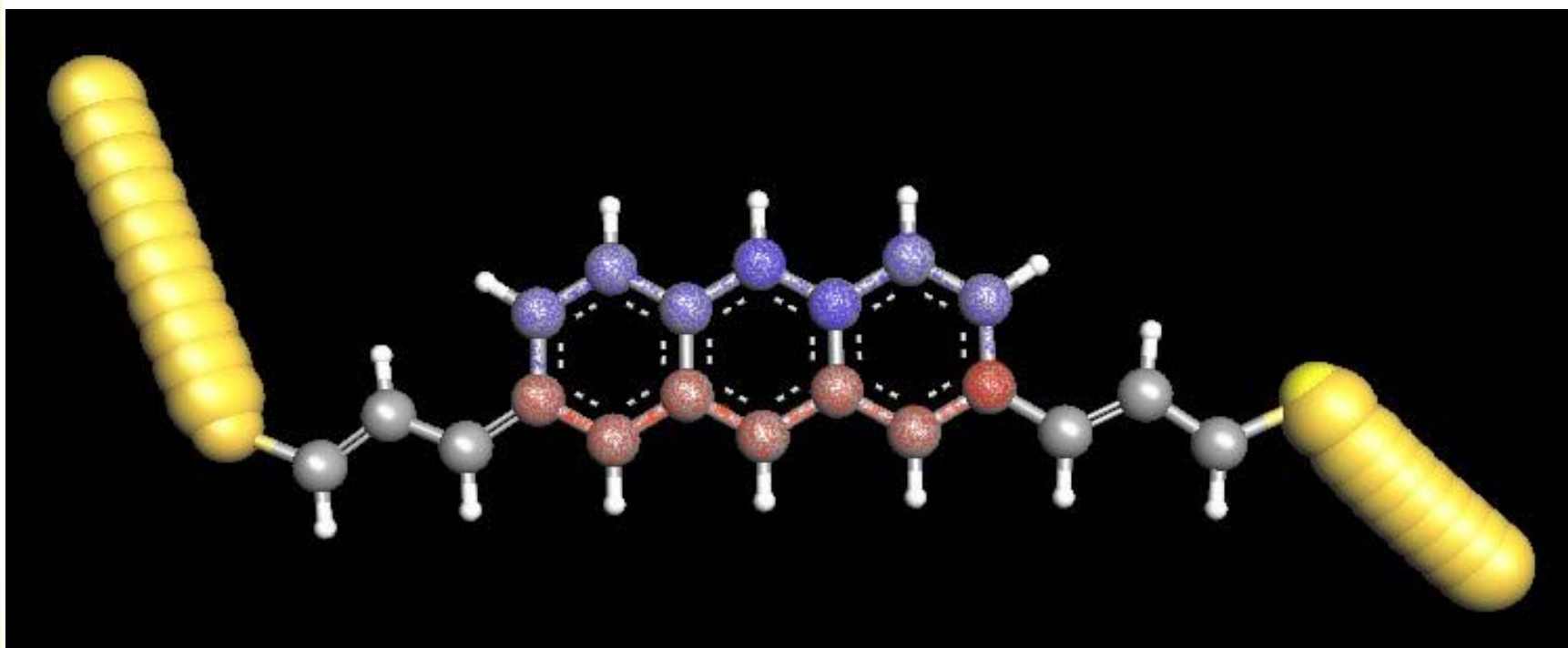
Fermi-Huckel Wave length
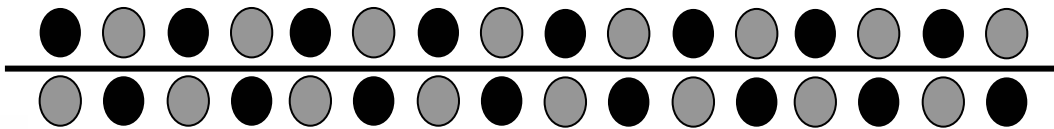
$\lambda = 2a$ — Anti-bonding
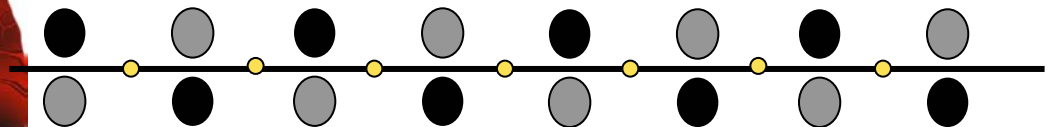
$\lambda_F = 4a$ — Half filling
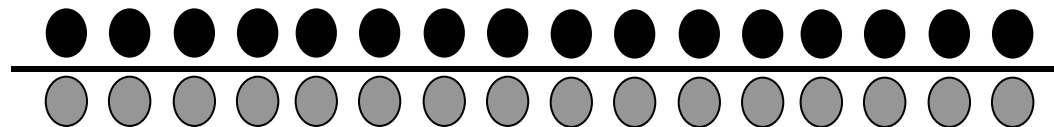
$\lambda = L$ — Bonding

$a = CC$

"Huckel" Interference
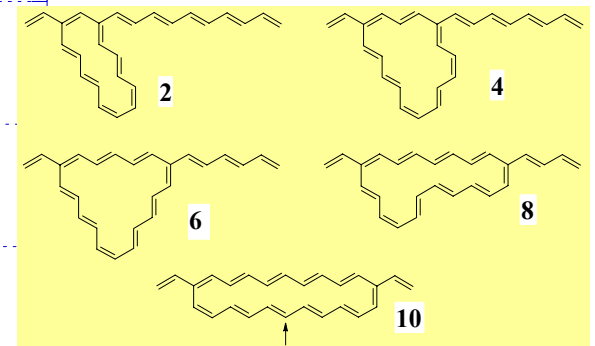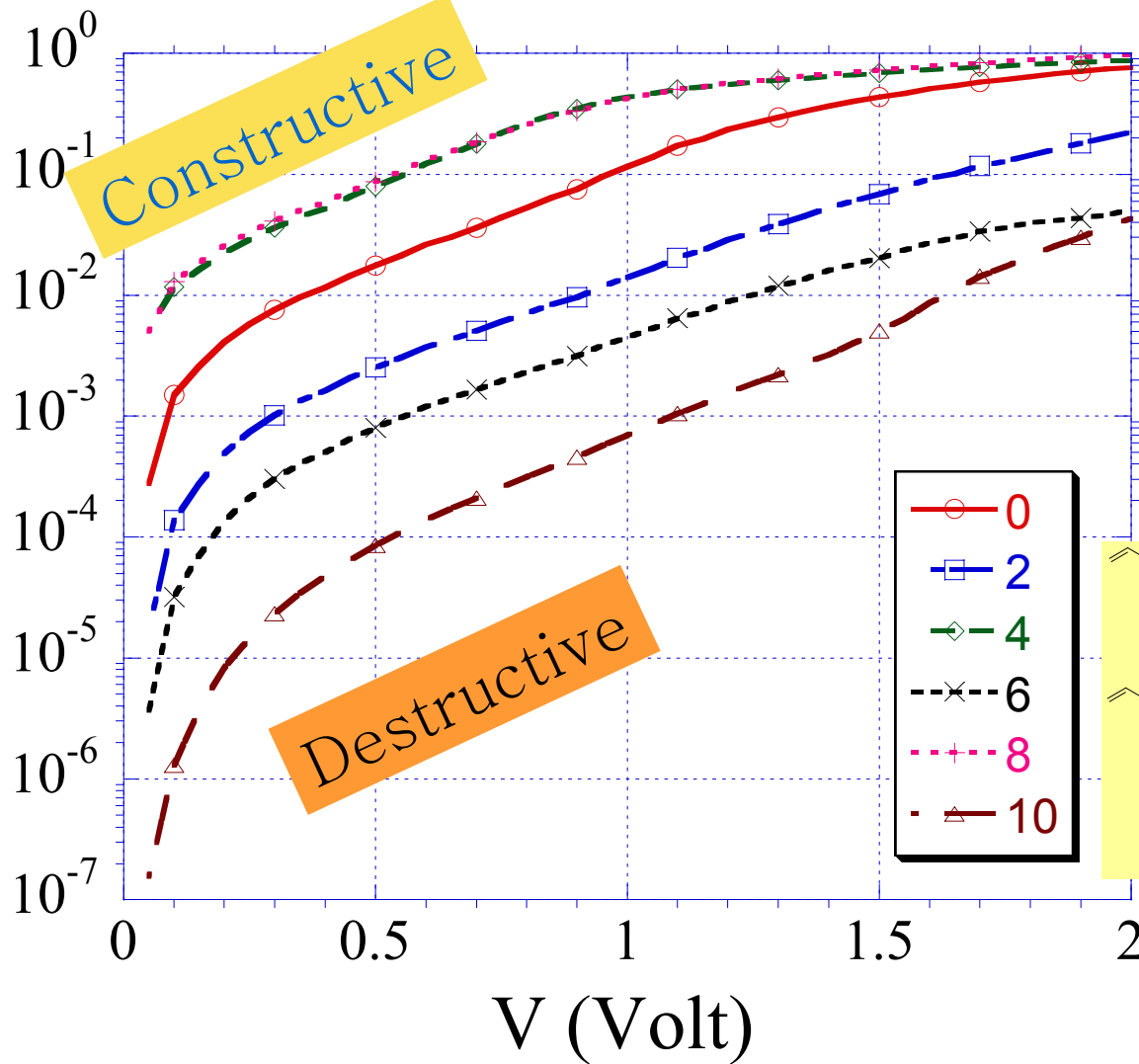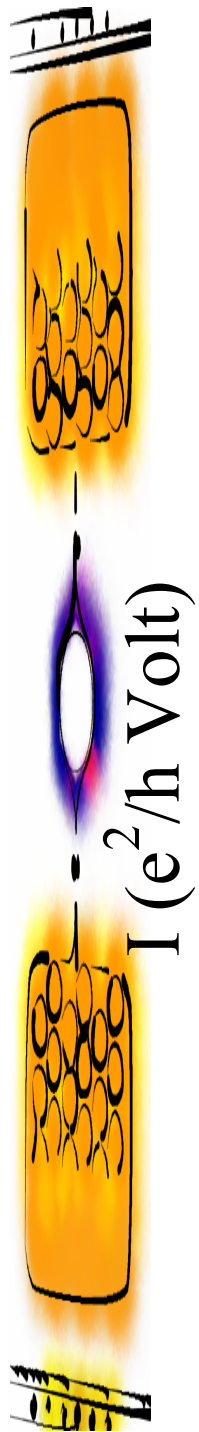
XOR gate based on interference...

Current I →

V_2

V_1
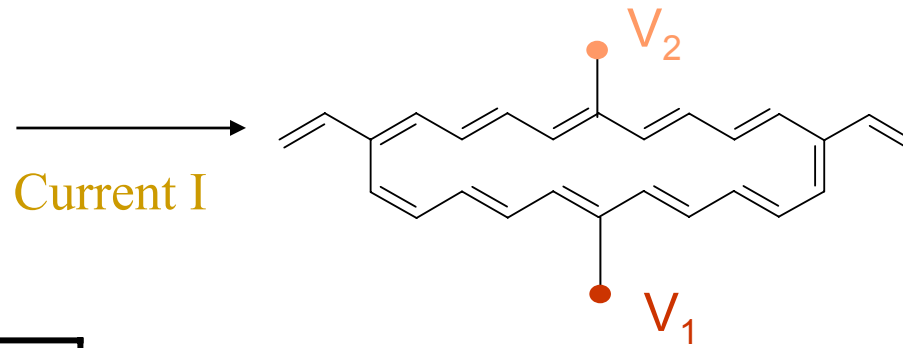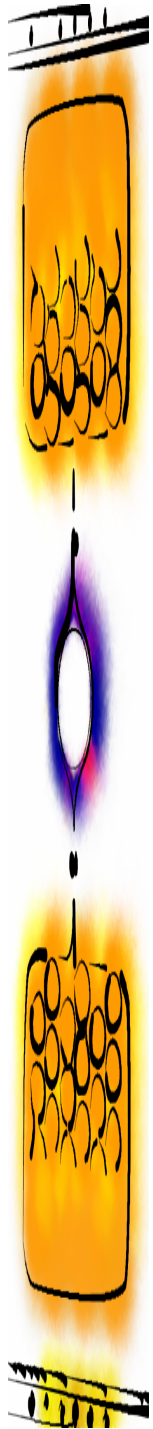
V_1	V_2	I
0	0	0
1	1	0
0	1	1
1	0	1

CIS Interference
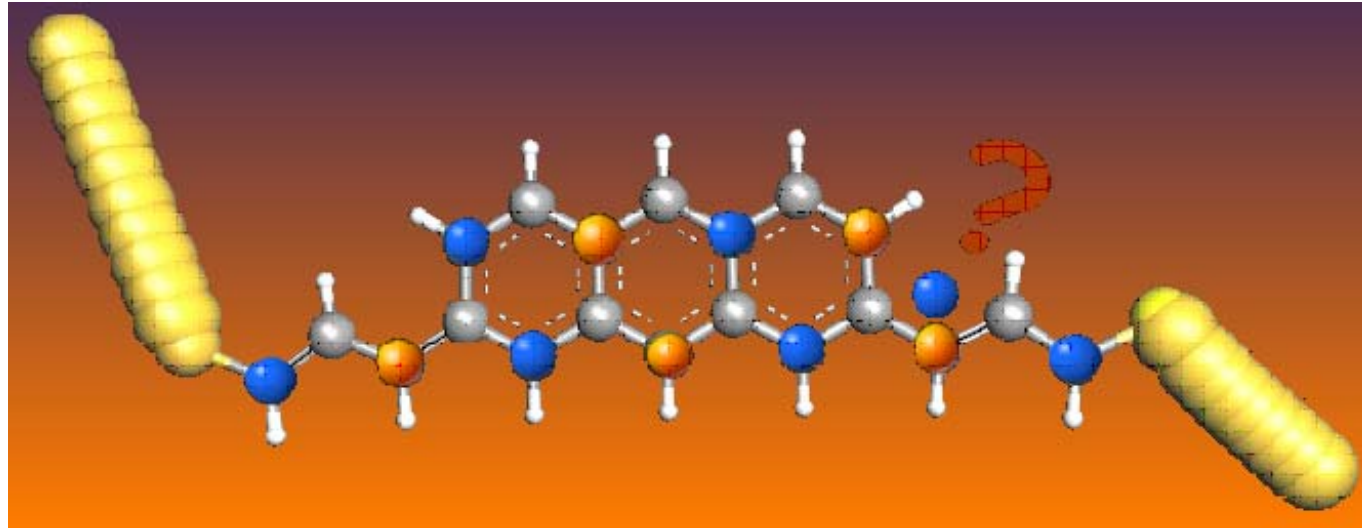
At the Fermi level:

destructive interference
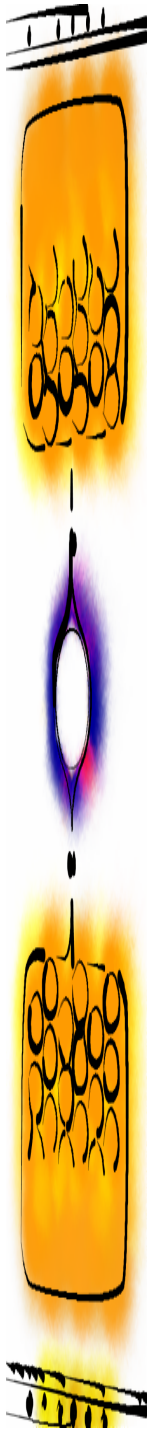
Trans Interference
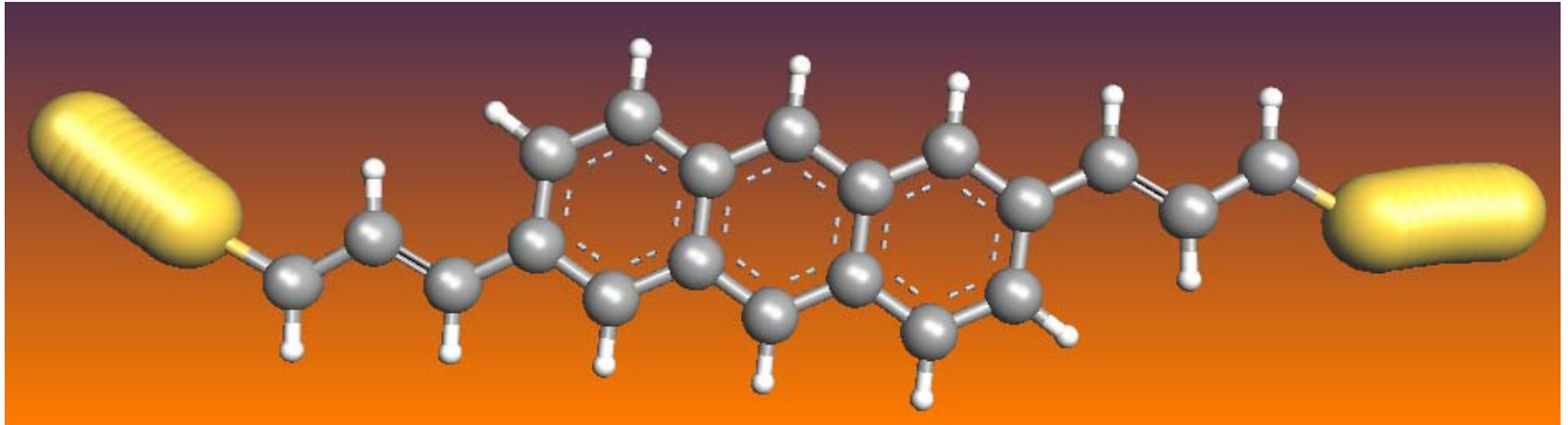
At the Fermi level:

constructive interference
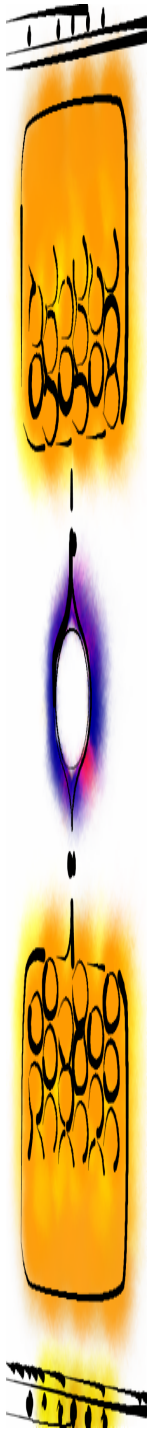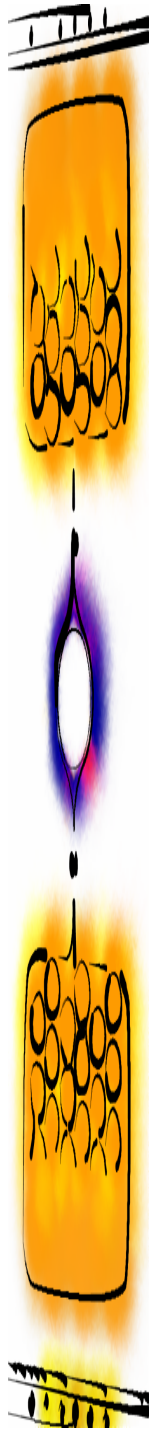
T(E) based on DFT
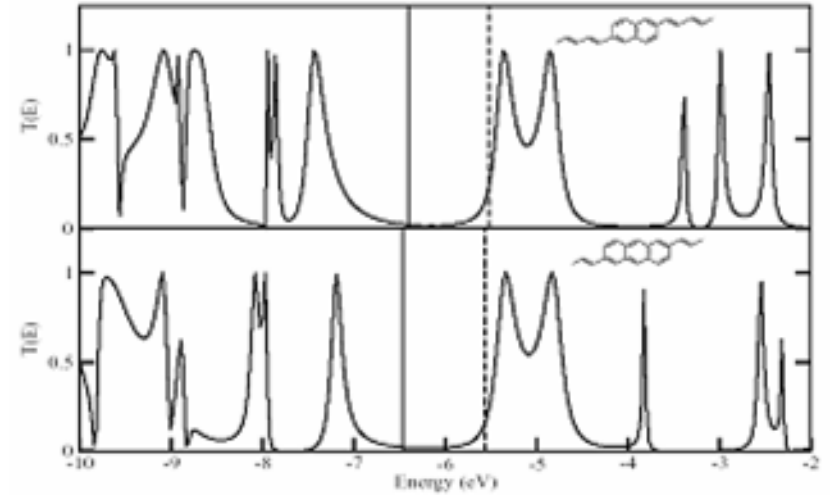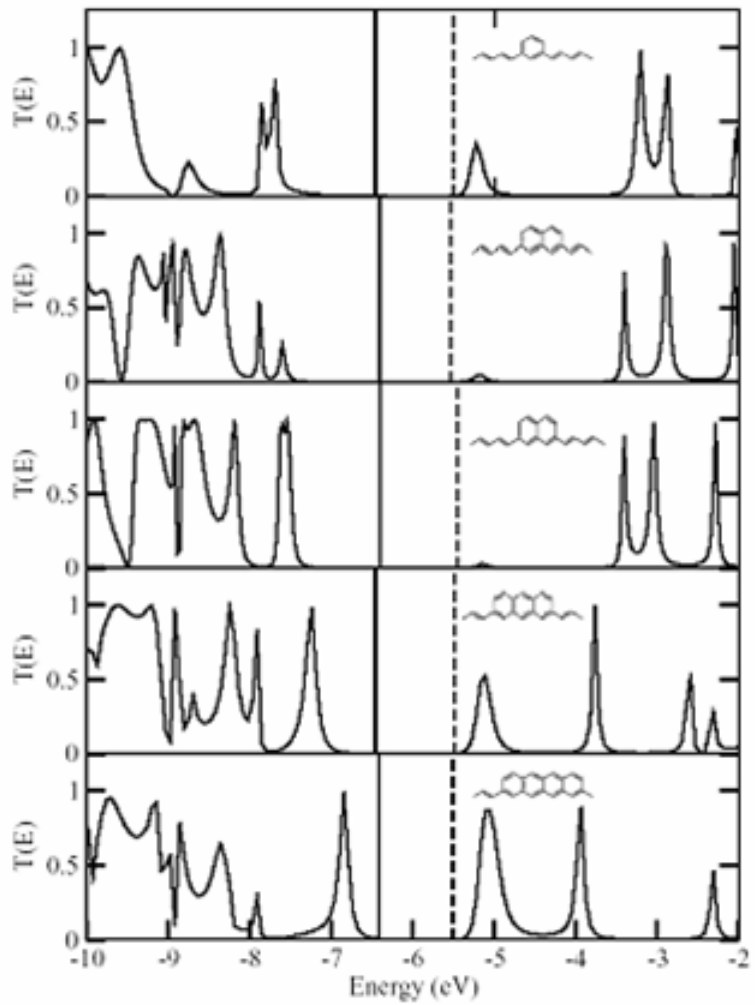
Molecular Electronics is Coming(?)

- Synthesis: can connect molecule to leads
- Analysis: can measure I-V curves (DC)
- Next: measure impedance?...

RESISTANCE   INDUCTANCE   CAPACITANCE
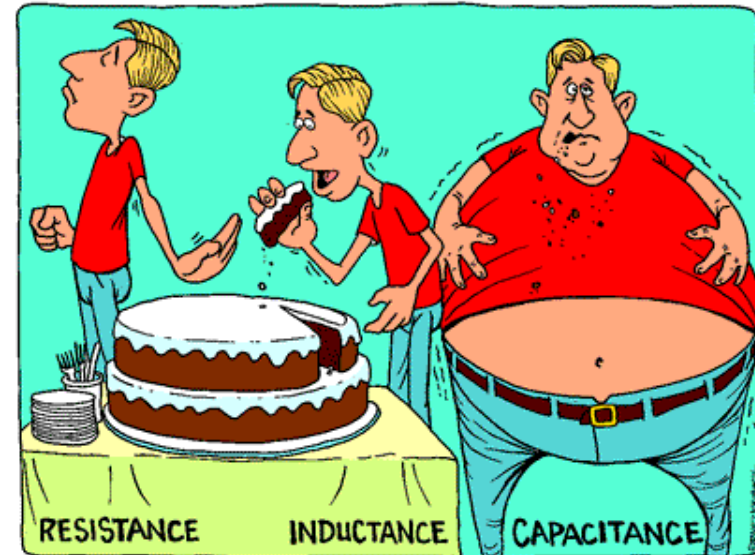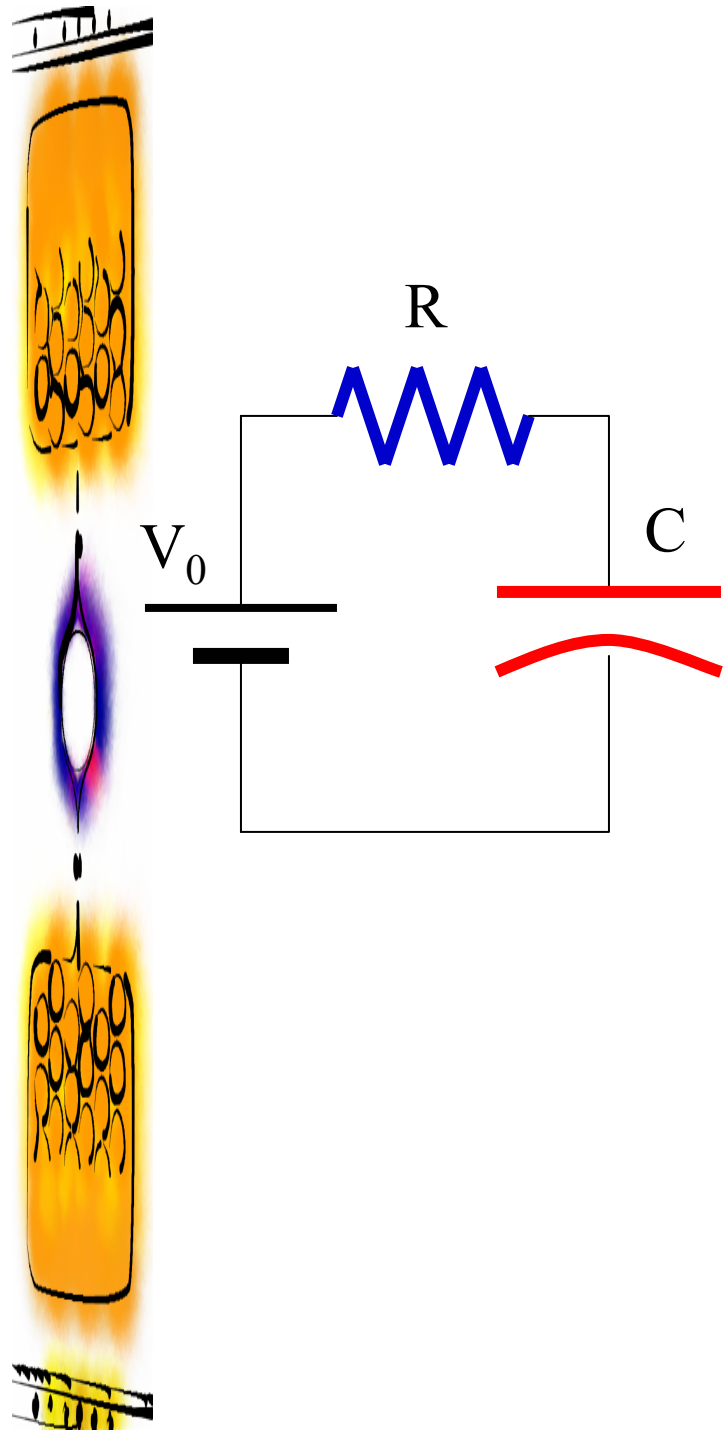
RC circuit

$$V_R = IR$$

$$Q = CV_C \qquad \dot{V}_C = I/C \qquad \left(I = \dot{Q}\right)$$

$$V_0 = V_R + V_C$$

$$\Rightarrow \dot{V}_0 = \dot{I}R + C^{-1}I$$

In frequency:

$$V_0(\omega) = I(\omega)\left(R + \frac{1}{i\omega C}\right)$$

RC circuit: high-pass filter

R

$$V_R(\omega) = I(\omega) R$$

$$V_0(\omega) = I(\omega)\left(R + \frac{1}{i\omega C}\right)$$

V_0
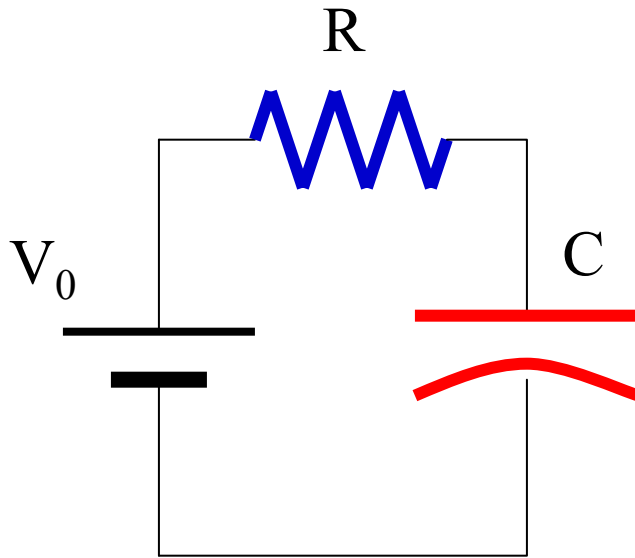
C

$$\left|\frac{V_R}{V_0}\right| = \frac{\omega(RC)}{\sqrt{\omega^2(RC)^2 + 1}}$$
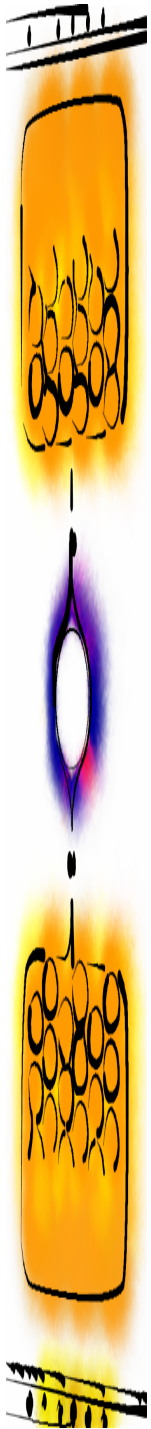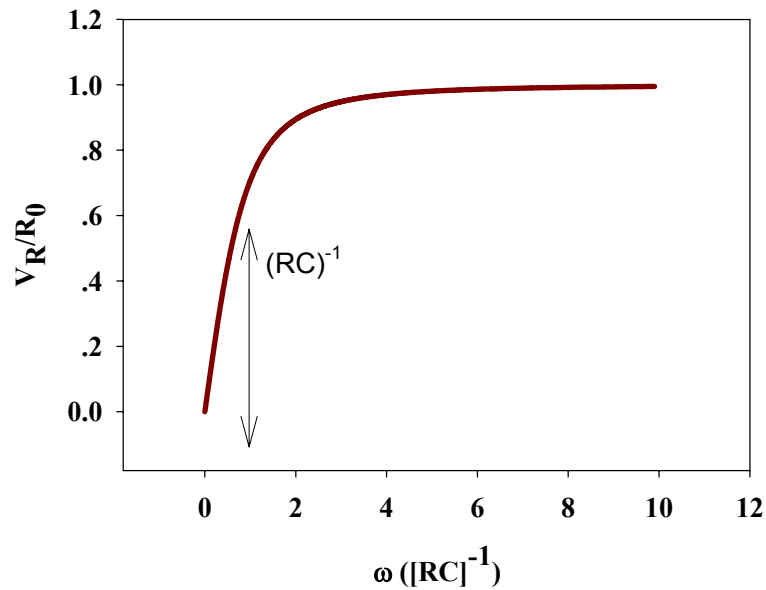
RL circuit

$$V_R = IR$$

$$V_L = L\dot{I}$$

$$V_0 = V_R + V_L$$

$$\Rightarrow V_0 = IR + L\dot{I}$$

In frequency:

$$V_0(\omega) = I(\omega)(R + i\omega L)$$
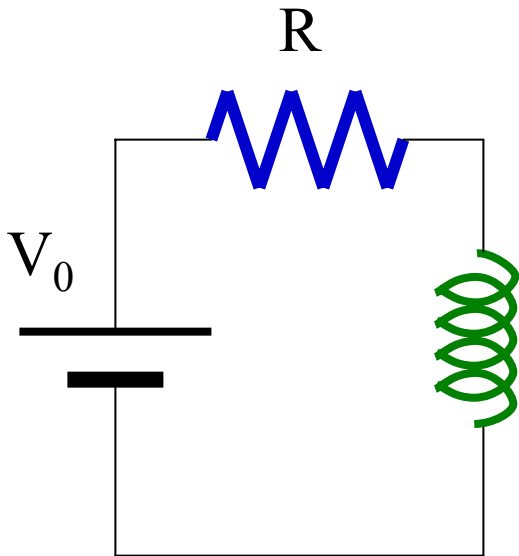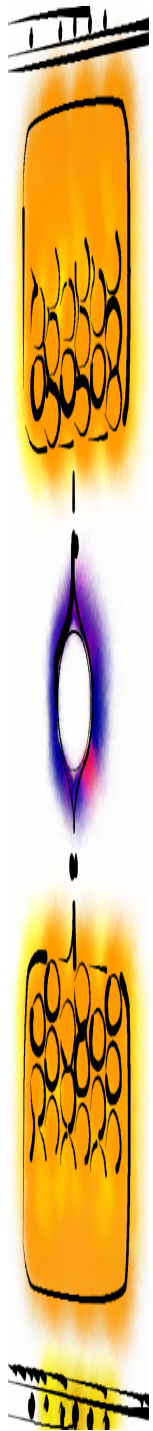
Moderator:

$$V_L = V_0 e^{-Rt/L}$$

$$V_R = V_0\left(1 - e^{-Rt/L}\right)$$

RLC circuits: Impedance

$$Z_I = i\omega L$$

$$Z_C = -i/\omega C$$

$$Z_R = R$$
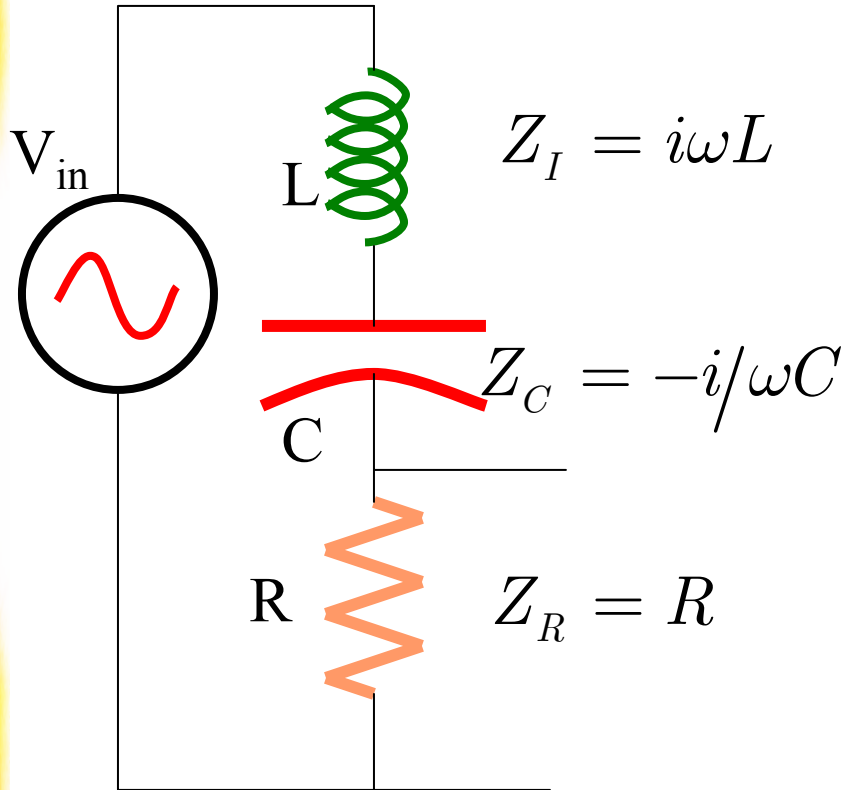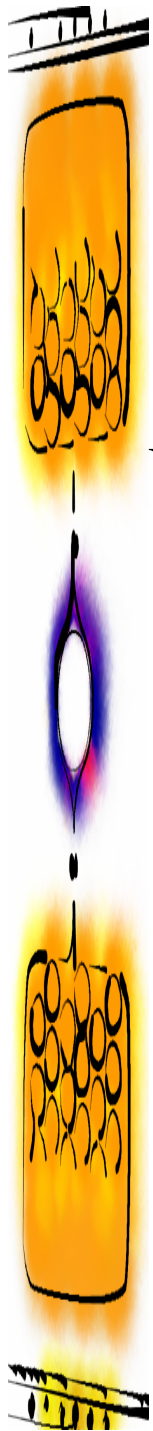
$$Z = R + i\left(\omega L - \frac{1}{\omega C}\right)$$

$$\left|\frac{V_R}{V_{in}}\right| = \left|\frac{Z_R}{Z}\right| = \frac{\omega RC}{\sqrt{\omega^2(RC)^2 + \left(\omega^2(LC) - 1\right)^2}}$$

V_{in}

L

C

R

Notch filter

$\omega = (LC)^{-1/2}$

R/L

V_R/V_{in}

ωRC
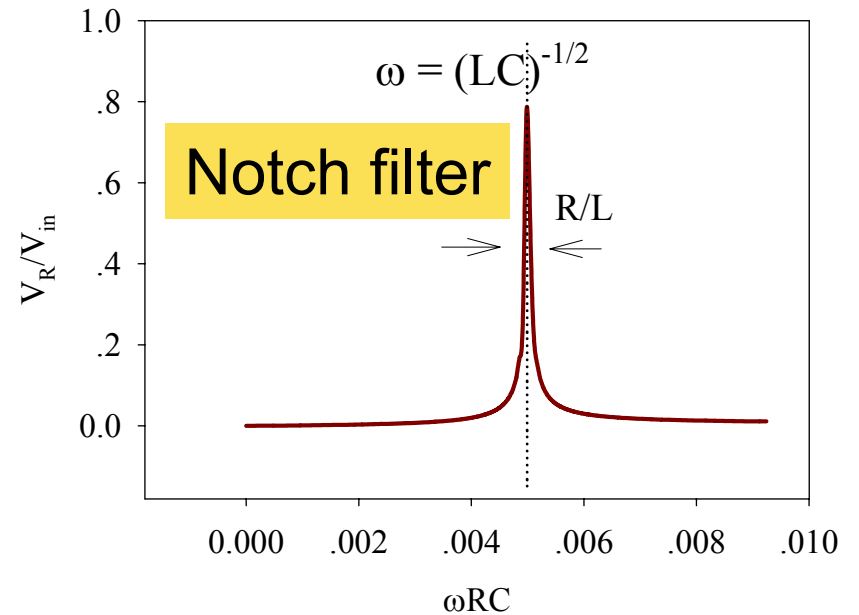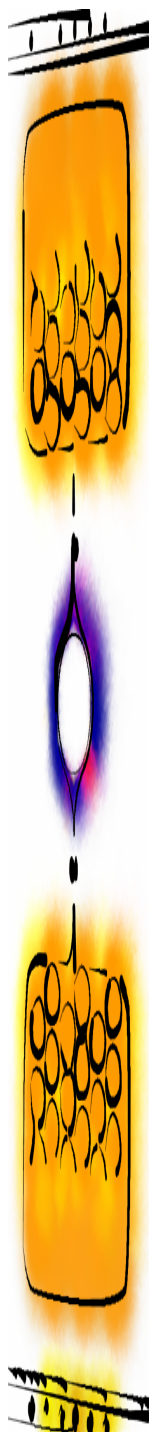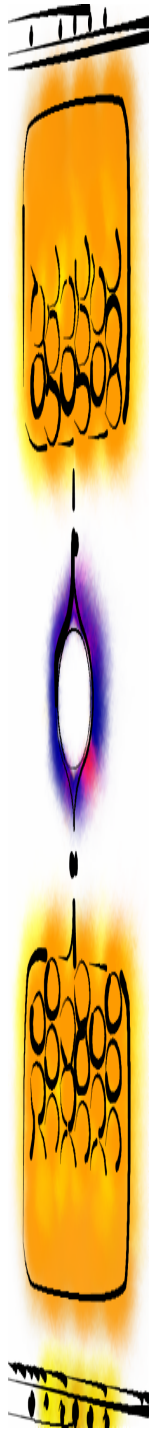
Can molecules do all that?

- If we work in high enough frequency yes
- We need to <u>understand</u> much more about conductance!
- This talk takes a benchmark system and tries to understand conductance:
  - Simple level: independent particle theory
  - Advanced level: time dependent DFT
- As a bonus we get AC impedance

T(E) of What???

- T(E) = cumulative "reaction probability"
- But what is the Hamiltonian?
- Simple picture

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + v_s(r)$$

- How to <u>compute</u> conductance from this
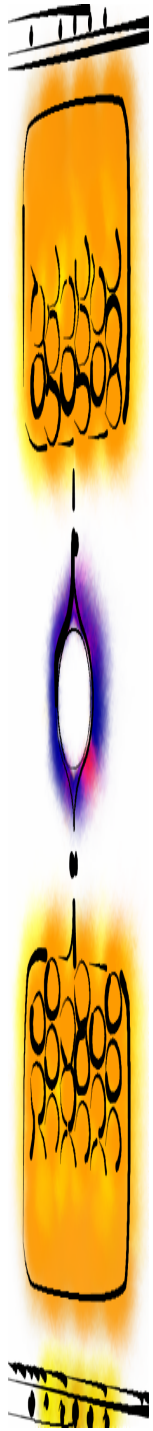
Benchmark: Two C$_6$ Systems

C
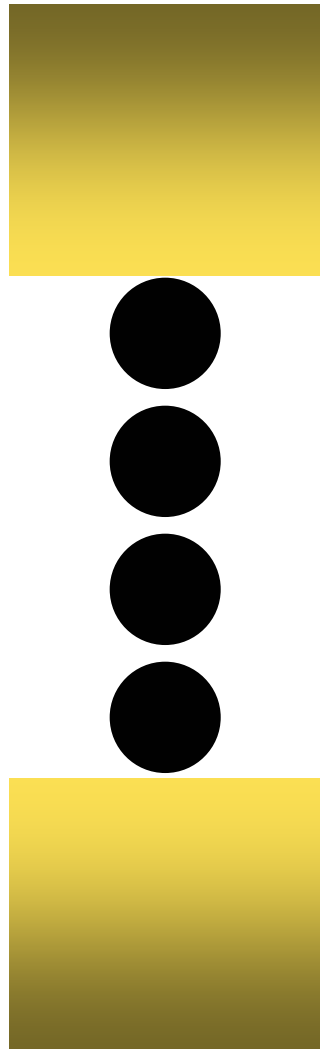
R
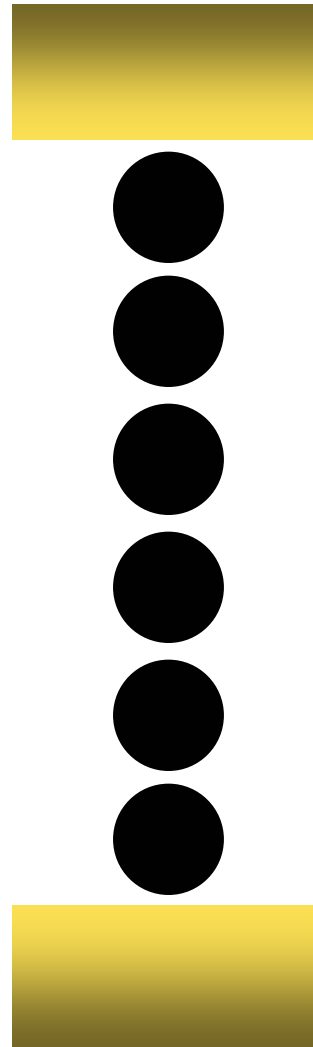
Benchmark in a Box

- Box with R-space grid $L_z = 64\ a_0$, $L_x = L_y = 10a_0$,

  $N_g = 20 \times 20 \times 128 = 51{,}200$

- FFT – do all the hard work

- Molecular wire:

  - Ionic cores – pseudopotentials (Fuchs +Scheffler PP98)

  - Realistic model

- Metal Leads:

  - a <u>uniform average</u> over the positive ionic charge of the metals

  - enough electrons to exactly neutralize

  - Not so realistic, but very well defined!
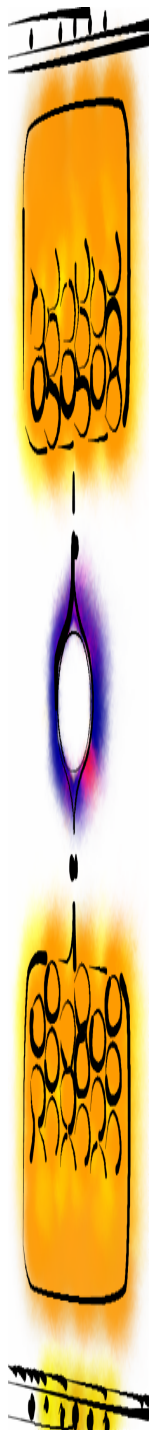
Simplified scheme

- Perform full DFT calculation

- in principle, also geometry

  - we did it, finding some Peierls dimerization

  - Effect not included here

- Give ε_F (HOMO energy)

- Then, using the Fock matrix H_{KS}…
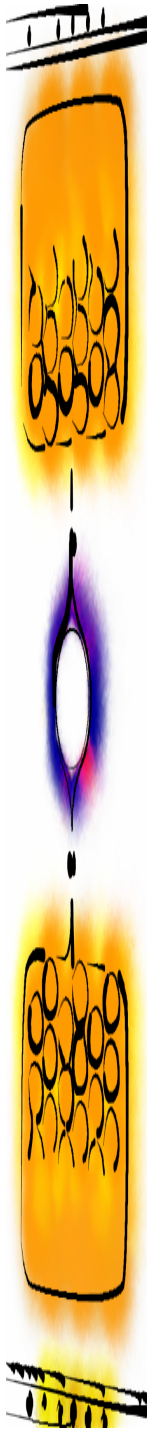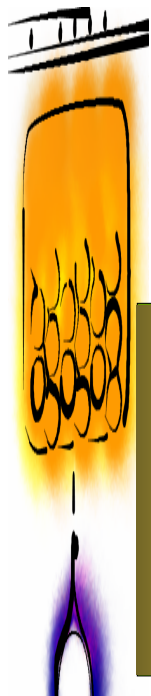
"Conductance after DFT"
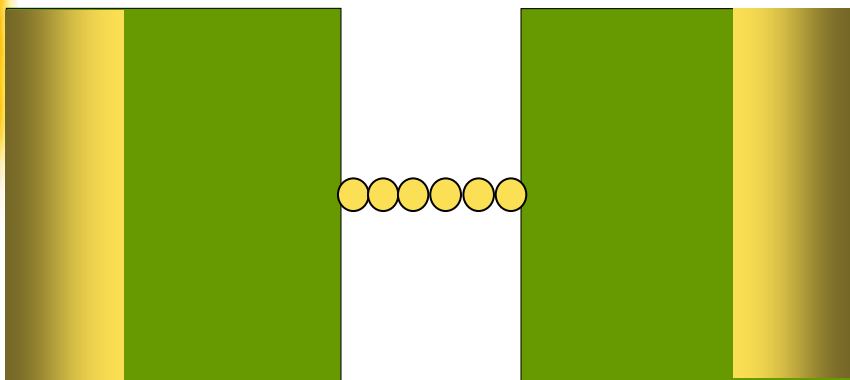
$$G = \frac{2e^2}{h} T(\varepsilon_F) \qquad T(E) = 4 tr \left\{ \Gamma_L \tilde{G}^\dagger(E) \Gamma_R \tilde{G}(E) \right\}$$

$$\tilde{G}(E) = \left(E - H_{KS} + i\Gamma_L + i\Gamma_R \right)^{-1}$$

$$\Downarrow\Downarrow$$

$$T(E) = tr \left\{ L^\dagger(E) L(E) \right\} \qquad L(E) = 2\sqrt{\Gamma_R} \tilde{G}(E) \sqrt{\Gamma_L}$$

Monte Carlo (with no sign problem):

$$tr L^\dagger L = \left\langle \left\langle \psi_\theta \left| L^\dagger L \right| \psi_\theta \right\rangle \right\rangle_\theta$$

$$\psi_\theta(r_m) = e^{i\theta_m}$$

$$G(C) = 0.4\ g_0$$
$$G(R) = 0.022\ g_0$$
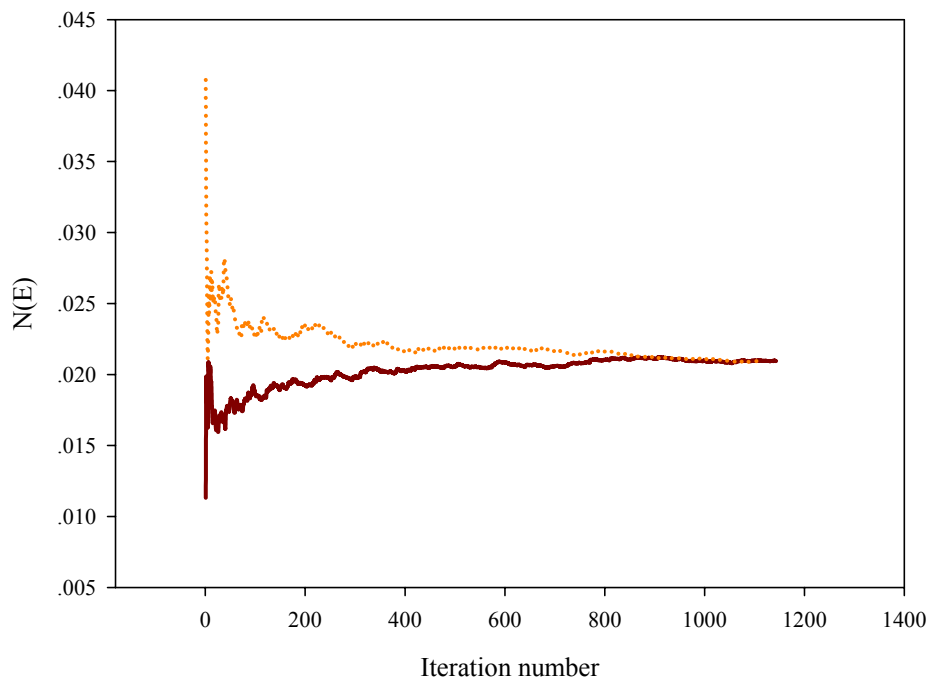
Neuhasuer and M.Baer, J. Chem .Phys. **90**, 4351 (1989).
Riss and Meyer, J. Chem .Phys. **105**, 1409 (1996).

Seideman and Miller, J. Chem .Phys. **97**, 2499 (1992).

Iitaka et al. Phys Rev E **56**, 1222 (1997).
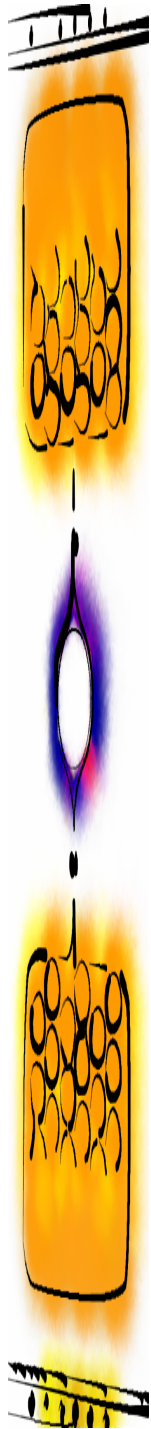
Monte Carlo method for trace

- Given an operator A, where Aψ is expensive compute

$$tr\{A\} = \sum_{n=1}^{N} \langle \psi_n | \hat{A} | \psi_n \rangle$$

- Solution:

$$tr\{A\} = \left\langle \left\langle \sum_{n=1}^{N} \psi_n e^{i\theta_n} \middle| \hat{A} \middle| \sum_{n=1}^{N} \psi_n e^{i\theta_n} \right\rangle \right\rangle_{\theta_1...\theta_N}$$

- Proof:

$$\left\langle \left\langle \sum_{n=1}^{N} \psi_n e^{i\theta_n} \middle| \hat{A} \middle| \sum_{n=1}^{N} \psi_n e^{i\theta_n} \right\rangle \right\rangle_{\theta_1...\theta_N} = \left\langle \sum_{m=1}^{N} \sum_{n=1}^{N} e^{i(\theta_m - \theta_n)} \langle \psi_n | \hat{A} | \psi_m \rangle \right\rangle_{\theta_1...\theta_N}$$

$$= \sum_{m=1}^{N} \sum_{n=1}^{N} \underbrace{\left\langle e^{i(\theta_m - \theta_n)} \right\rangle_{\theta_1...\theta_N}}_{\delta_{nm}} \langle \psi_n | \hat{A} | \psi_m \rangle$$

$$= \sum_{m=1}^{N} \langle \psi_n | \hat{A} | \psi_m \rangle = tr(A)$$

Benchmark: Two C_6 Systems
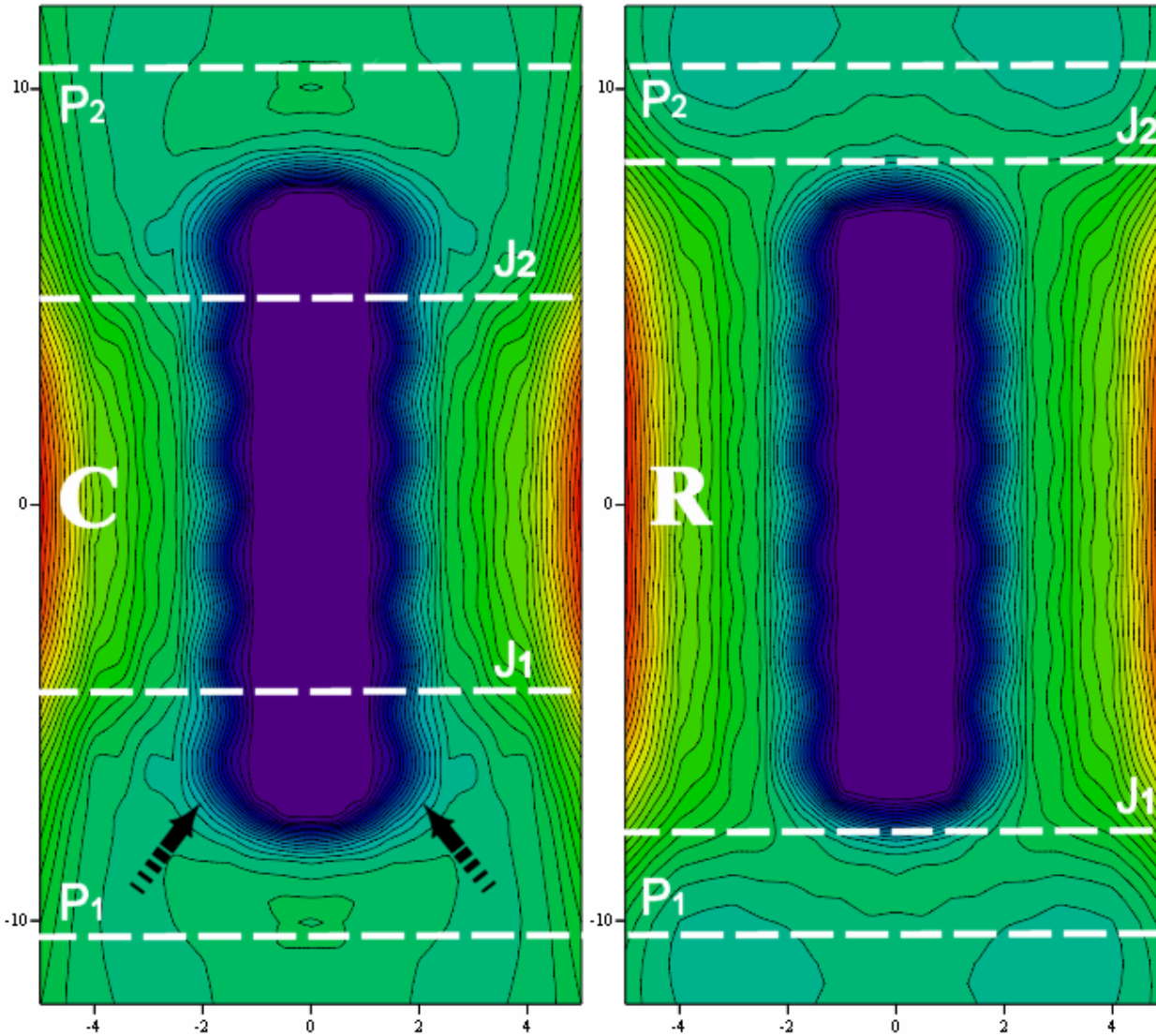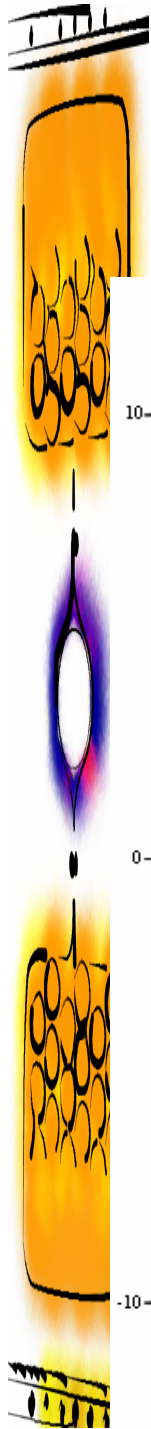
- Channel has no barrier on the contrary – deep

- In R system, small entrance barrier=1.5 eV

- Fermi electron kinetic energy is 5.5 eV.

- But.. X/Y coordinates need to squeeze into the narrow channel.

- Costs ~2.5 eV, and need good x/y accelaration

- C system will conduct better: sticks out so goo x/y acceleartion
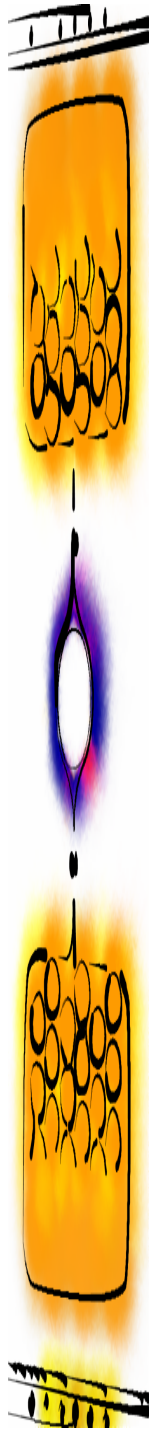
But… Things are NOT so simple

- V_{ks} is missing the bias
- Electrodes metallic $\rightarrow$ bias localized on junction
- Solution: put in a bias potential $H_{bias} = H_{KS} + V_{bias}$
- Problem 1: what is V_{bias}??
- Problem 2: screening of the bias???
- Issues raised recently by Datta, Ratner, Nitzan, Lang
- Popular method to deal with these: Non eq. Greens F
- We present a different approach that encompases this and adds more

Do what the experimentalist does

- Connect a molecule to leads ("junction")
- Turn on bias
- Measure potential difference $V_{12}(t)$
- Measure current through junction $I(t)$
- Fourier transform

- DFT GS electrons +Ions +Jellium+ NIP
- Add $v_{ext}(\mathbf{r},t)$ and propagate
- Calculate $n(r,t)$

$$V_{12}(t) = v_e(r_1,t) - v_e(r_2,t)$$

- Calculate $I(t) = \int_S \mathbf{j} \cdot d\mathbf{S}$
- Fourier transform

$$Z_{12}(\omega) = \frac{V_{12}(\omega)}{I(\omega)}$$
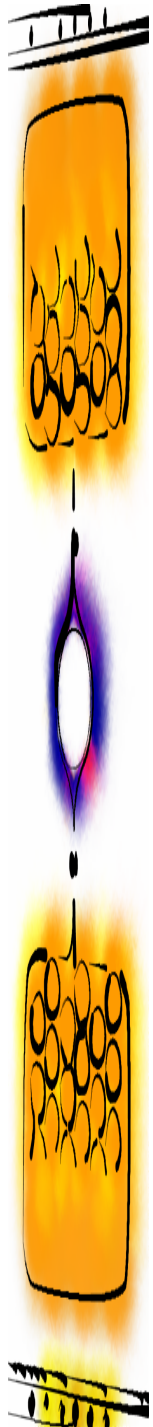
TDDFT in Real time

- Density is represented by orbitals:

$$n\left(\mathbf{r},t\right) = \sum_{n=1}^{N_e} \left|\phi_n\left(\mathbf{r},t\right)\right|^2$$

- Orbitals must obey

$$i\hbar\dot{\phi}_n\left(\mathbf{r},t\right) = \left\{-\frac{\hbar^2}{2\mu_e}\nabla^2 + v_s\left(\mathbf{r},t\right)\right\}\phi_n\left(\mathbf{r},t\right)$$

- The potential v_s is given by the Euler equation:

$$v_s\left(\mathbf{r},t\right) = v\left(\mathbf{r},t\right) + v_H\left[n\right]\left(\mathbf{r},t\right) + v_{xc}\left[n\right]\left(\mathbf{r},t\right)$$

$$v_H\left(\mathbf{r},t\right) = \frac{\delta S_H}{\delta n\left(\mathbf{r},t\right)} = \int \frac{n\left(\mathbf{r}',t\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}d^3r' \qquad v_{xc}\left(\mathbf{r},t\right) = \frac{\delta S_{xc}}{\delta n\left(\mathbf{r},t\right)}$$
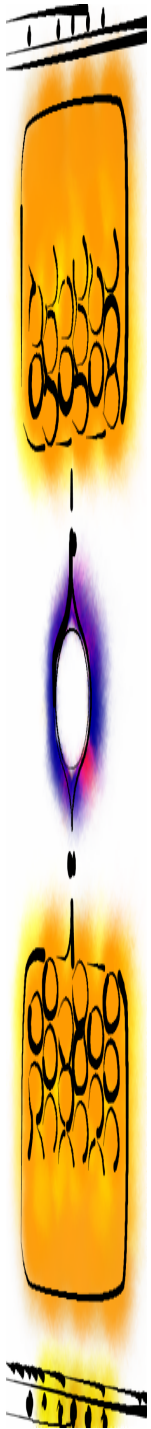
Basic xc-functional: ALDA

$$S_{xc}[n] = \int_0^{t_f} \int \varepsilon_{LDA}\big(n(\mathbf{r},t)\big)\, n(\mathbf{r},t)\, d^3r\, dt$$

$$v_{xc}[n](\mathbf{r},t) = v_{LDA}\big(n(\mathbf{r},t)\big)$$

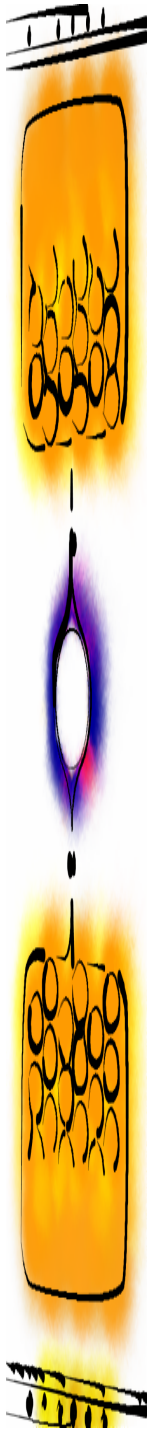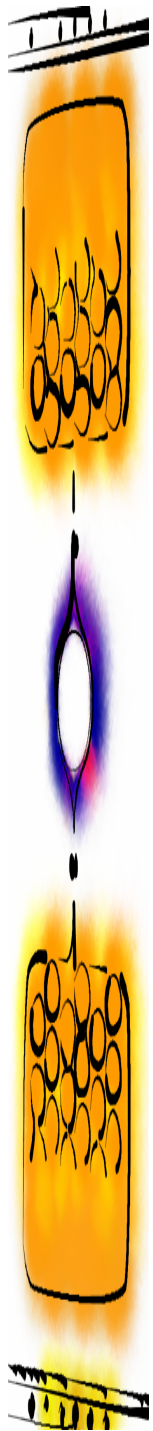$$v_{LDA}(n) = \varepsilon_{LDA}(n) + \varepsilon'_{LDA}(n)\, n$$

Slight change in NIP

- We have a many electron system
- NIP will gobble up the electrons
- So, we use projection operator far from the junction (in principle, should be very deep in leads, in practice, mildly deep):
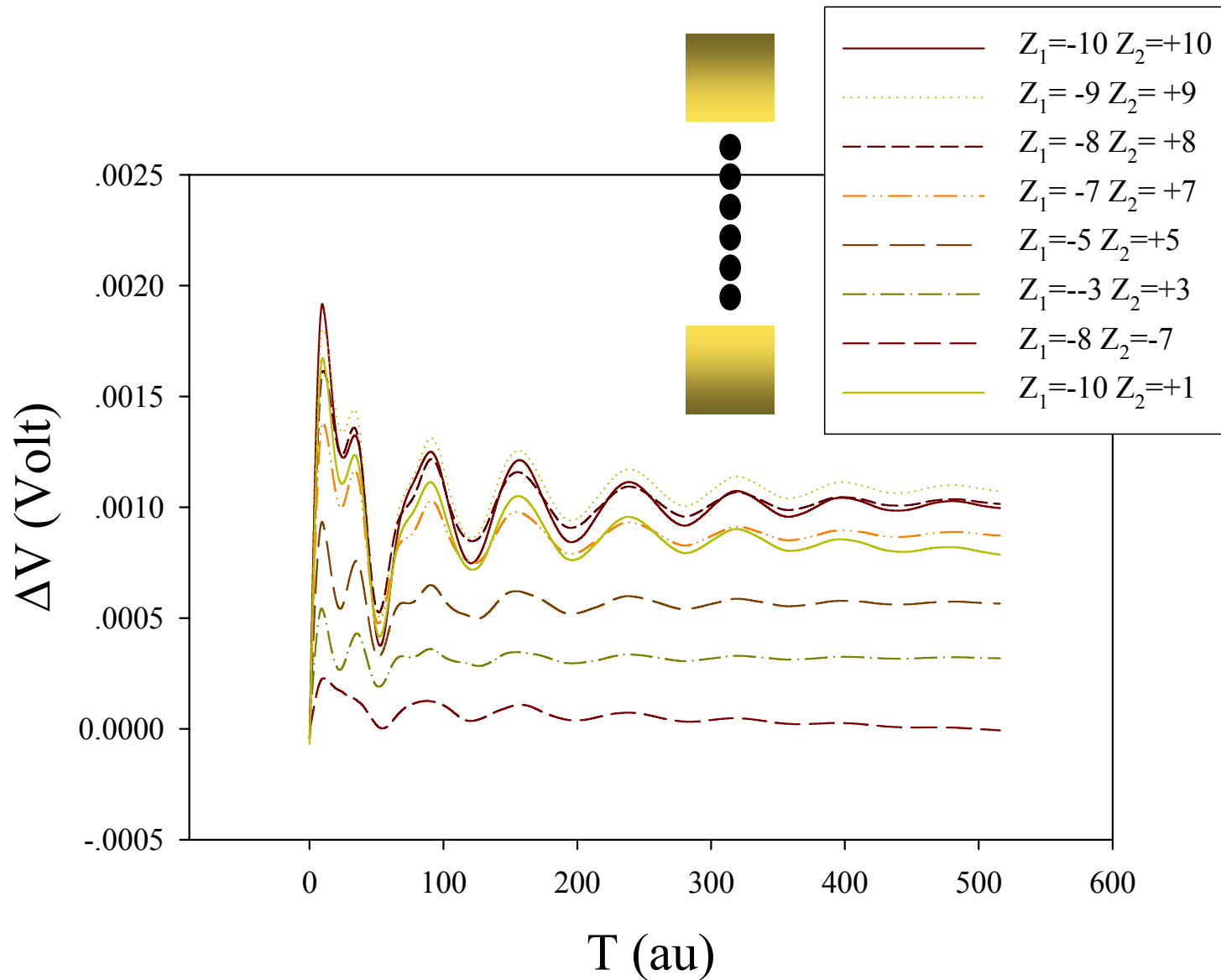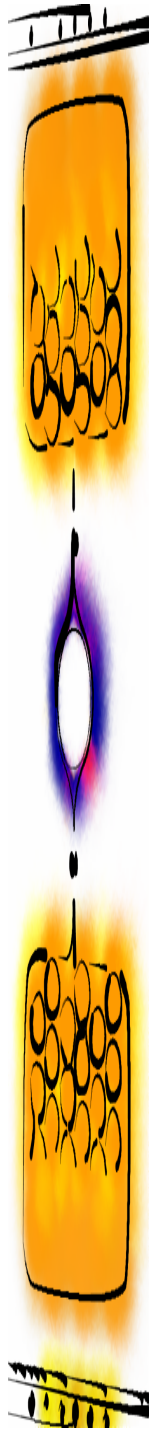
$$\hat{V}_{NIP} = Q^\dagger v_{NIP} Q$$

$$\hat{Q} = 1 - \sum_{n \in occ} \left| \psi_n^{KS} \right\rangle \left\langle \psi_n^{KS} \right|$$

Typical voltage differences

Legend:
- $Z_1 = -10$ $Z_2 = +10$
- $Z_1 = -9$ $Z_2 = +9$
- $Z_1 = -8$ $Z_2 = +8$
- $Z_1 = -7$ $Z_2 = +7$
- $Z_1 = -5$ $Z_2 = +5$
- $Z_1 = --3$ $Z_2 = +3$
- $Z_1 = -8$ $Z_2 = -7$
- $Z_1 = -10$ $Z_2 = +1$

Y-axis: ΔV (Volt)

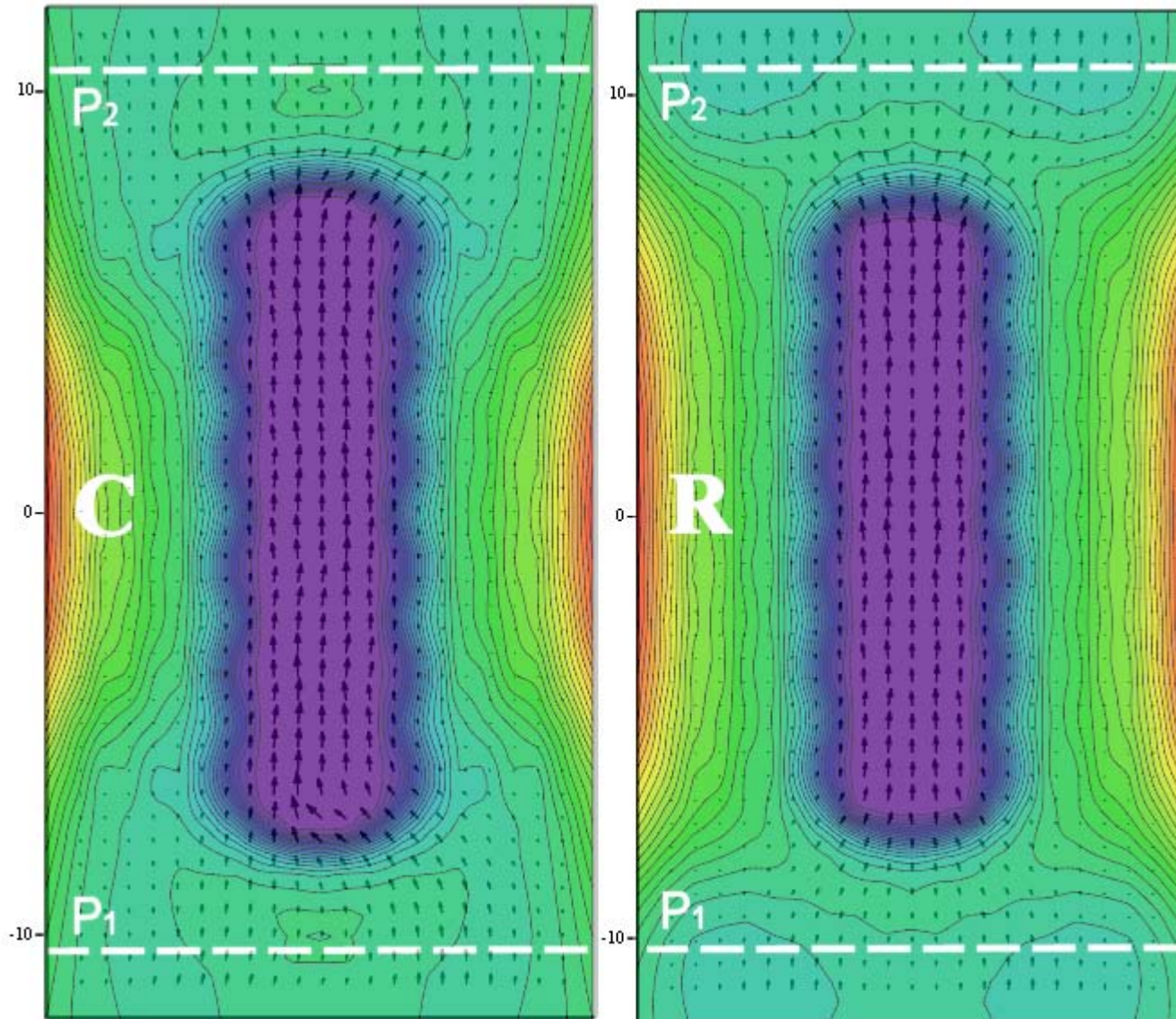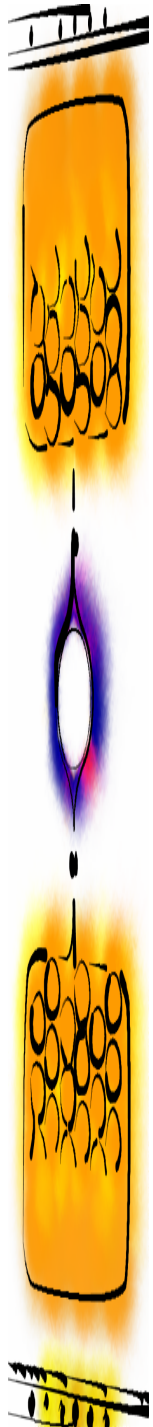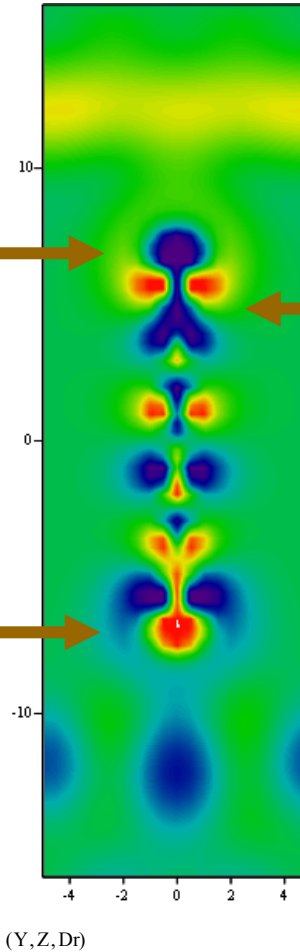X-axis: T (au)

DC conduction with TDLDA

DC Charge Density: screening

Buildup of
Negative charge

Buildup of
Positive charge

$$\delta n\left(r\right) = 4\sum_{i=1}^{N_e} \psi_i\left(r\right)\mathrm{Re}\left(\delta\psi_i\left(r\right)\right)$$

$$\pi \rightarrow \pi^*$$

$$\left(p_1 + p_2\right)\left(p_1 - p_2\right) = p_1^2 - p_2^2$$

(Y, Z, Dr)
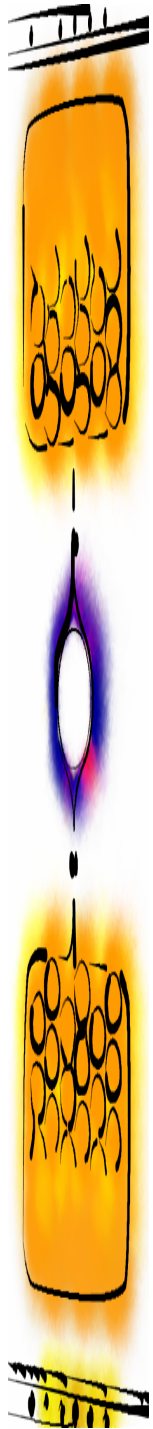
DC conductance using TDLDA

	Landauer	*TDLDA*
$g(C)\big/g_0$	0.38	1.30
$g(R)\big/g_0$	0.02	0.12
$g(C)\big/g(R)$	19.00	10.80

Quantum fluctuations of the Current
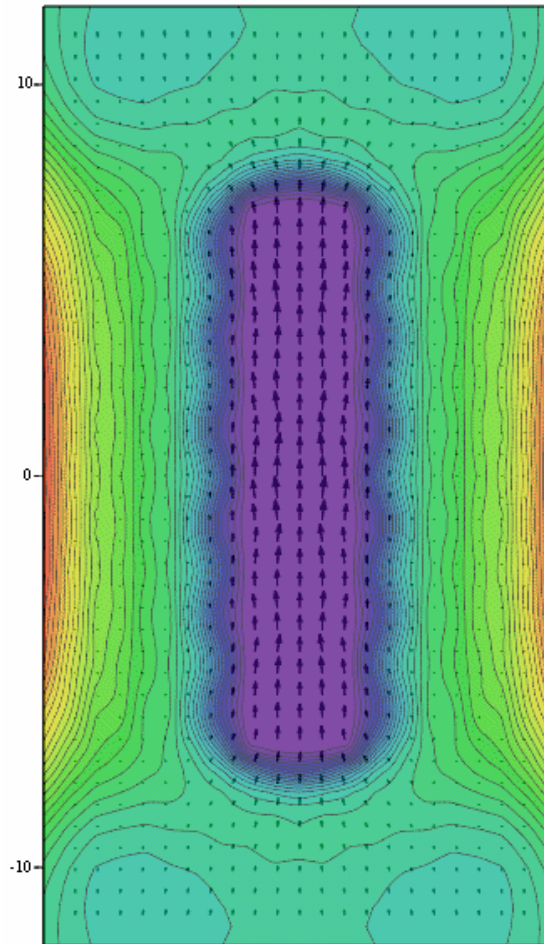
Shown, the current for R system:

$$\Delta J\left(r,t\right) = J\left(r,t\right) - J_{DC}\left(r,t\right)$$

(Each frame is 0.5 fs)
Apparent: uniformity,
like collective excitations
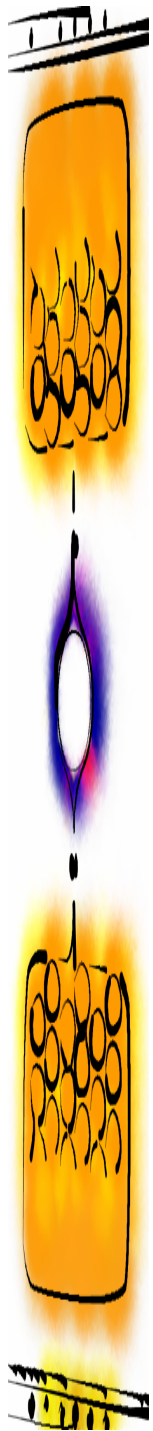
Absorption spectrum of components
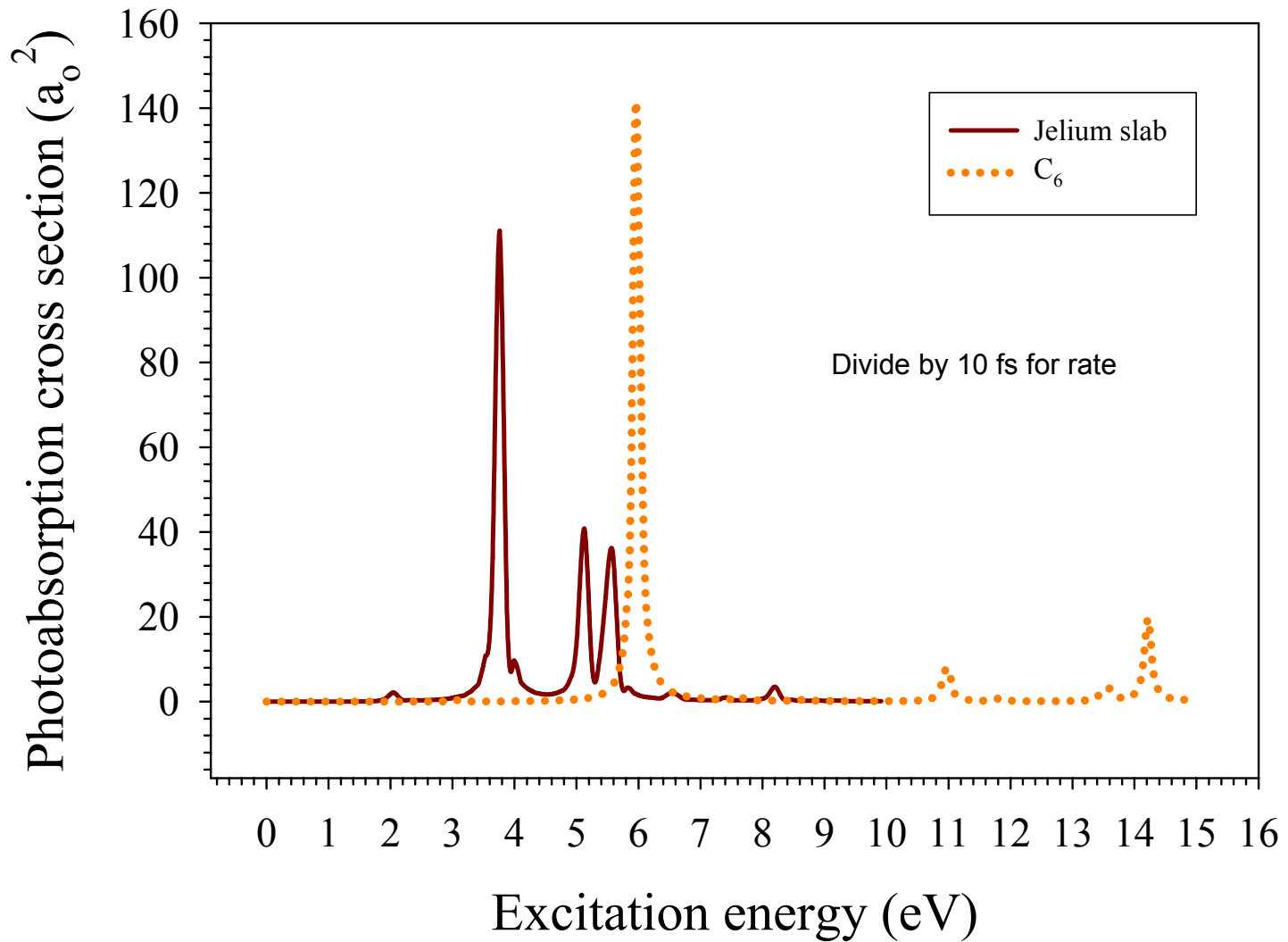

Plot axes: Photoabsorption cross section (a_o^2) vs Excitation energy (eV)

Legend:
- Jelium slab
- C_6

Divide by 10 fs for rate
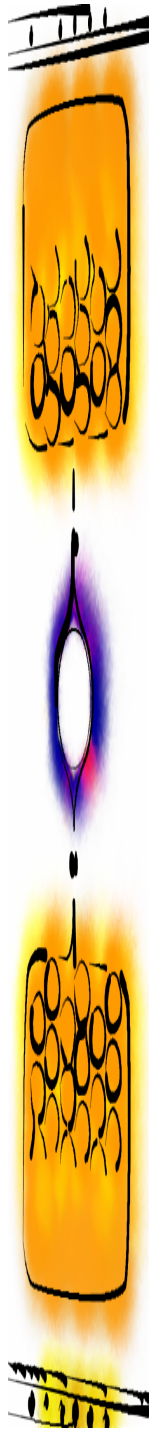
Fourier spectrum of current
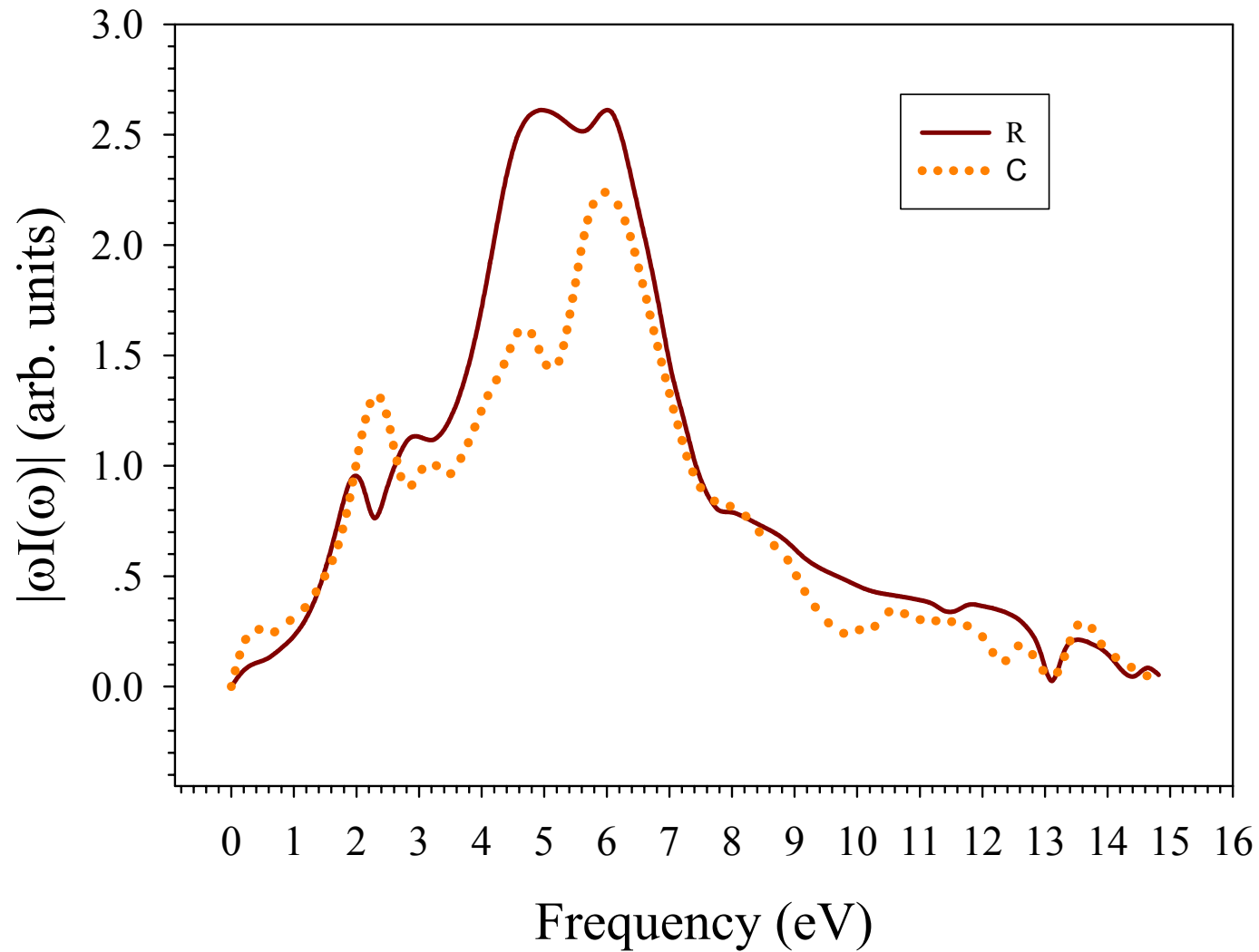
Impedance
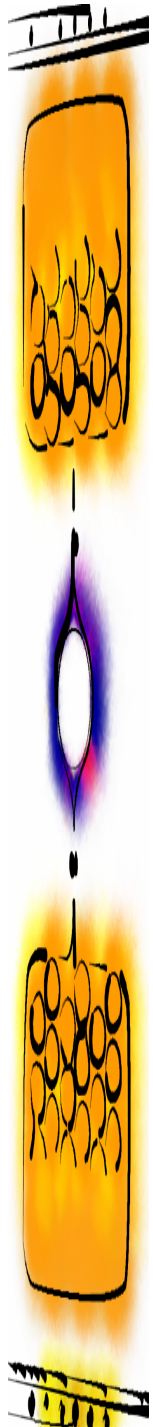
R system

$Z\,(g_0^{-1})$

Resistor-inductor

C system

$Z\,(g_0^{-1})$

$\omega = 6.2$ eV

$\omega = 2.3$ eV

$\omega = 4.4$ eV

$Z_L = -10a_0$ $Z_R = 10a_0$
$Z_L = -9a_0$ $Z_R = 9a_0$
$Z_L = -8a_0$ $Z_R = 8a_0$

$Z_L = -10a_0$ $Z_R = 10a_0$
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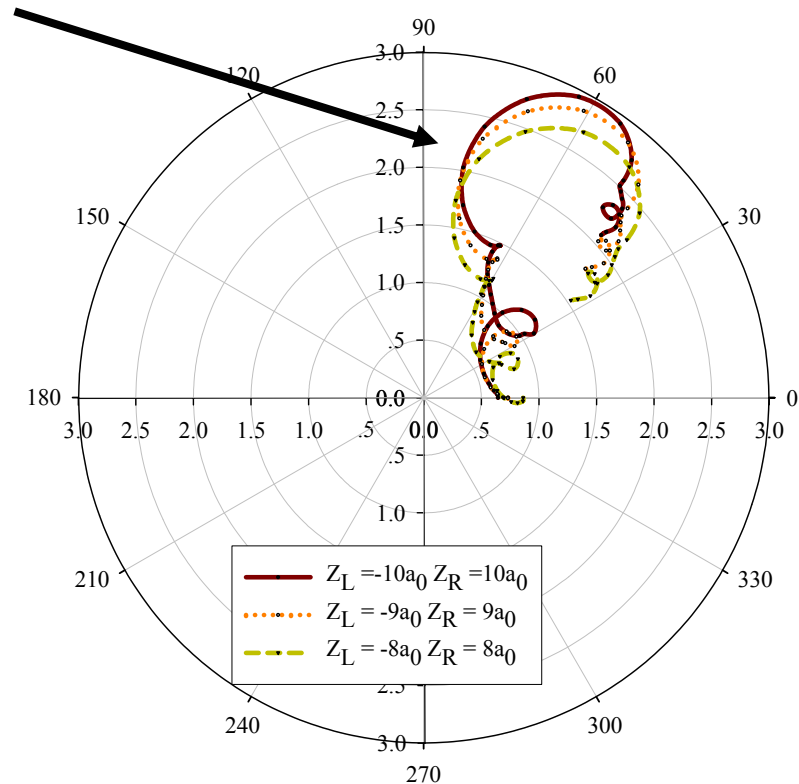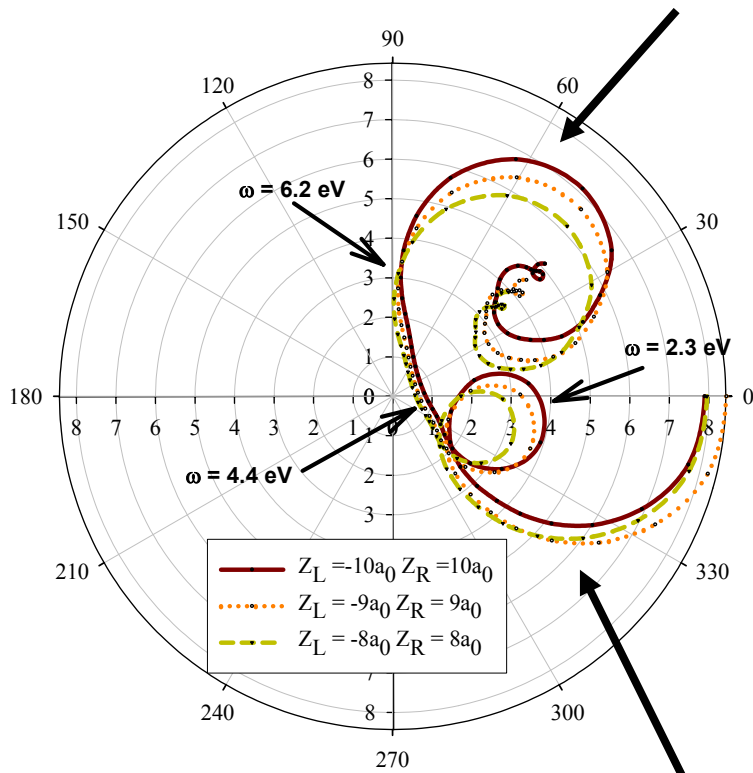
Resistor-capacitor

Summary

- Understanding conductance:
  - Simple theory for conductance
  - Efficient Monte Carlo method
  - Vks Mechanism for difference in conductance (no orbital picture!)
- Reshuffled all!
  - The bias potential
  - Dynamic screening
- A definition of conductance: more like the experiment
  - Application using TD-ALDA
  - Large difference in results from simple theory
- Novel observable: AC impedance
  - Impedance very different in both systems.
  - R system has strong RC at low freq. and strong RL at high frequency
  - C system has no R-C behavior (C infinite) and strong RL at high frequency.
  - Geometric description in the complex plane (circles etc).
- To Do's:
  - Self interaction
  - "Current density functional theory", large bias
  - Nuclear motion (via Ehrenfest molecular dynamics)
  - More new applications
  - More realistic Leads (...)