Time-dependence in quantum transport through nanostructures

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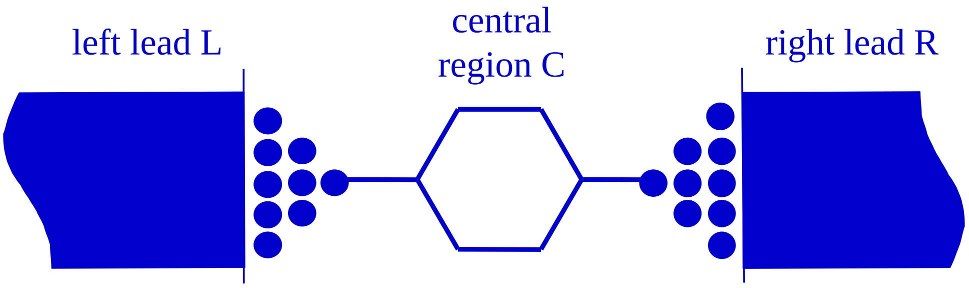
Molecular Electronics

Dream: Use single molecules as basic units (transistors, diodes, …) of electronic devices



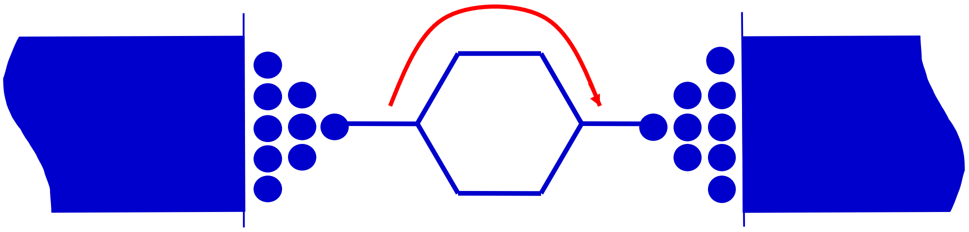
Bias between L and R is turned on: U(t) ⟶ V for large t

A steady current, I, may develop as a result.

- **Calculate current-voltage characteristics I(V)**
- **Control path of current through molecule by laser**

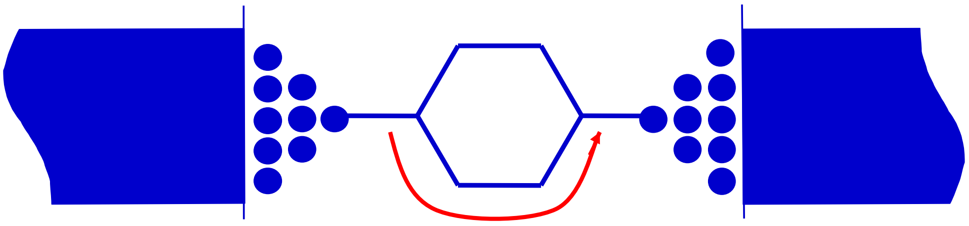
Molecular Electronics

Control the path of the current with laser

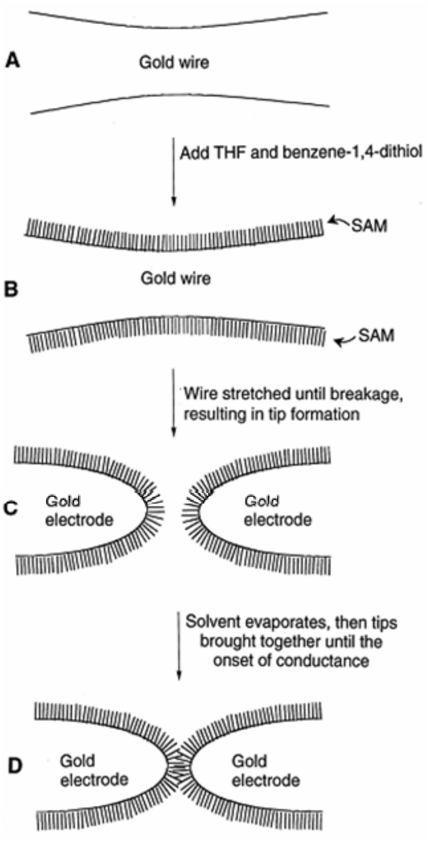


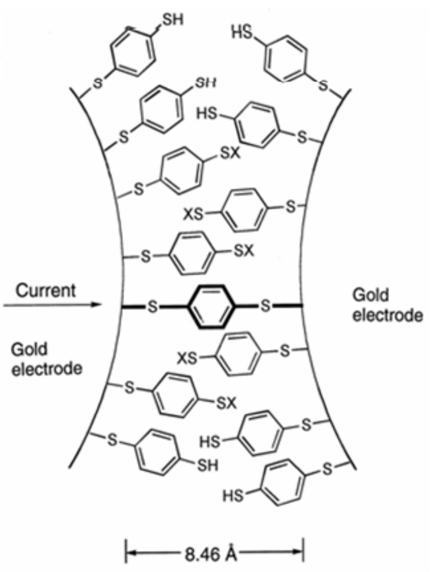
Molecular Electronics

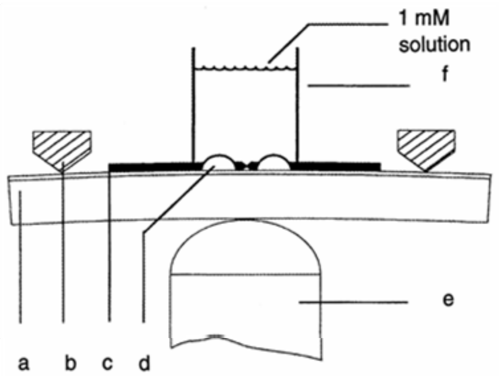
Control the path of the current with laser



Break junction experiment

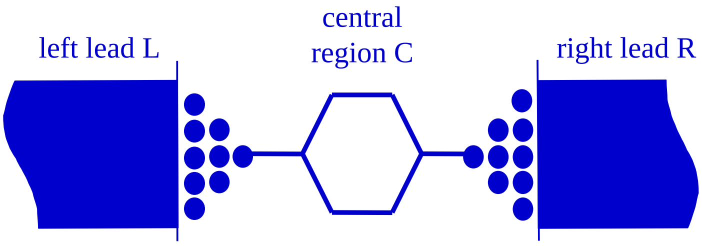






Outline

- Traditional Landauer approach
- Why time-dependent transport?
- Computational issues (open, nonperiodic system)
- Numerical examples for model systems
  - Recovering Landauer steady state
  - Transients and AC bias
  - Electron pumping
- Does a system always evolve into a steady state?



Standard approach: Landauer formalism plus static DFT

$$\boxed{I(V)=\frac{e}{h}\int dE\, T(E,V)\left[f(E-\mu_1)-f(E-\mu_2)\right]}$$

Transmission function T(E,V) calculated from static (ground-state) DFT

$$\boxed{\mu_{1,2}=E_F\mp\frac{eV}{2}}$$

Comparison with experiment: Qualitative agreement, BUT conductance often 1-3 orders of magnitued too high.

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eigenstates of static KS Hamiltonian of the complete system (no periodicity!)

$$\begin{pmatrix} H_{LL}^{stat} & H_{LC}^{stat} & 0 \\ H_{CL}^{stat} & H_{CC}^{stat} & H_{CR}^{stat} \\ 0 & H_{RC}^{stat} & H_{RR}^{stat} \end{pmatrix}\begin{pmatrix}\varphi_L\\ \varphi_C\\ \varphi_R\end{pmatrix}=E\begin{pmatrix}\varphi_L\\ \varphi_C\\ \varphi_R\end{pmatrix}$$

Define Green's functions of the static leads

$$\left(E-H_{LL}^{stat}\right)G_L^{stat}(E)=\mathbb{1}$$

$$\left(E-H_{RR}^{stat}\right)G_R^{stat}(E)=\mathbb{1}$$

Substitute φ_L and φ_R in equation for central region

$$\boxed{(H_{CL}G_LH_{LC} + H_{CC} + H_{CR}G_RH_{RC})\,\varphi_C = E\,\varphi_C}$$

Effective KS equation for the central region

$$\Sigma_L := H_{CL}\,G_L\,H_{LC} \qquad \Sigma_R := H_{CR}\,G_R\,H_{RC}$$

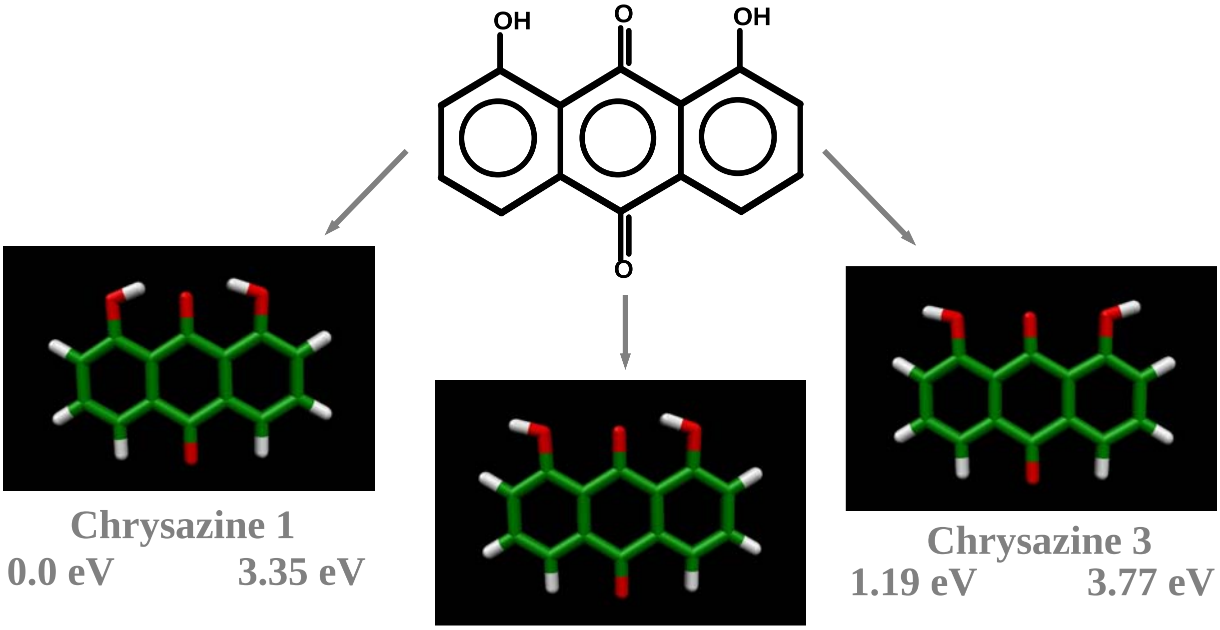
$$g = (E - H_{CC} - \Sigma_L - \Sigma_R)^{-1}$$

$$\Gamma_L = i\left(\Sigma_L - \Sigma_L^{+}\right) \qquad \Gamma_R = i\left(\Sigma_R - \Sigma_R^{+}\right)$$

$$T = \mathrm{trace}\left(\Gamma_L\, g\, \Gamma_R\, g^{+}\right)$$

Chrysazine

Relative Total Energies and **HOMO-LUMO Gaps**



Chrysazine 1
0.0 eV 3.35 eV

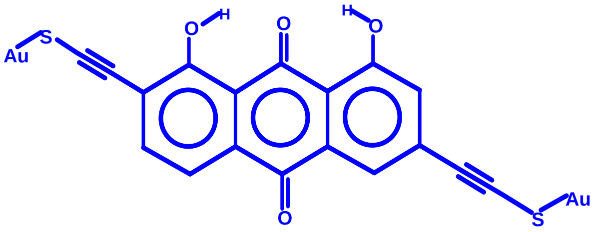
Chrysazine 2
0.54 eV 3.41 eV

Chrysazine 3
1.19 eV 3.77 eV

Relative Total Energies and HOMO-LUMO Gaps

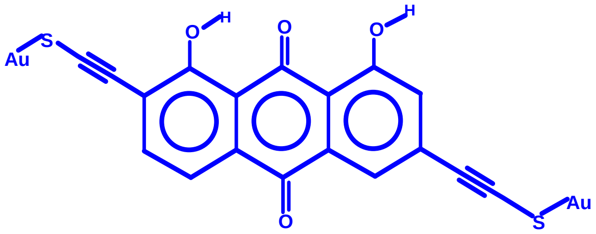
Chrysazine 1

0.0 eV 1.93 eV



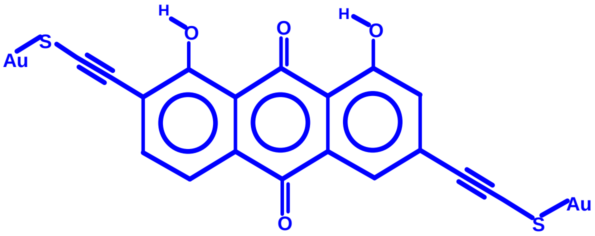
Chrysazine 2a

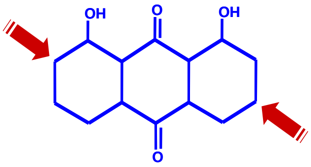
0.70 eV 1.67 eV

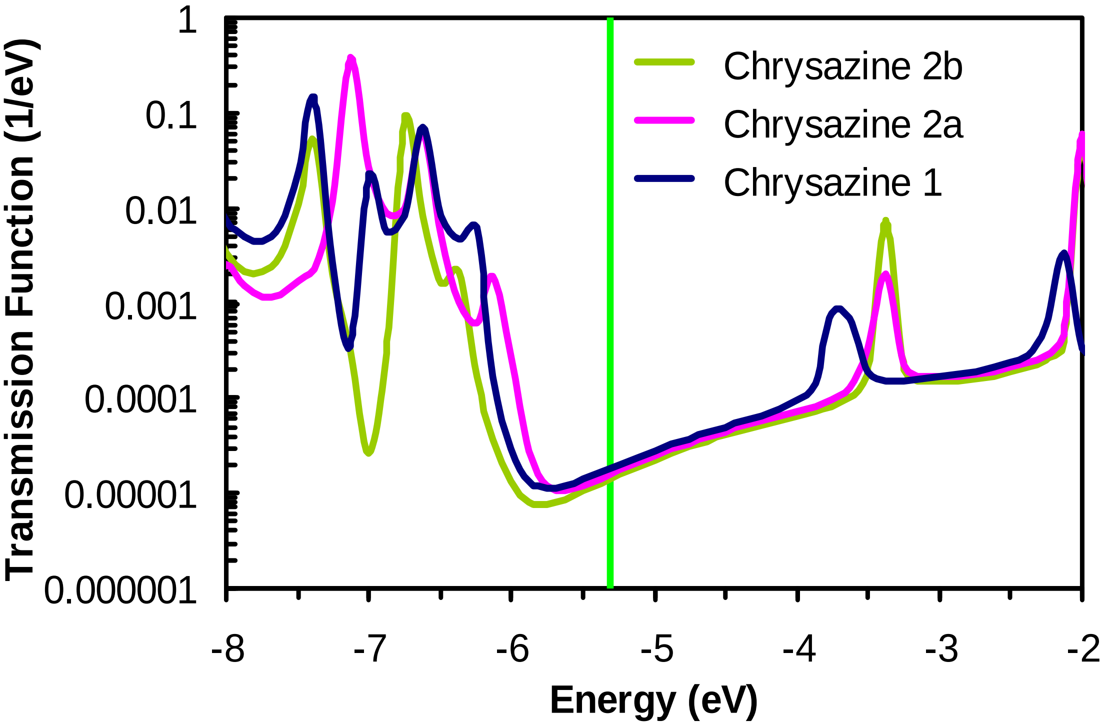


Chrysazine 2 b

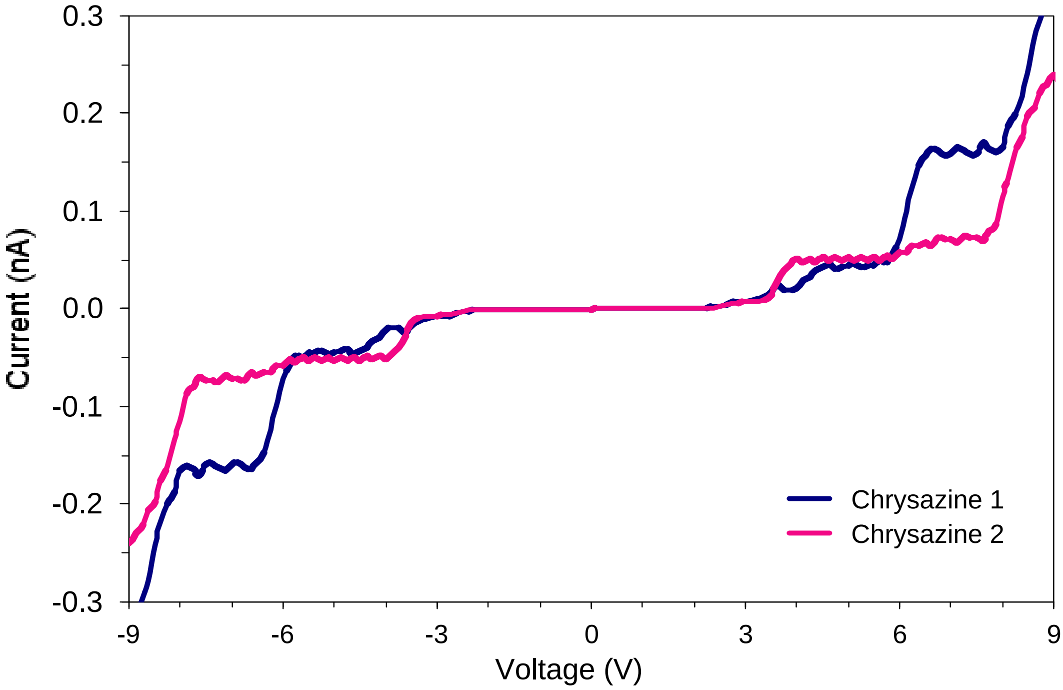
0.57 eV 1.79 eV







$$I(V) = \frac{e}{h}\int dE\, T(E,V)\left[f(E-\mu_1) - f(E-\mu_2)\right]$$



Chryzazine: A possible optical switch

Summary of standard approach

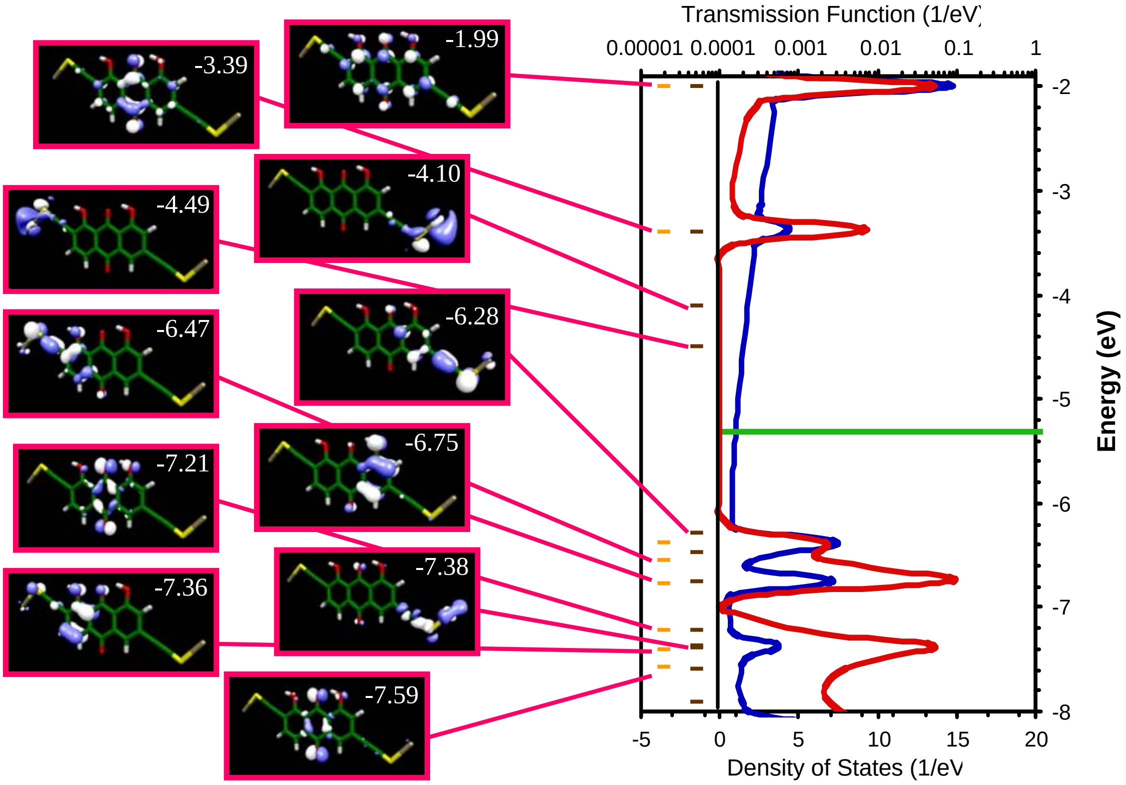
- Use ground-state DFT within Landauer formalism
- Fix left and right chemical potentials
- Solve self-consistently for KS Green’s function
- Transmission function has resonances at KS levels
- No empirical parameters, suggests confidence level of ground-state DFT calculations

Why time-dependent transport?

- allows the study of transients: How does the steady state evolve, does it appear at all?
- AC effects
- laser-induced isomerization
- optimal control of current

- TDDFT allows proper inclusion of e-e interaction effects:
  Note: When static DFT is used for effective potential together with Landauer formula → resonant tunneling occurs at the wrong energies.

Chrysazine 2 b



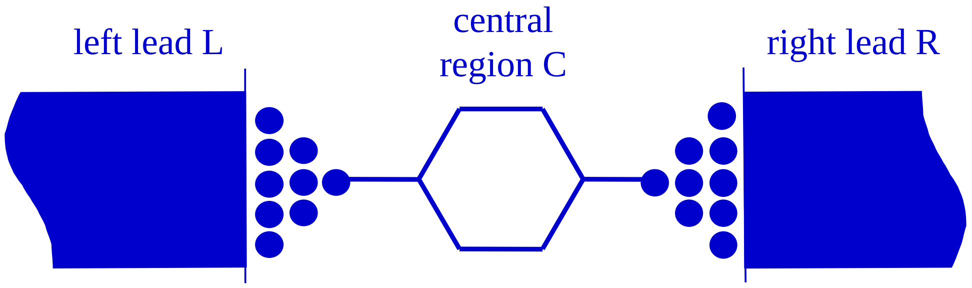
- Landauer theory is for non-interacting electrons. If static DFT is used for effective potential → resonant tunneling occurs at the wrong energies → Landauer current does not give true current even for the exact exchange-correlation potential of static DFT. → **[Landauer + static DFT]-approach in principle wrong.**

How serious is this problem?

Atom	Experimental Excitation Energies $^1S \to {}^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	TDDFT response (Ry)
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

Molecular Electronics with TDDFT



TDKS equation

$$i\frac{\partial}{\partial t}\begin{pmatrix}\varphi_L(t)\\ \varphi_C(t)\\ \varphi_R(t)\end{pmatrix}=\begin{pmatrix}H_{LL}(t) & H_{LC}(t) & H_{LR}(t)\\ H_{CL}(t) & H_{CC}(t) & H_{CR}(t)\\ H_{RL}(t) & H_{RC}(t) & H_{RR}(t)\end{pmatrix}\begin{pmatrix}\varphi_L(t)\\ \varphi_C(t)\\ \varphi_R(t)\end{pmatrix}$$

Propagate TDKS equation on spatial grid

- $\varphi_A(t) = \text{vector}\left(\varphi(r_1,t),\varphi(r_2,t),\ldots\right)$ with grid points r_1, r_2, … in region A (A = L, C, R)
- $H_{AB}(t) = \text{corresponding grid-blocks of TDKS Hamiltonian}$

$H_{AB}(t)$ for $\underline{A \neq B}$ is purely kinetic, because KS potential is local

$H_{CL}, H_{LC}, H_{CR}, H_{RC}$ are time-independent

$H_{LR} = H_{RL} = 0$

$$i\frac{\partial}{\partial t}\begin{pmatrix}\varphi_L(t)\\ \varphi_C(t)\\ \varphi_R(t)\end{pmatrix} = \begin{pmatrix} H_{LL}(t) & H_{LC}\cancel{(t)} & \cancel{H_{LR}}(t) \\ H_{CL}\cancel{(t)} & H_{CC}(t) & H_{CR}\cancel{(t)} \\ \cancel{H_{RL}}(t) & H_{RC}\cancel{(t)} & H_{RR}(t)\end{pmatrix}\begin{pmatrix}\varphi_L(t)\\ \varphi_C(t)\\ \varphi_R(t)\end{pmatrix}$$

Hence:

$$\left(i\frac{\partial}{\partial t} - H_{LL}(t)\right)\varphi_L(t) = H_{LC}\,\varphi_C(t) \qquad Ⓛ$$

$$i\frac{\partial}{\partial t}\varphi_C(t) = H_{CL}\,\varphi_L(t) + H_{CC}(t)\varphi_C(t) + H_{CR}\,\varphi_R(t) \qquad Ⓒ$$

$$\left(i\frac{\partial}{\partial t} - H_{RR}(t)\right)\varphi_R(t) = H_{RC}\,\varphi_C(t) \qquad Ⓡ$$

Next step: Solve inhomogeneous Schrödinger equations Ⓛ, Ⓡ for φ_L, φ_R using Green's functions of L, R, leads

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Define Green's Functions of left and right leads:

$$\left(i\frac{\partial}{\partial t} - H_{LL}(t)\right)G_L(t,t') = \delta(t-t') \qquad \left(i\frac{\partial}{\partial t} - H_{RR}(t)\right)G_R(t,t') = \delta(t-t')$$

$$\Rightarrow \quad \varphi_L = \hat{G}_L\left[\text{r.h.s. of Ⓛ}\right] + \left[\text{solution of hom. SE } \left(i\frac{\partial}{\partial t} - H_{LL}(t)\right)\psi = 0\right]$$

$$\varphi_R = \hat{G}_R\left[\text{r.h.s. of Ⓡ}\right] + \left[\text{solution of hom. SE } \left(i\frac{\partial}{\partial t} - H_{RR}(t)\right)\psi = 0\right]$$

<u>explicity</u>:

$$\varphi_L(t) = \int_0^t dt'\,G_L(t,t')H_{LC}\varphi_C(t') + iG_L(t,0)\varphi_L(0)$$

$$\varphi_R(t) = \int_0^t dt'\,G_R(t,t')H_{RC}\varphi_C(t') + iG_R(t,0)\varphi_R(0)$$

insert this in equation Ⓒ

Effective TDKS Equation for the central (molecular) region

S. Kurth, G. Stefanucci, C.O. Almbladh, A. Rubio, E.K.U.G.,
Phys. Rev. B 72, 035308 (2005)

$$\boxed{\begin{aligned} i\frac{\partial}{\partial t}\varphi_C(t) &= H_{CC}(t)\varphi_C(t) \\ &\quad + \int_0^t dt'\left[H_{CL}G_L(t,t')H_{LC} + H_{CR}G_R(t,t')H_{RC}\right]\varphi_C(t') \\ &\quad + iH_{CL}G_L(t,0)\varphi_L(0) + iH_{CR}G_R(t,0)\varphi_R(0) \end{aligned}}$$

source term: L → C and R → C charge injection

memory term: C → L → C and C → R → C hopping

<u>Necessary input to start time propagation</u>:

- lead Green’s functions G_L, G_R
- initial orbitals $\varphi_C(0)$ in central region as initial condition for time propagation
- initial orbitals $\varphi_L(0)$, $\varphi_R(0)$ in leads (for source terms)

Calculation of lead Green's functions:

$$\left(i\frac{\partial}{\partial t}-H_{LL}(t)\right)G_L(t,t')=\delta(t-t')$$

$$H_{LL}(t)=\Big[T+V_{nucl}(r)+V_{Hxc}[\rho]\ (r,t)+V_{ext}(r,t)\Big]_{\text{left lead}}$$

Simplest situation: Bias acts as spatially uniform potential in leads (instantaneous metallic screening)

$$H_{LL}(t)=\Big[T+V_{nucl}(r)+V^{stat}_{Hxc}[\rho_{g.s.}]\ (r)+U(t)\Big]_{\text{left lead}}=H^{stat}_{LL}+U_L(t)$$

likewise $H_{RR}(t)=H^{stat}_{RR}+U_R(t)$, $U_L(t)-U_R(t)=$ total potential drop across central region

initial lead states are calculated as linear combinations of periodic bulk states

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initial orbitals in C region

eigenstates of static KS Hamiltonian of the complete system (no periodicity!)

$$\begin{pmatrix} H^{stat}_{LL} & H^{stat}_{LC} & 0 \\ H^{stat}_{CL} & H^{stat}_{CC} & H^{stat}_{CR} \\ 0 & H^{stat}_{RC} & H^{stat}_{RR} \end{pmatrix}\begin{pmatrix}\varphi^{(0)}_L \\ \varphi^{(0)}_C \\ \varphi^{(0)}_R\end{pmatrix}=E\begin{pmatrix}\varphi^{(0)}_L \\ \varphi^{(0)}_C \\ \varphi^{(0)}_R\end{pmatrix}$$

Define Green’s functions of the static leads

$$\left(E - H_{LL}^{stat}\right) G_{L}^{stat}(E) = \mathbb{1}$$

$$\left(E - H_{RR}^{stat}\right) G_{R}^{stat}(E) = \mathbb{1}$$

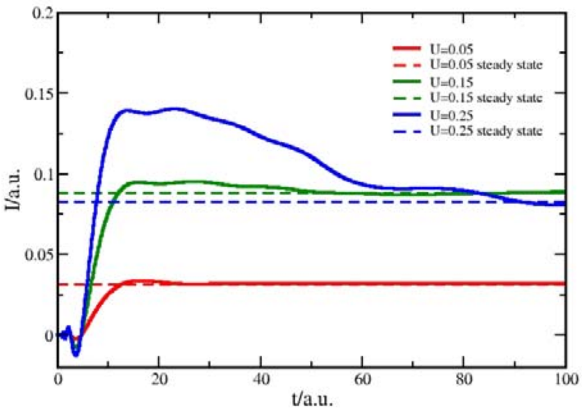
Effective static KS equation for central region

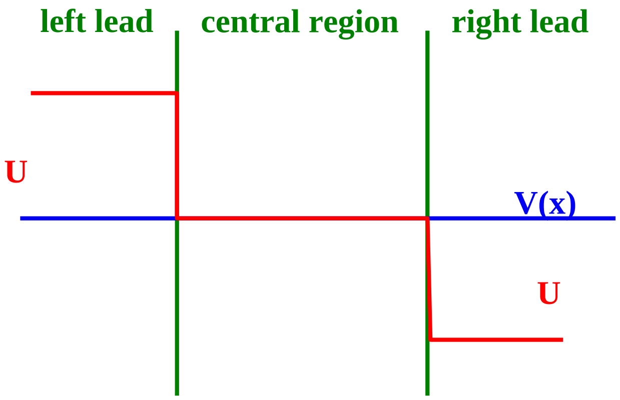
$$\left(H_{CC}^{stat} + H_{CL}^{stat} G_{L}^{stat}(E) H_{LC}^{stat} + H_{CR}^{stat} G_{R}^{stat}(E) H_{RC}^{stat}\right) \varphi_{C}^{(0)} = E \varphi_{C}^{(0)}$$

In the traditional Landauer + static DFT approach, this equation is used to calculate the transmission function. Here we use it only to calculate the initial states in the C-region.

Numerical examples for non-interacting electrons

Recovering the Landauer steady state





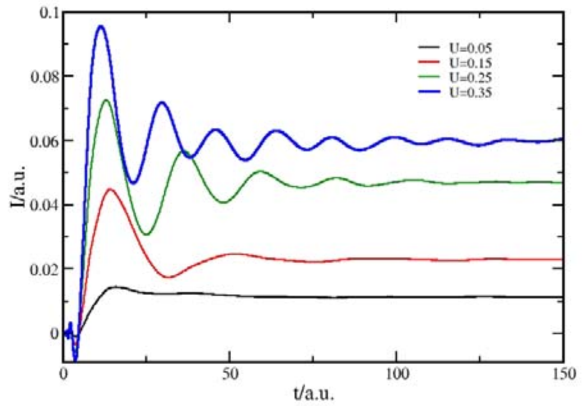
Time evolution of current in response to bias switched on at time t = 0,

Fermi energy $\varepsilon_F = 0.3$ a.u.

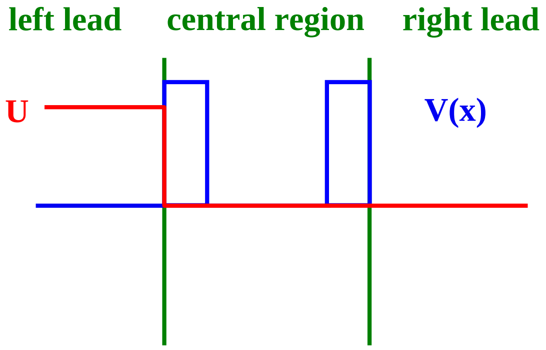
Steady state coincides with Landauer formula

and is reached after a few femtoseconds

Charge accumulation in device



Time evolution of current

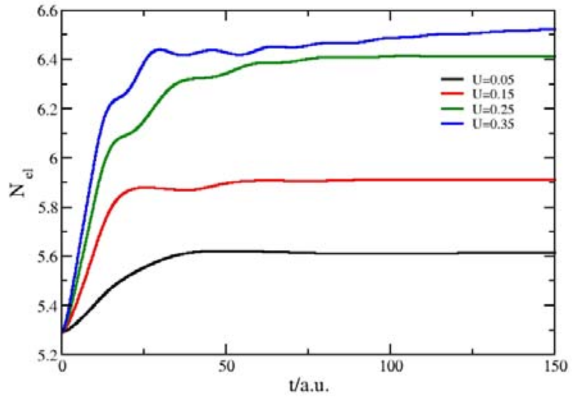


left lead **central region** **right lead**

U

V(x)

barrier height: 0.5 a.u.
$\in_F = 0.3$ a.u.



Time evolution of total number of electrons in central region

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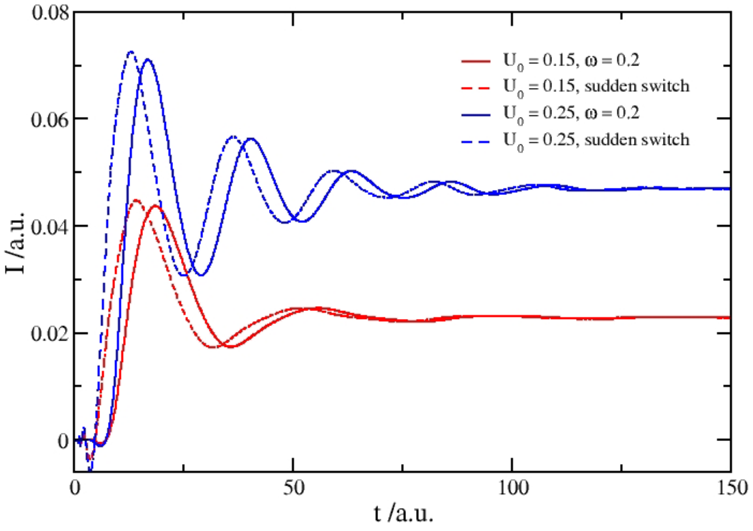
Transients

Current through double square barrier for different ways to switch on the bias

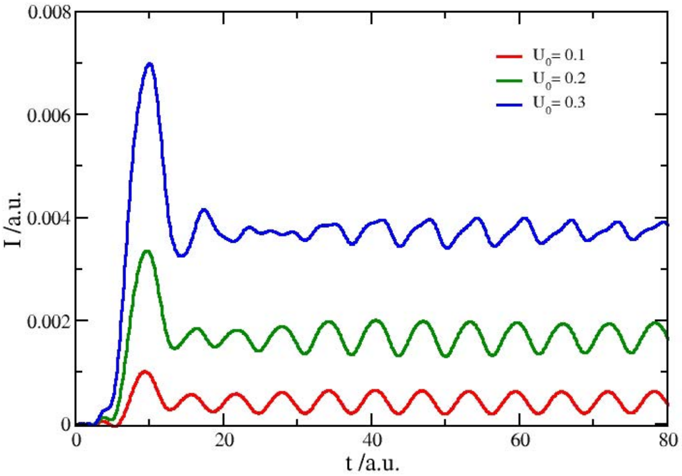
solid lines: $$U_L(t) = \begin{cases} U_0 \sin^2(\omega t) & \text{for } 0 \le t \le \pi/(2\omega) \\ U_0 & \text{for } t > \pi/(2\omega) \end{cases}$$



same steady state!

Time-dependent bias

Current through square potential barrier for AC bias



$$U_L(t) = U_0 \sin(\omega t)$$

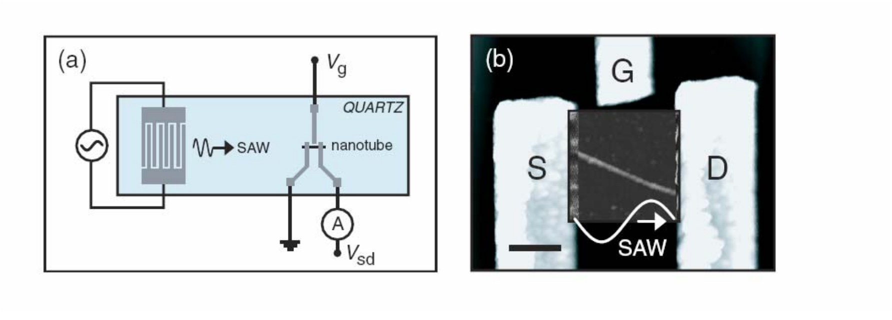
with ω= 1.0 a.u.

barrier height: 0.6 a.u.
Fermi energy: 0.5 a.u.

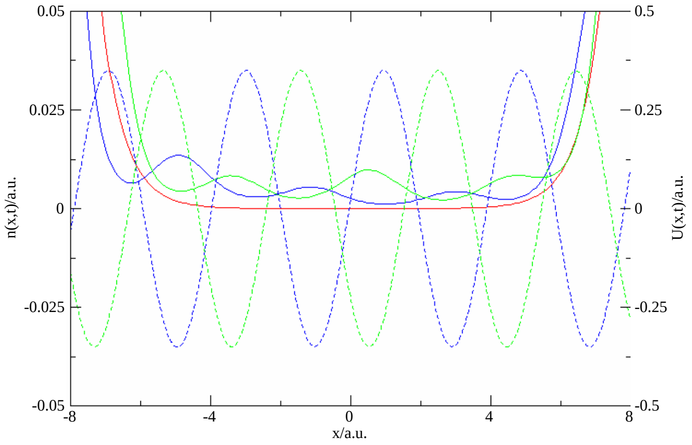
ELECTRON PUMP

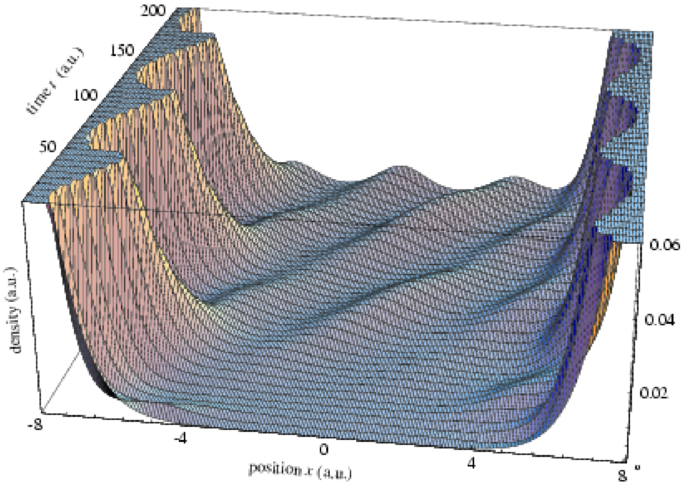
Device which generates a net current between two electrodes (with no static bias) by applying a time-dependent potential in the device region

Recent experimental realization : Pumping through carbon nanotube by surface acoustic waves on piezoelectric surface (Leek et al, PRL 95, 256802 (2005))

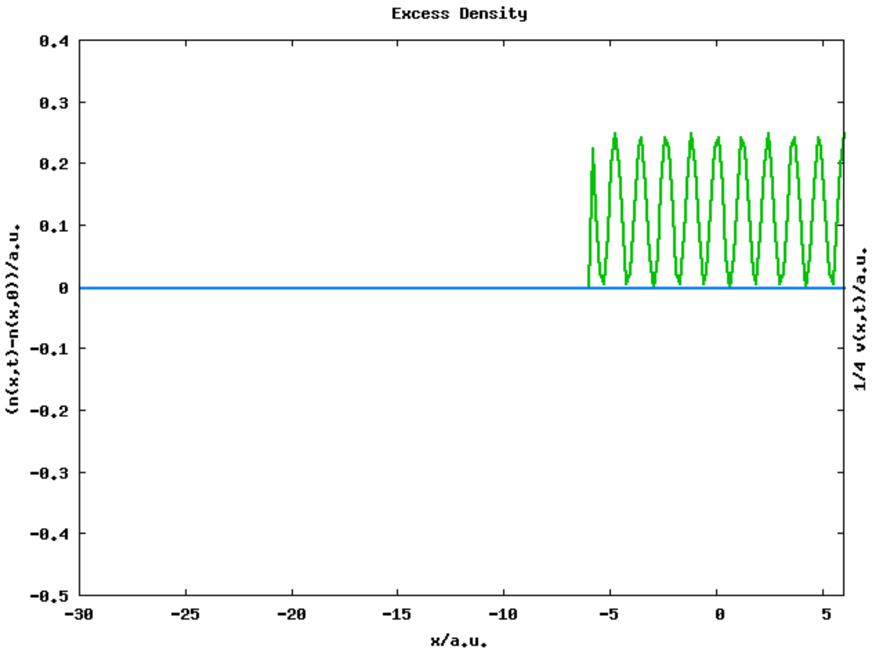


Pumping through a square barrier (of height 0.5 a.u.) using a travelling wave in device region
$U(x,t) = U_o \sin(kx-wt)$
($k = 1.6$ a.u., $w = 0.2$ a.u.
Fermi energy = 0.3 a.u.)



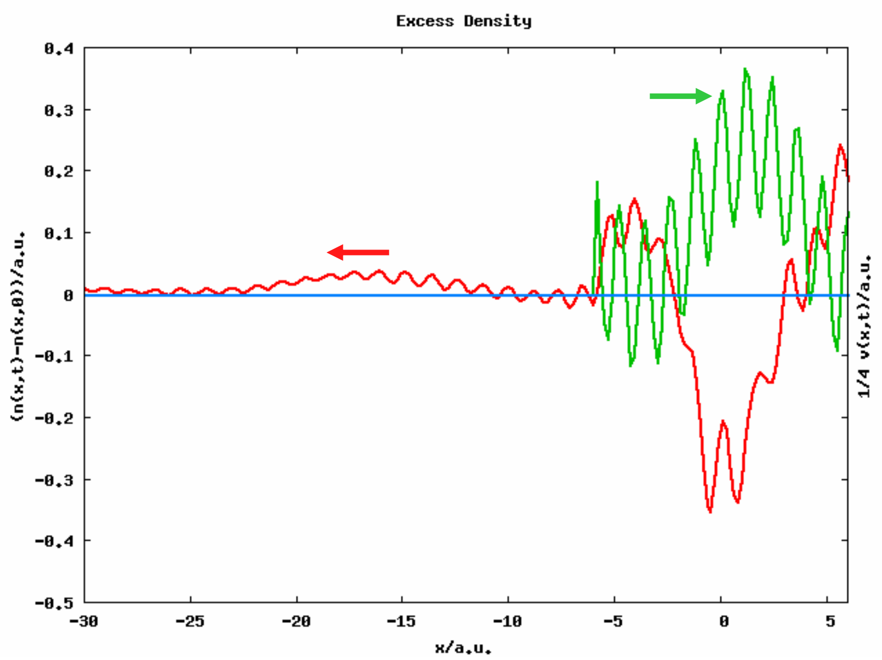


Patent: Archimedes (250 b.c.)



Simple 1-D model showing current inversion:
Superimpose travelling wave on static potential with corrugation which appears to be crucial to obtain current inversion

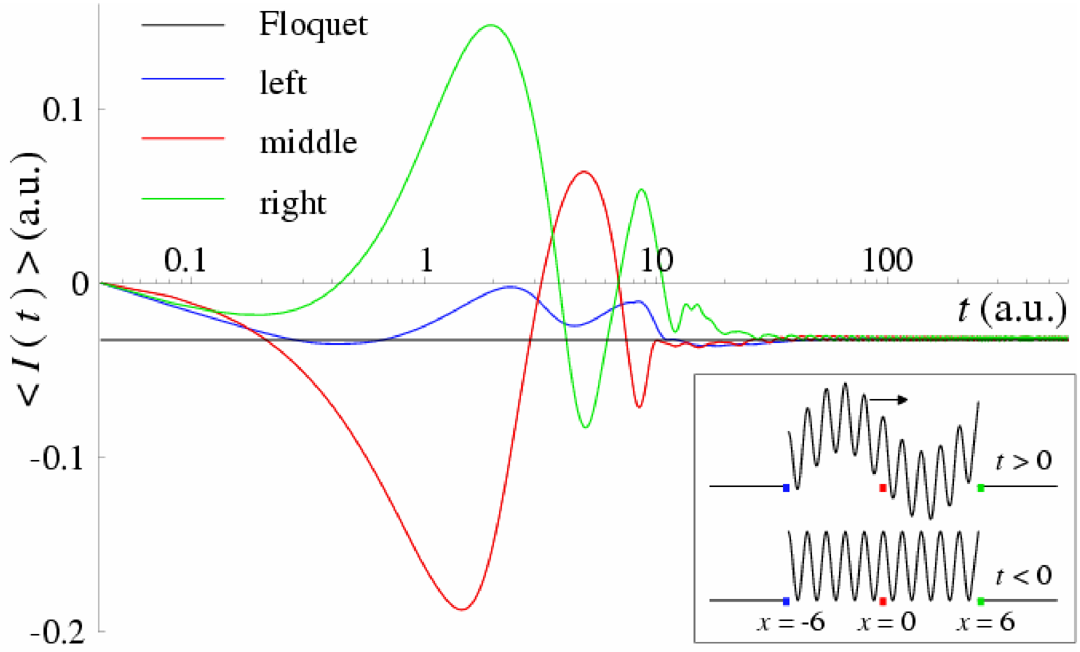
Static potential for $|x|<6$: $V(x) = V_0\,(1 + \cos(kx))$, $V_0=0.5$ a.u., $k=5.2$ a.u.
Travelling wave only for $|x|<6$:
$U(x,t) = U_o \sin(qx-\omega t)$ ($U_o= 0.5$a.u.,$q = 0.6$ a.u., $\omega = 0.8$ a.u., Fermi energy: 0.3 a .u.)



Current goes in direction opposite to the external field !!

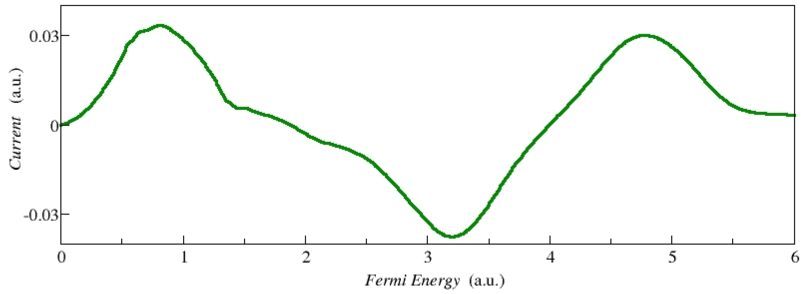
Position dependence of current

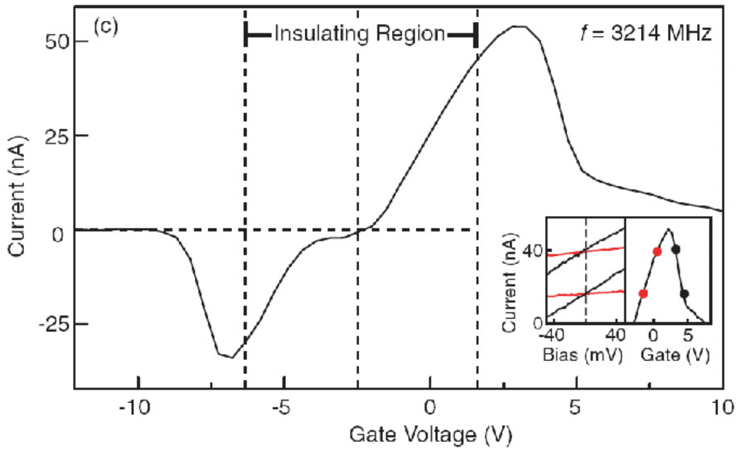
TD current averaged over one period of traveling wave



Time-averaged current

G. Stefanucci, S. Kurth, A. Rubio, E.K.U.G., cond-mat/0701279.





Experimental result:

Bound state oscillations and memory effects

Analytical: G. Stefanucci, Phys. Rev. B, 195115 (2007))

Numerical: G. Stefanucci, S. Kurth, A. Rubio, E.K.U.G., cond-mat/0701279

If Hamiltonian of a (non-interacting) biased system in the long-time limit supports two or more bound states → total current in long-time limit has two parts

$$\lim_{t\to\infty} I_\alpha(t) = I_\alpha^{(S)} + I_\alpha^{(D)}(t)$$

Steady-state part $I_\alpha^{(S)}$ and dynamical part

$$I_\alpha^{(D)}(t) = 2\sum_{b,b'} f_{bb'}\Lambda^{\alpha}_{bb'} \sin[(\varepsilon_b - \varepsilon_{b'})t]$$

sum runs over the bound states of the biased Hamiltonian in the long-time limit.

Note: - $\Lambda_{bb'}$ depends on history of time-dependent Hamiltonian (memory!)

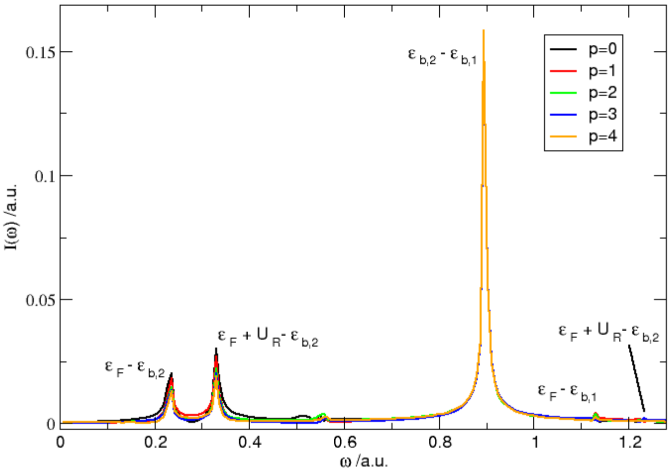
- Landauer/DFT approach to transport rests on the assumption of a time-independent KS potential in the long-time limit

1-D model:

Simple square well: $V(x) = -1.4$ a.u. for $|x|<1.2$ a.u., 0 otherwise → two bound states
At t=0 switch on static bias $U_R=0.1$ a.u. in right lead, also the biased Hamiltonian has two bound states → current oscillations

Time-Frequency Analysis of Time-Dependent Current

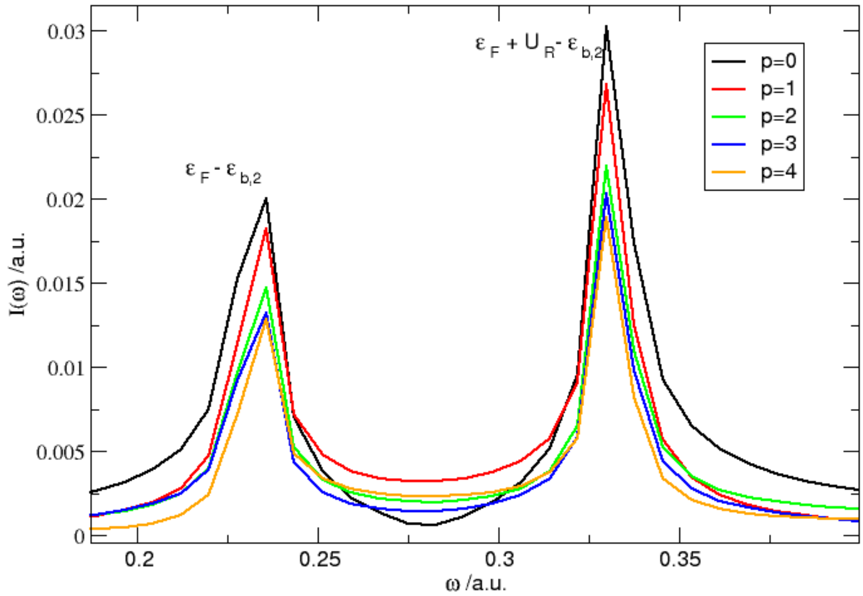
Fourier transform of TD current for finite time interval with $T_0=800$ a.u.
and (t_p,t_p+T_0), $t_p=(2+p)\times 100$ a.u.



Amplitude of oscillation with frequency of transition between bound states is independent of t_p !

Time-Frequency Analysis of Time-Dependent Current

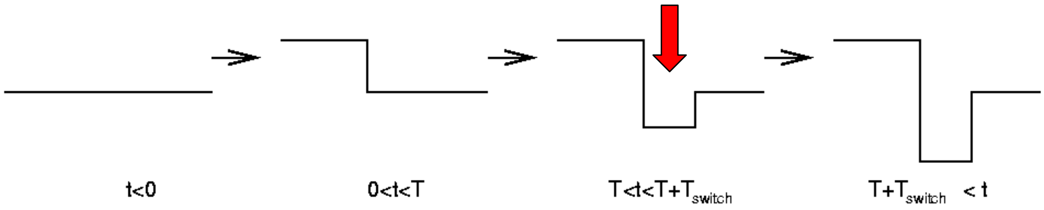
Zoom in on transitions between bound states and continuum



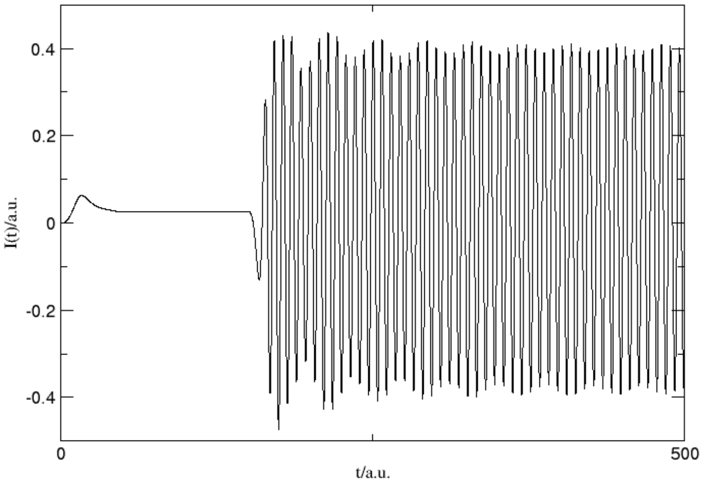
Amplitude of bound-continuum transitions decay slowly (~1/t) with time

History dependence of undamped oscillations

1-D model:
start with flat potential, switch on constant bias, wait until transients die out, switch on gate potential with different switching times to create two bound states



note: amplitude of bound-state oscillations may not be small compared to steady-state current



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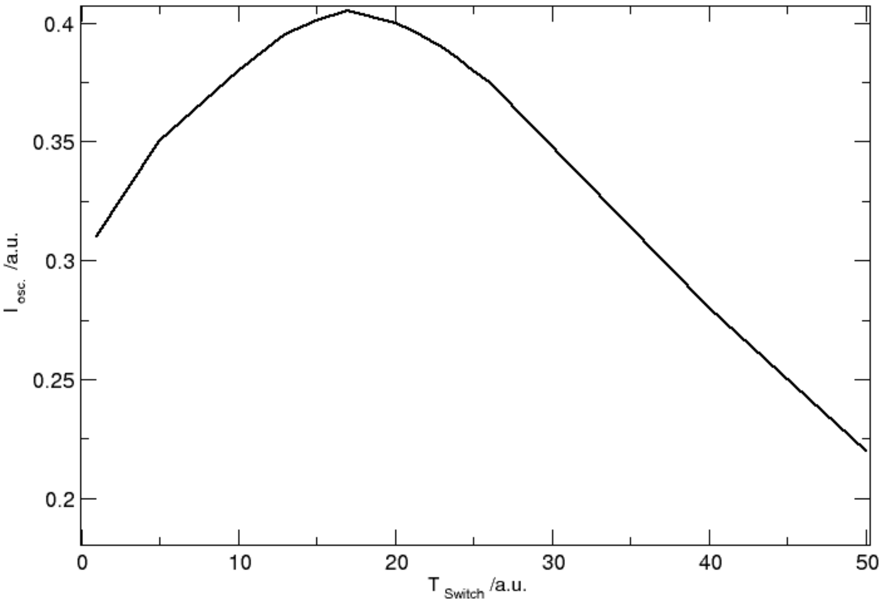
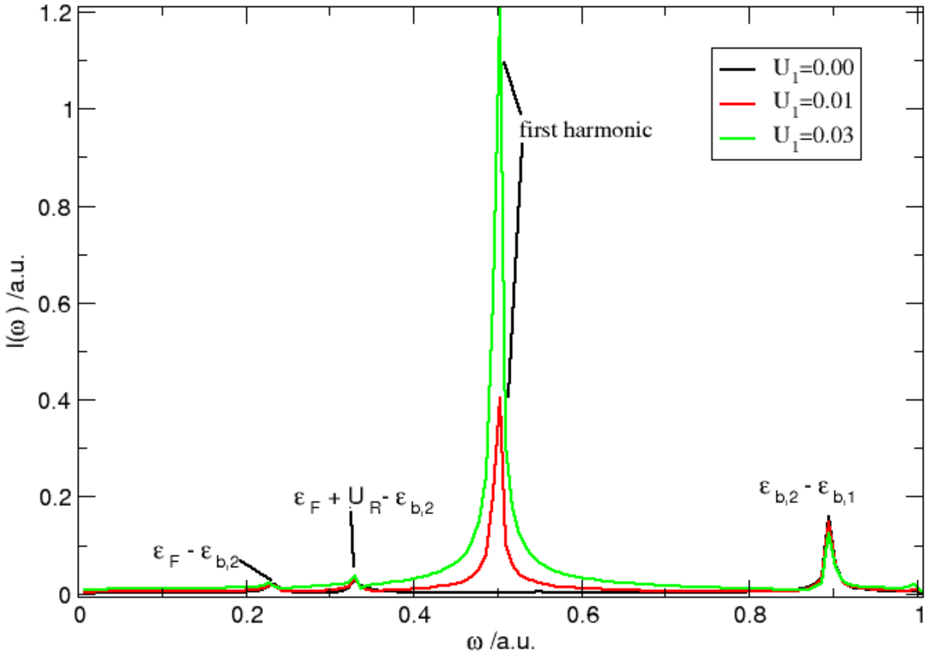
amplitude of current oscillations as function of switching time of gate



question: what is the physical reason behind the maximum of oscillation amplitude ?

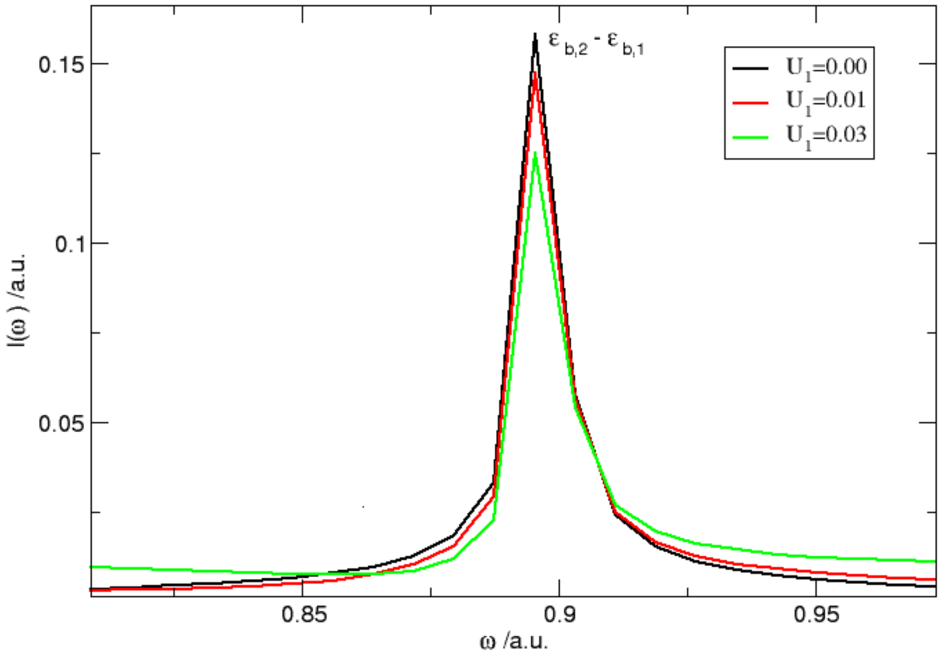
Pumping by travelling wave: Fourier Analysis of Time-Dependent Current

Frequency decomposition of current for different amplitudes, U_1, of pump wave



Fourier Analysis of Time-Dependent Current (with Pumping)

Oscillations originating from transitions between bound states: Dependence on amplitude of pump wave



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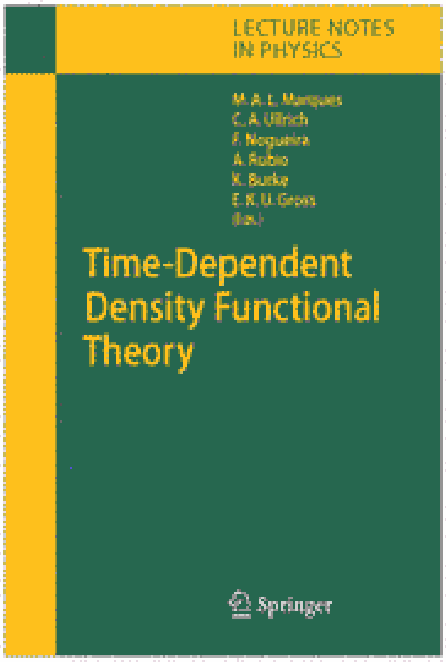
LECTURE NOTES IN PHYSICS

M. A. L. Marques
C. A. Ullrich
F. Nogueira
A. Rubio
K. Burke
E. K. U. Gross
(Eds.)

Time-Dependent Density Functional Theory

Springer

Lecture Notes in Physics 706
(Springer, August 2006)

Conclusions

- Standard approach to molecular transport: static DFT + Landauer
  - -- Chrysazine may serve as an optical switch

- TDDFT approach to transport properties
- Algorithm for time propagation of open systems
- Electron pumping
- Persistent current oscillations from transition between bound states
- Memory effect: amplitude of oscillations depends on history of the system

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In progress

- Spin transport
- Inclusion of (nonlinear) Hxc potentials
  - --Does a steady state exist?
  - -- If so, is it unique or does it depend on the switching-on
- Implementation for realistic 3D molecules
- Inclusion of nuclear motion: Local heating, current-induced isomerization
- Combination with superconducting leads (treated with TD-SCDFT)
  - --Molecular Josephson effect
  - --Molecluar proximity effect