Time-dependence and optimal control of quantum transport

E.K.U. Gross

Max-Planck Institute for Microstructure Physics

web: http://users.physik.fu-berlin.de/~ag-gross

Broader context of topic:
Experiments shift from static to time-resolved probes

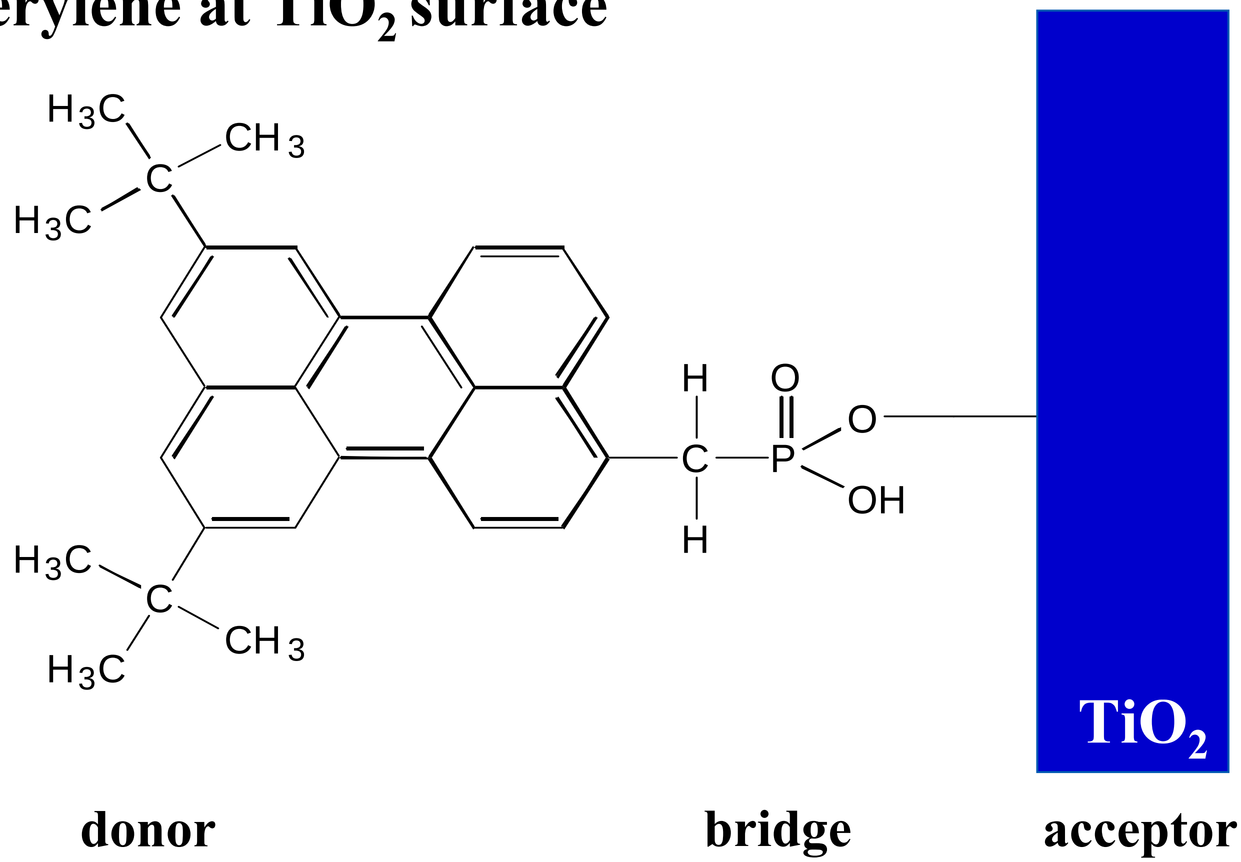
Traditionally:

- **optical spectrum, photo-electron spectrum, oscillator strengths,….**
- **ionisation rates**
- **steady-state current in nano-scale junctions**

Recently:

- **time-resolved spectroscopy**
- **pump-probe experiments**
- **time-dependence of current through nano-scale junctions**

Perylene at TiO_2 surface



Time-resolved photo-absorption experiment: Frank Willig (HMI Berlin)
Much richer information, important in the design of photo-voltaic materials

Three different ab-initio approaches

- **TD many-body perturbation theory (Kadanoff-Baym equation)**

- **TD denstity-functional theory (TD Kohn-Sham equation)**

- **TD wave-function approaches (TD many-body Schrödinger equation)**

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OUTLINE

- TDDFT approach to electron transport through nano-scale junctions
  - -- electron pumps
  - -- bound-state oscillations
  - -- TD picture of Coulomb blockade

- Optimal control of
  - -- currents
  - -- path of wave packet in real space

THANKS

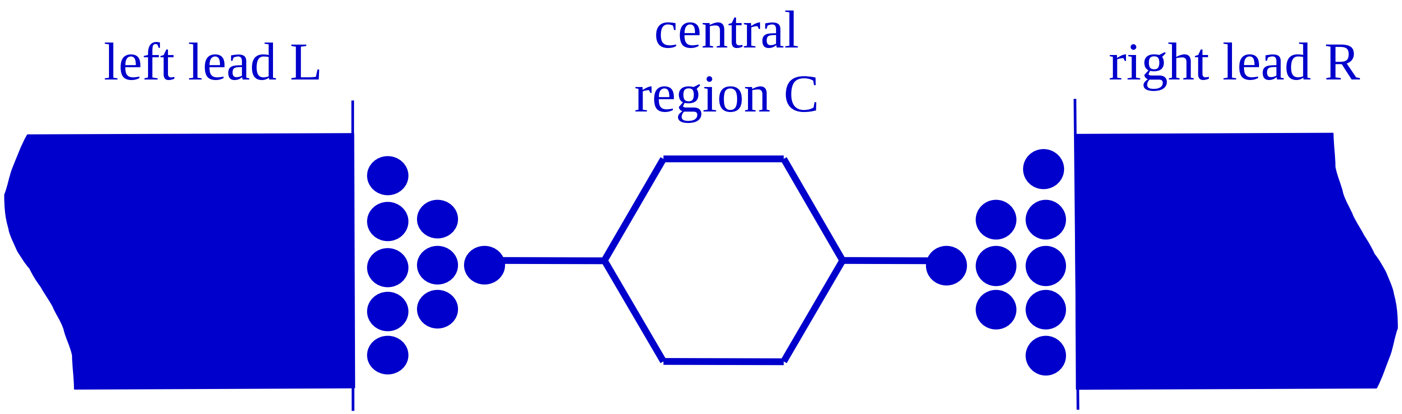
Stefan Kurth
Gianluca Stefanucci
Claudio Verdozzi
Elham Khosravi
Angelica Zacarias
Danilo Nitsche

Jan Werschnik
Ioana Serban
Esa Räsänen
Alberto Castro
Kevin Krieger

Angel Rubio

Molecular Electronics

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



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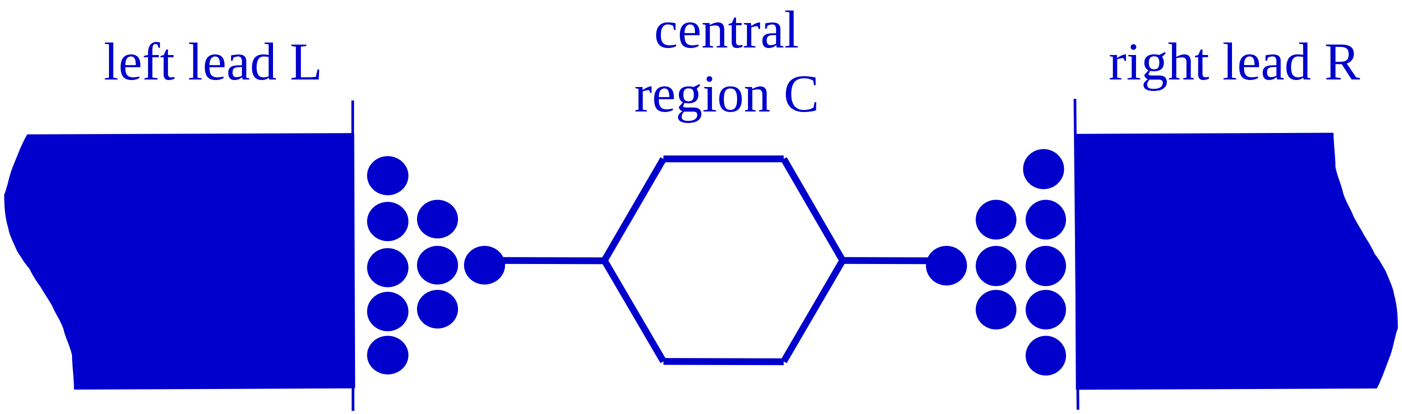

Bias between L and R is turned on: U(t) $\longrightarrow$ V for large t

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

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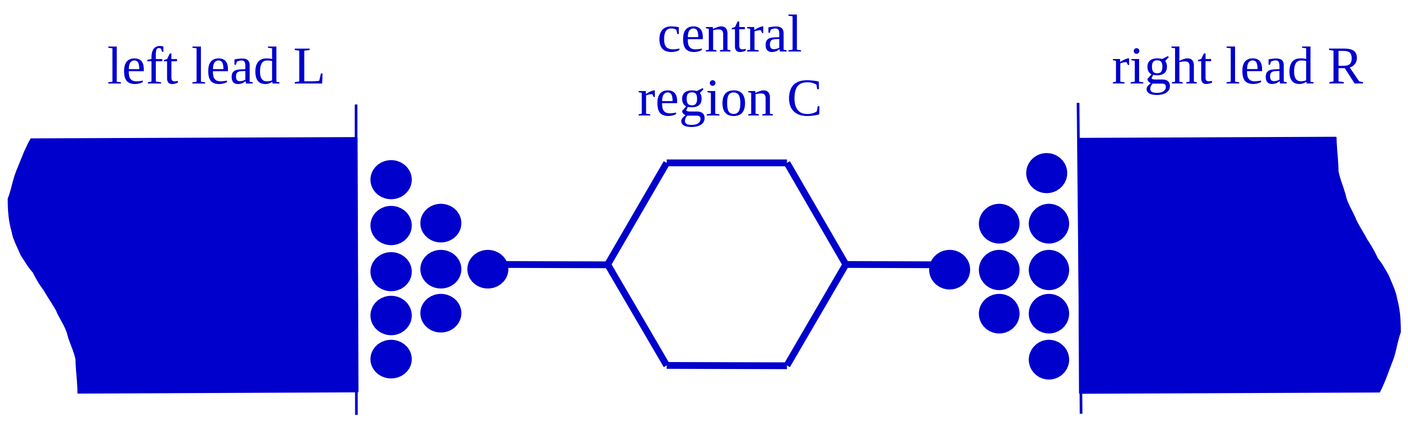

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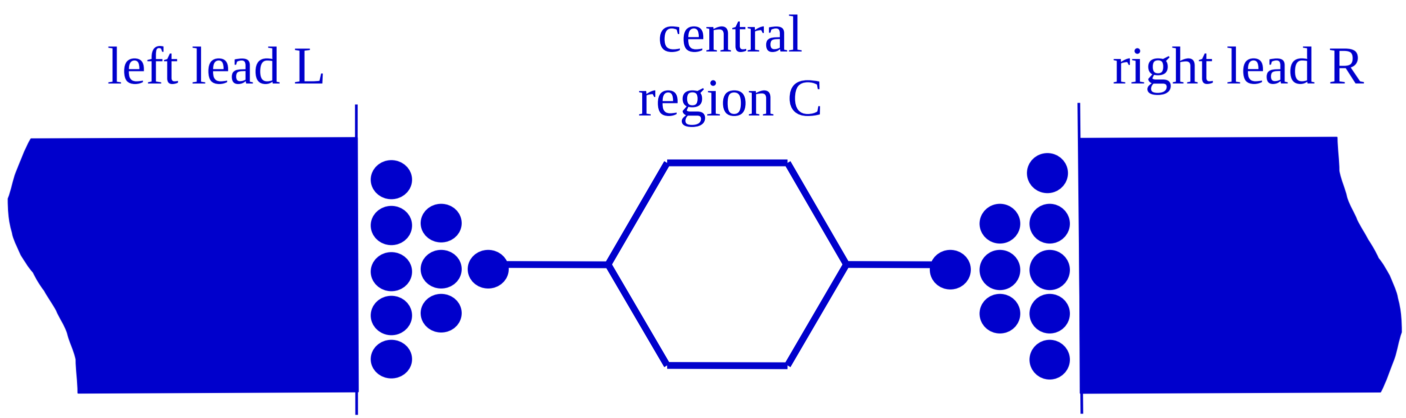

Bias between L and R is turned on: U(t) $\longrightarrow$ V for large t

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<u>Goal 1:</u> Calculate current-voltage characteristics I(V)
<u>Goal 2:</u> Analyze how steady state is reached, determine if there is steady state at all and if it is unique

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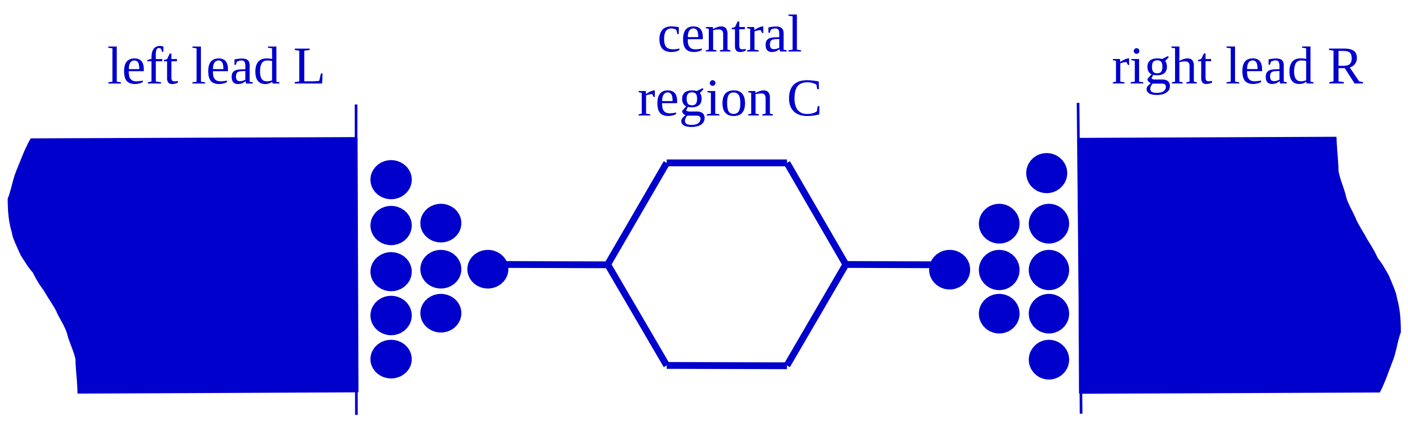

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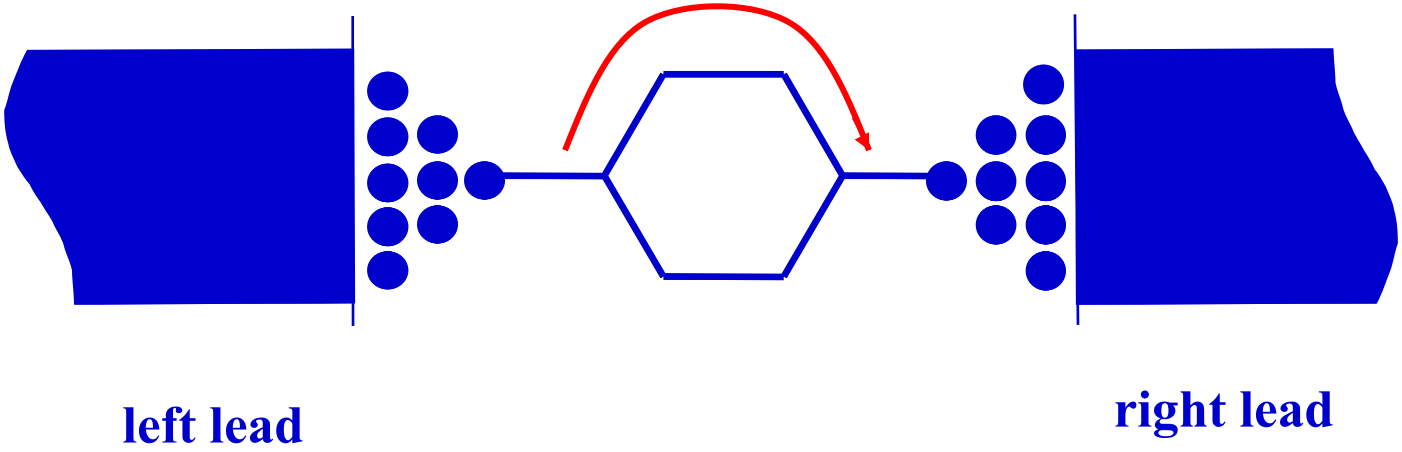
<u>Goal 3:</u> Control path of current through molecule by laser

Molecular Electronics

Control the path of the current with laser



Molecular Electronics

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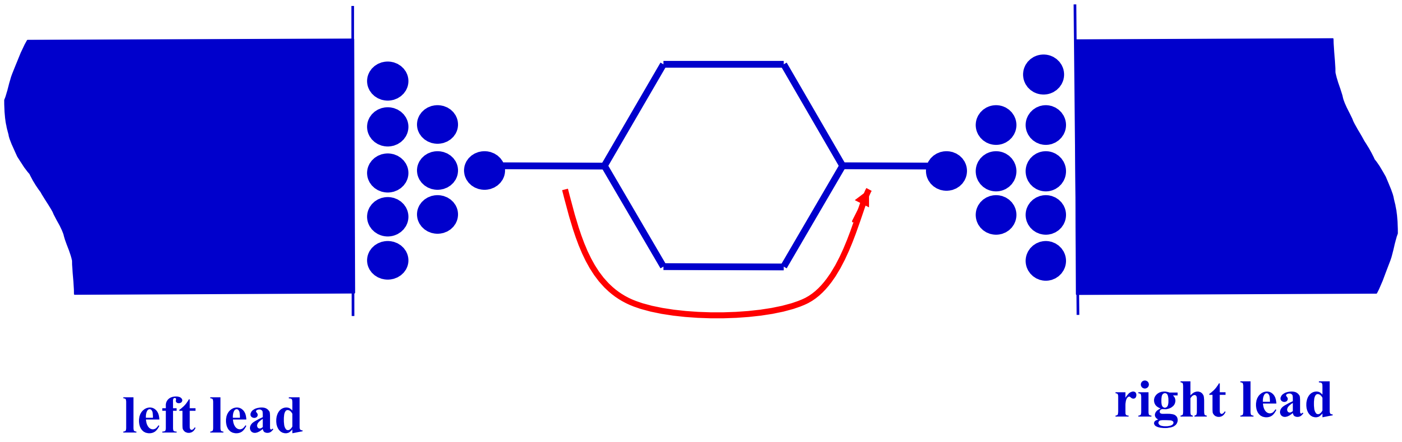

Molecular Electronics

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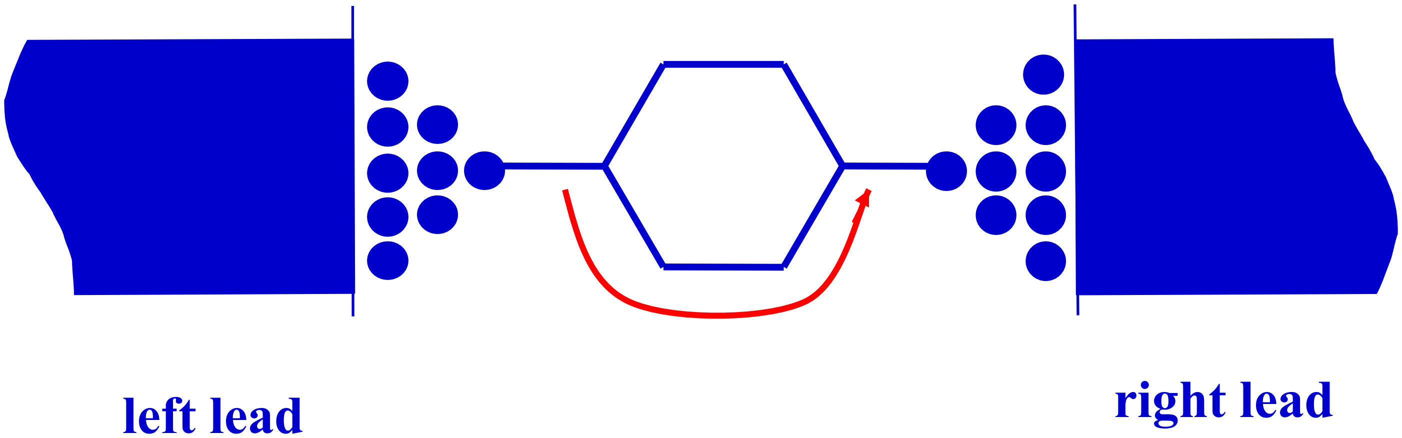
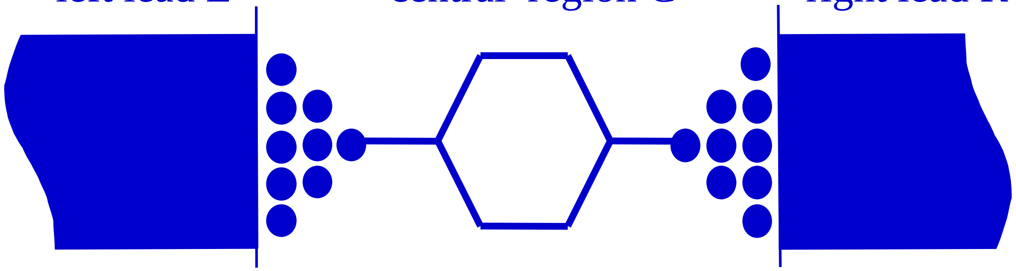


<u>Necessary</u>: Algorithm to calculate shape of optimal laser pulse



Standard approach: Landauer formalism plus static DFT

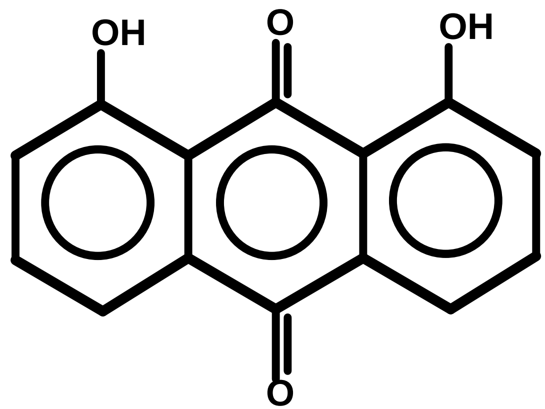
$$I(V) = \frac{e}{h} \int dE \, T(E,V) \left[f\left(E - \mu_1\right) - f\left(E - \mu_2\right) \right]$$

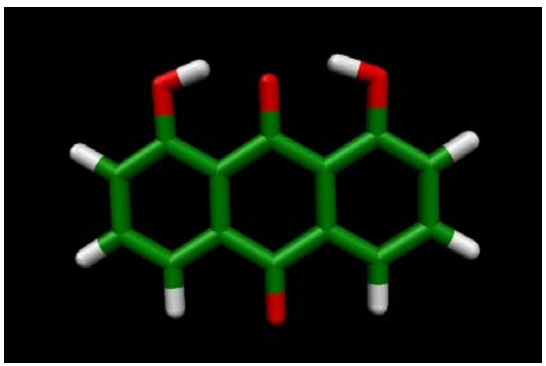
Transmission function T(E,V) calculated from <u>static (ground-state) DFT</u>

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

Chrysazine

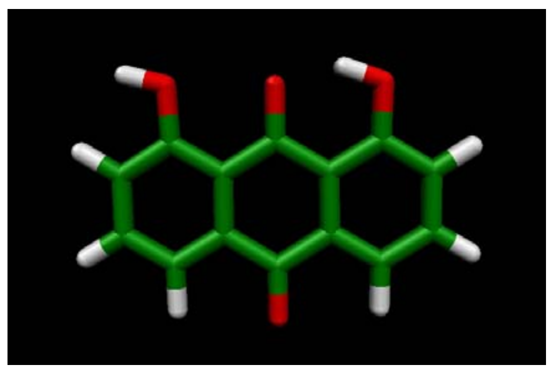
Relative Total Energies and **HOMO-LUMO Gaps**





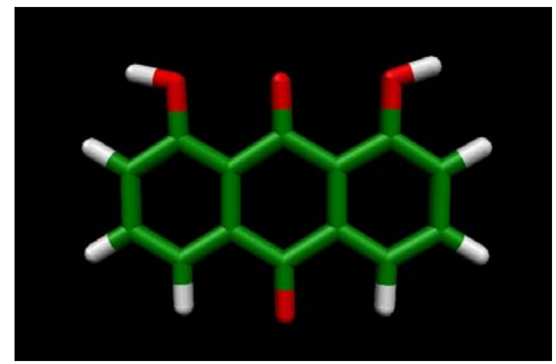
Chrysazine (a)

0.0 eV 3.35 eV



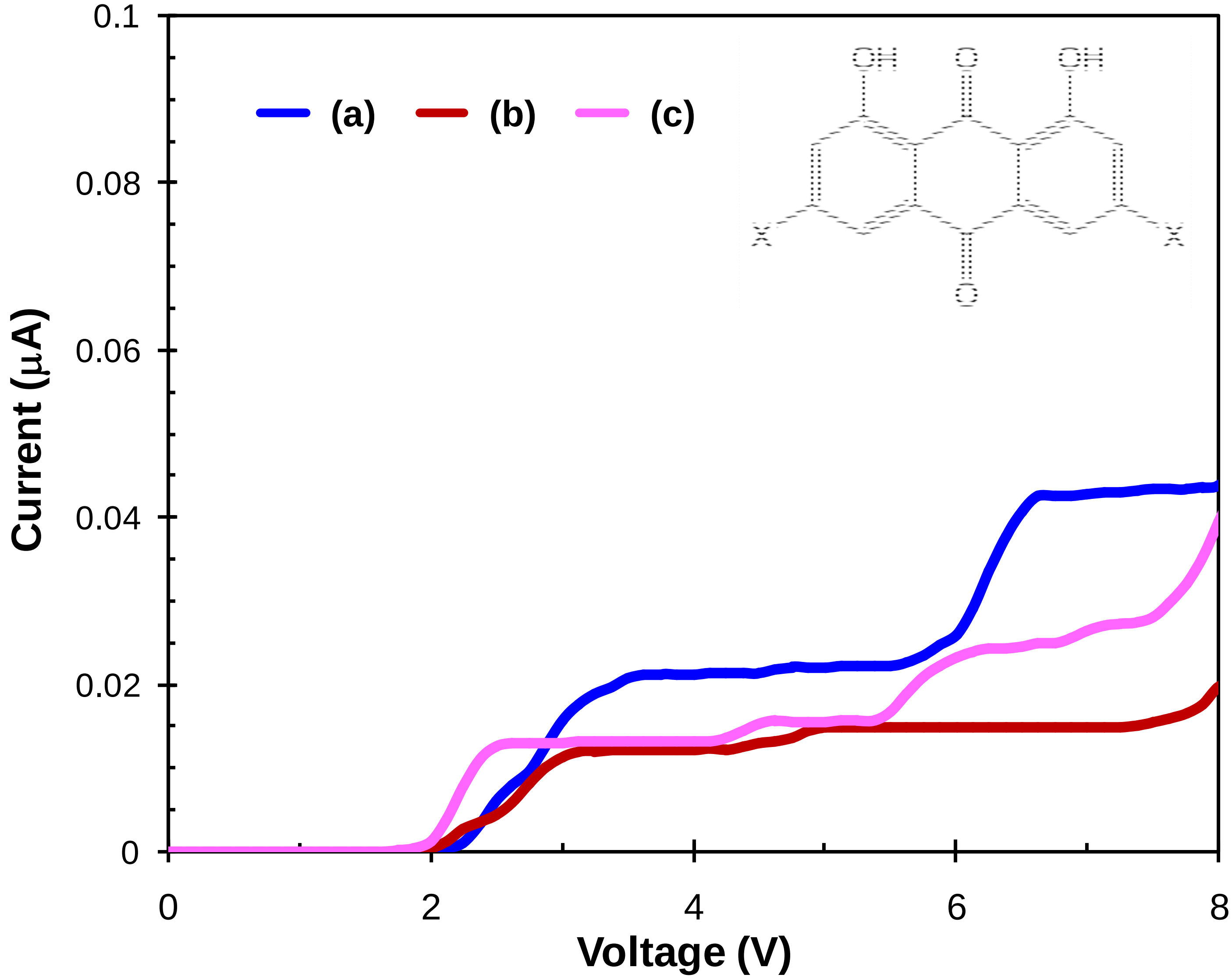
Chrysazine (b)

0.54 eV 3.41 eV



Chrysazine (c)

1.19 eV 3.77 eV



Possible use: Optical switch

A.G. Zacarias, E.K.U. Gross, TCAC (Jan 2010)

Motivation to develop a time-dependent approach:

Two conceptual issues:

☠ **Assumption that upon switching-on the bias a steady state is reached**

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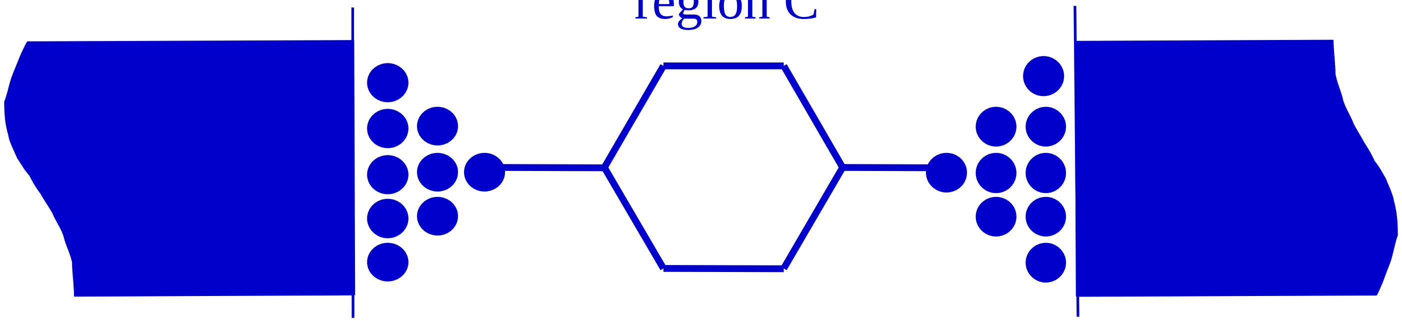
One practical issue:

- ☠ TD external fields, AC bias, laser control, etc, cannot be treated within the static approach

Molecular Electronics with TDDFT

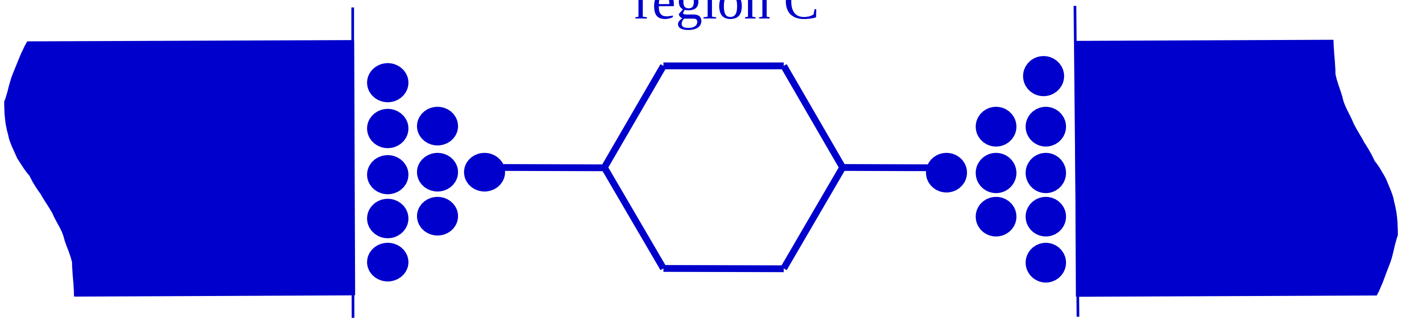


TDKS equation (E. Runge, EKUG, PRL **52**, 997 (1984))

$$i\hbar \frac{\partial}{\partial t}\varphi_j(rt) = \left(-\frac{\hbar^2 \nabla^2}{2m} + v_{KS}[\rho](rt) \right) \varphi_j(rt)$$

$$v_{KS}[\rho(r't')](rt) = v(rt) + \int d^3r' \frac{\rho(r't)}{|r-r'|} + v_{xc}[\rho\,(r't')](r\,t)$$

Molecular Electronics with TDDFT



TDKS equation

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

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)

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

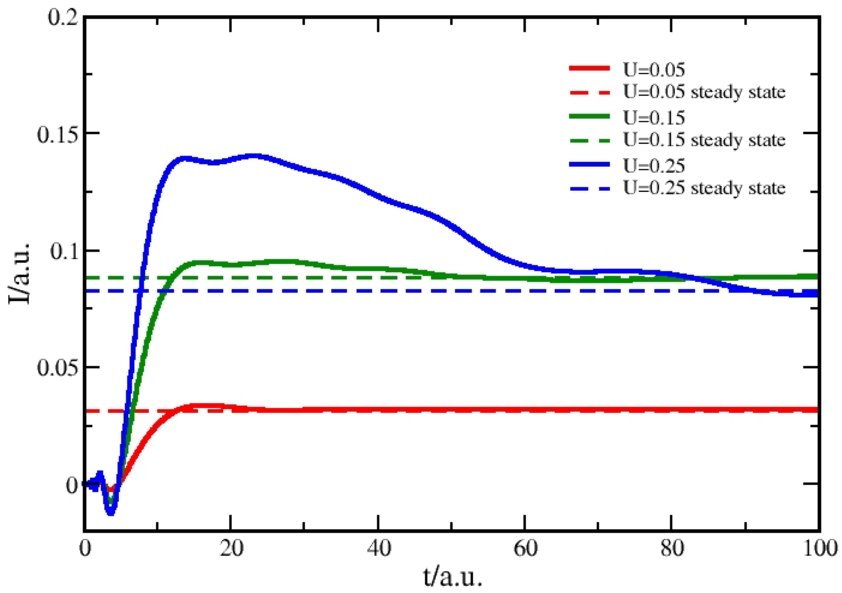
source term: $L \rightarrow C$ and $R \rightarrow C$ charge injection

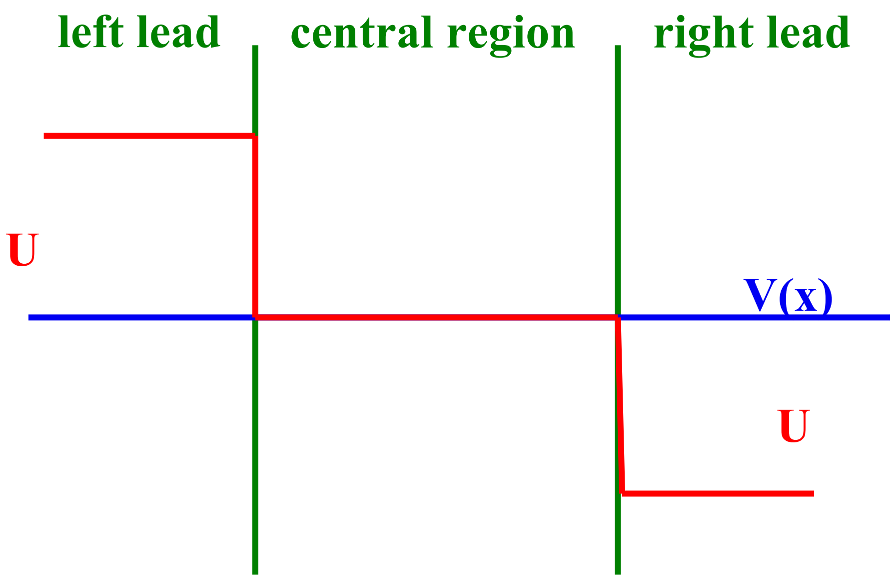
memory term: $C \rightarrow L \rightarrow C$ and $C \rightarrow R \rightarrow C$ hopping

<u>Note</u>: So far, no approximation has been made.

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.

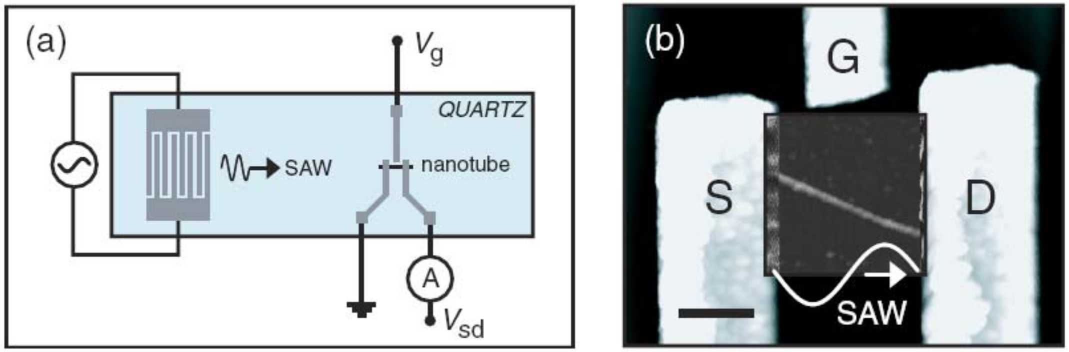
Steady state coincides with Landauer formula

and is reached after a few femtoseconds

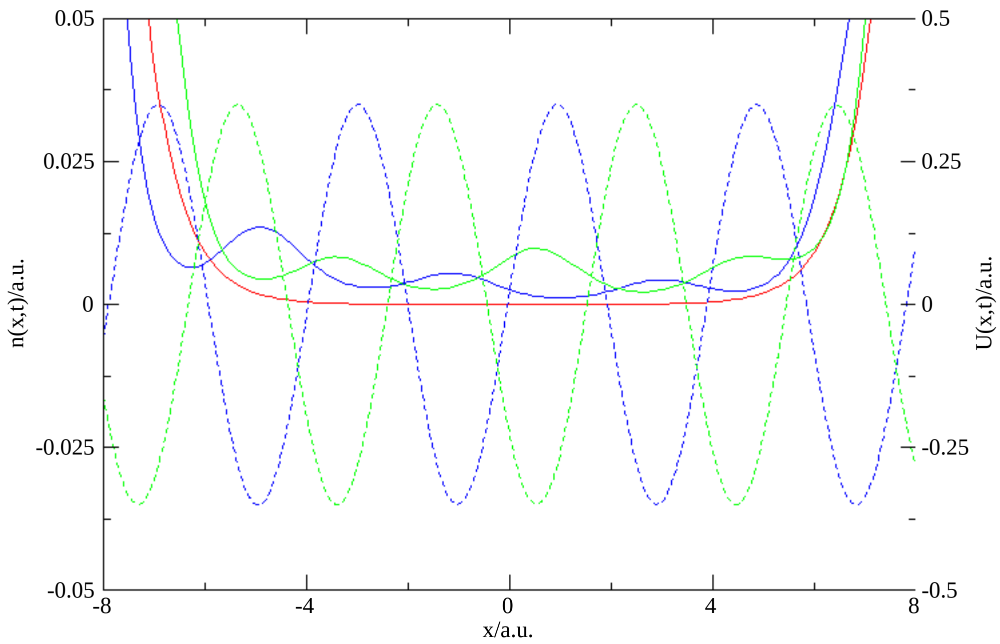
ELECTRON PUMP

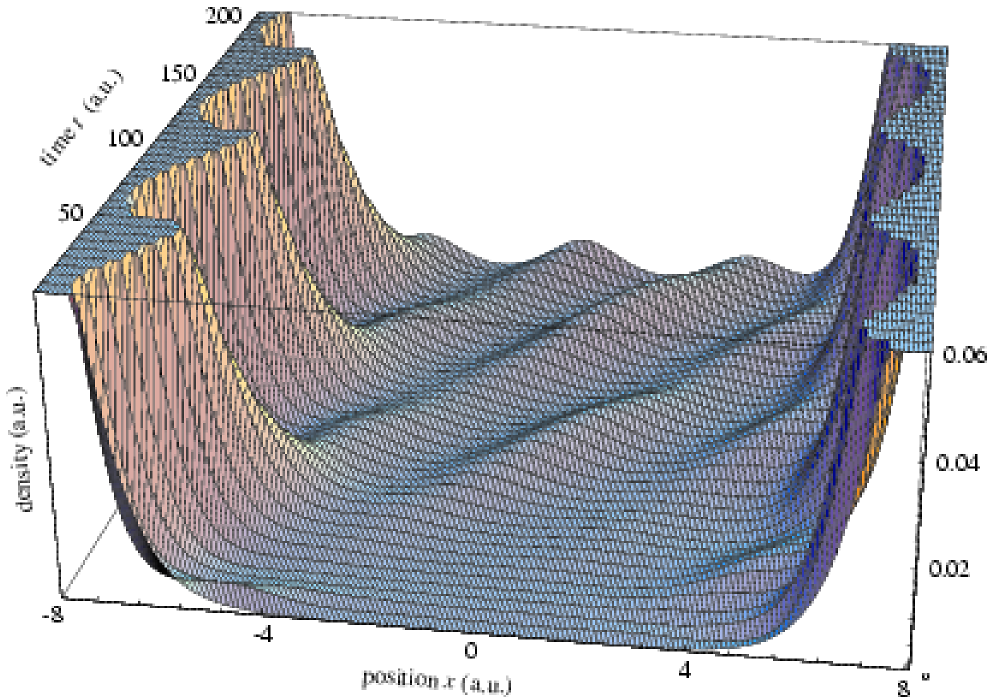
Device which generates a net current between two electrodes (with <u>no</u> static bias) by applying a time-dependent potential in the device region

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



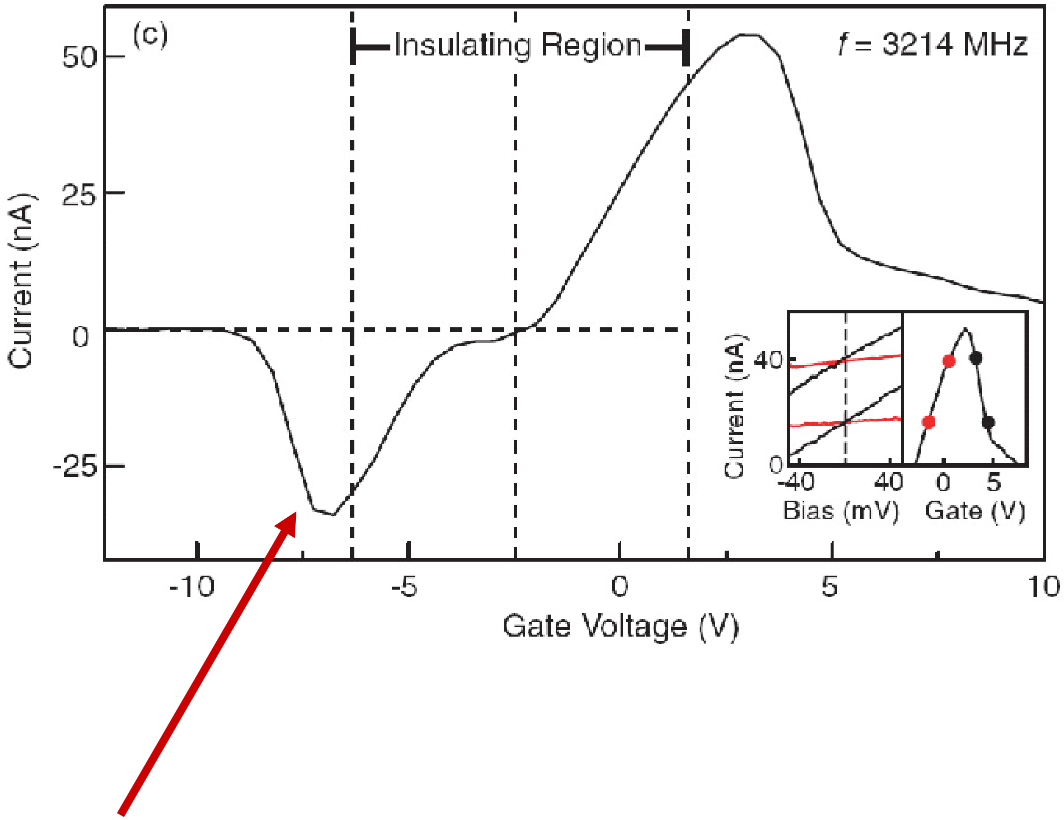
Pumping through a square barrier (of height 0.5 a.u.) using a travelling wave in device region
$U(x,t) = U_o \sin(kx-wt)$
($k = 1.6$ a.u., $w = 0.2$ a.u.
Fermi energy = 0.3 a.u.)



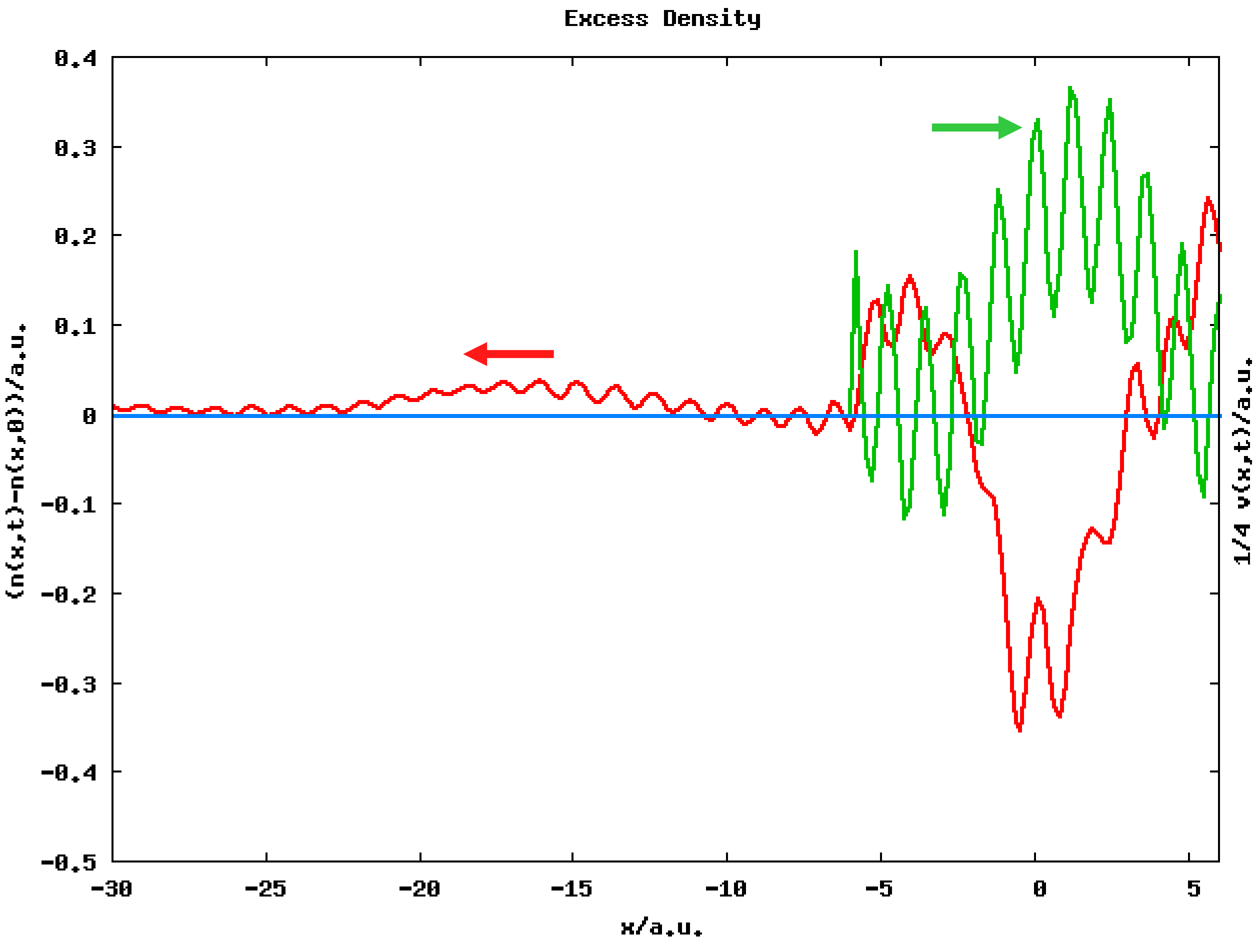


Patent: Archimedes (250 b.c.)

Experimental result:



Current flows in direction opposite to sound wave



Current goes in direction opposite to the external field !!

Bound state oscillations and memory effects

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

Numerical: E. Khosravi, S. Kurth, G. Stefanucci, E.K.U.G., Appl. Phys. A**93**, 355 (2008)

If Hamiltonian of a (non-interacting) biased system in the long-time limit supports two or more bound states then current has steady, $I^{(S)}$, and dynamical, $I^{(D)}$, parts:

$$\boxed{I(t \to \infty) = I^{(S)} + I^{(D)}(t)}$$

$$\boxed{I^{(D)}(t) = \sum_{b,b'} \Lambda_{bb'} \sin[(\varepsilon_b - \varepsilon_{b'})t]}$$

Sum over bound states of biased Hamiltonian

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

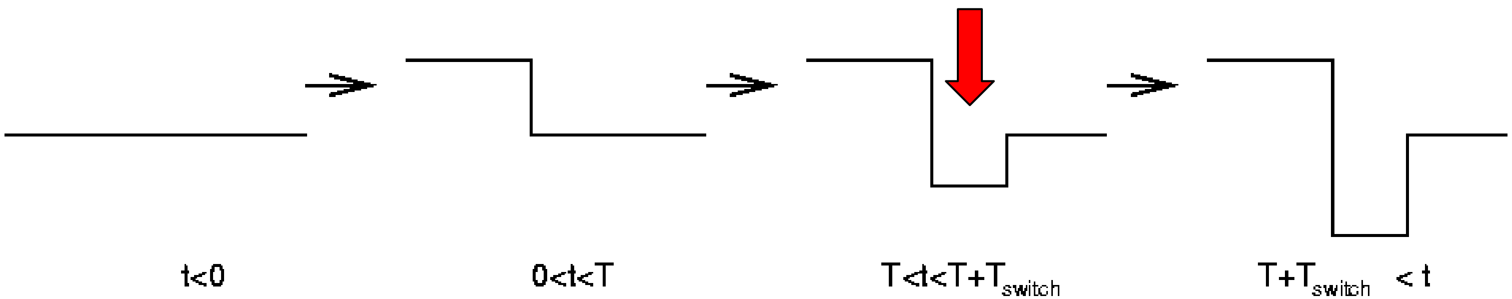
Questions: -- How large is $I^{(D)}$ vs $I^{(S)}$?

-- How pronounced is history dependence?

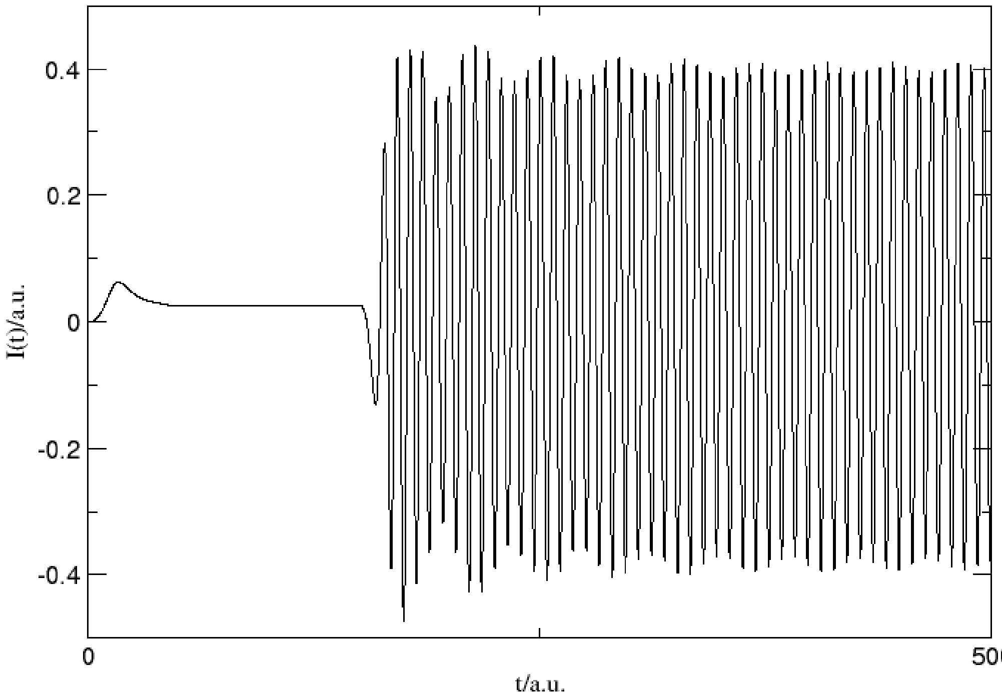
History dependence of undamped oscillations

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

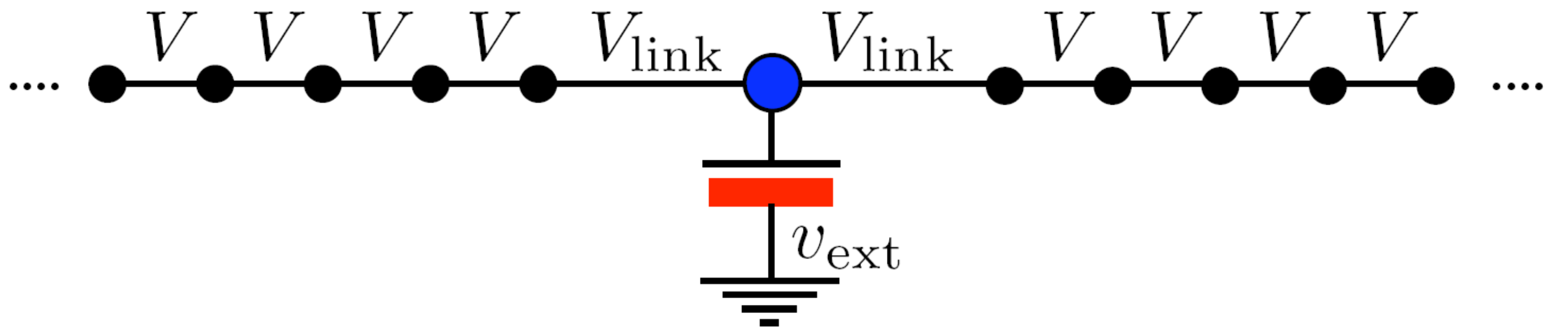


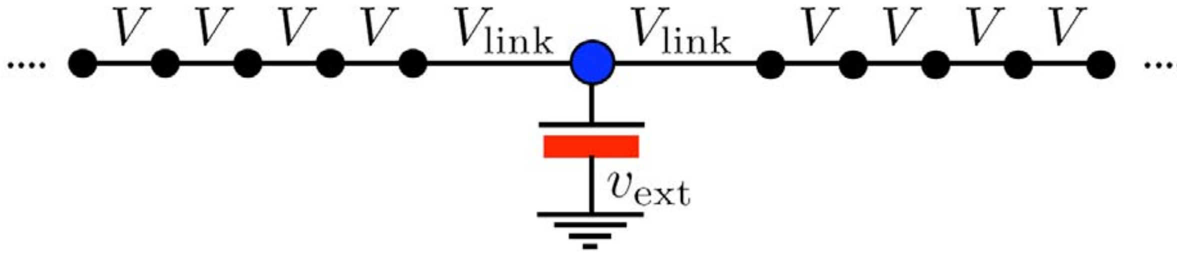
So far: systems without e-e interaction

Next step: TDKS, i.e. inclusion of e-e- interaction via approximate xc potential

→ **time-dependent picture of Coulomb blockade**

Model system





$$\hat{H}(t) = \hat{H}_{QD} + \sum_{\alpha=L,R} \hat{H}_{\alpha} + \hat{H}_{T} + \hat{H}_{bias}(t)$$

$$\hat{H}_{QD} = v_{ext} \sum_{\sigma} \hat{n}_{0\sigma} + U \hat{n}_{0\uparrow} \hat{n}_{0\downarrow}$$

$$\hat{H}_{\alpha}(t) = -\sum_{\sigma} \sum_{i=1}^{\infty} \left(V \hat{c}_{i+1\alpha,\sigma} \hat{c}_{i\alpha,\sigma} + h.c. \right)$$

$$\hat{H}_{T} = -\sum_{\alpha,\sigma} \sum_{i=1}^{\infty} \left(V_{link} \hat{c}^{\dagger}_{1\alpha,\sigma} \hat{c}_{0\sigma} + h.c. \right)$$

$$\hat{H}_{bias}(t) = -\sum_{\alpha,\sigma} \sum_{i=1}^{\infty} W_{\alpha}(t) \hat{n}_{i\alpha,\sigma}$$

Solve TDKS equations (instead of fully interacting problem):

$$\hat{H}_{KS}(t) = \hat{H}_{QD,KS}(t) + \sum_{\alpha=L,R} \hat{H}_{\alpha} + \hat{H}_{T} + \hat{H}_{bias}(t)$$

$$\hat{H}_{QD,KS}(t) = \sum_{\sigma} v_{KS}\left[n_0(t)\right]\hat{n}_{0\sigma}$$

$$n_0(t) = \sum_{\sigma} n_{0\sigma}(t)$$

$$v_{KS}\left[n_0(t)\right] = v_{ext} + \frac{1}{2}Un_0(t) + v_{xc}\left[n_0(t)\right]$$

LDA functional for v_{xc} is available from exact Bethe-ansatz solution of the 1D Hubbard model.

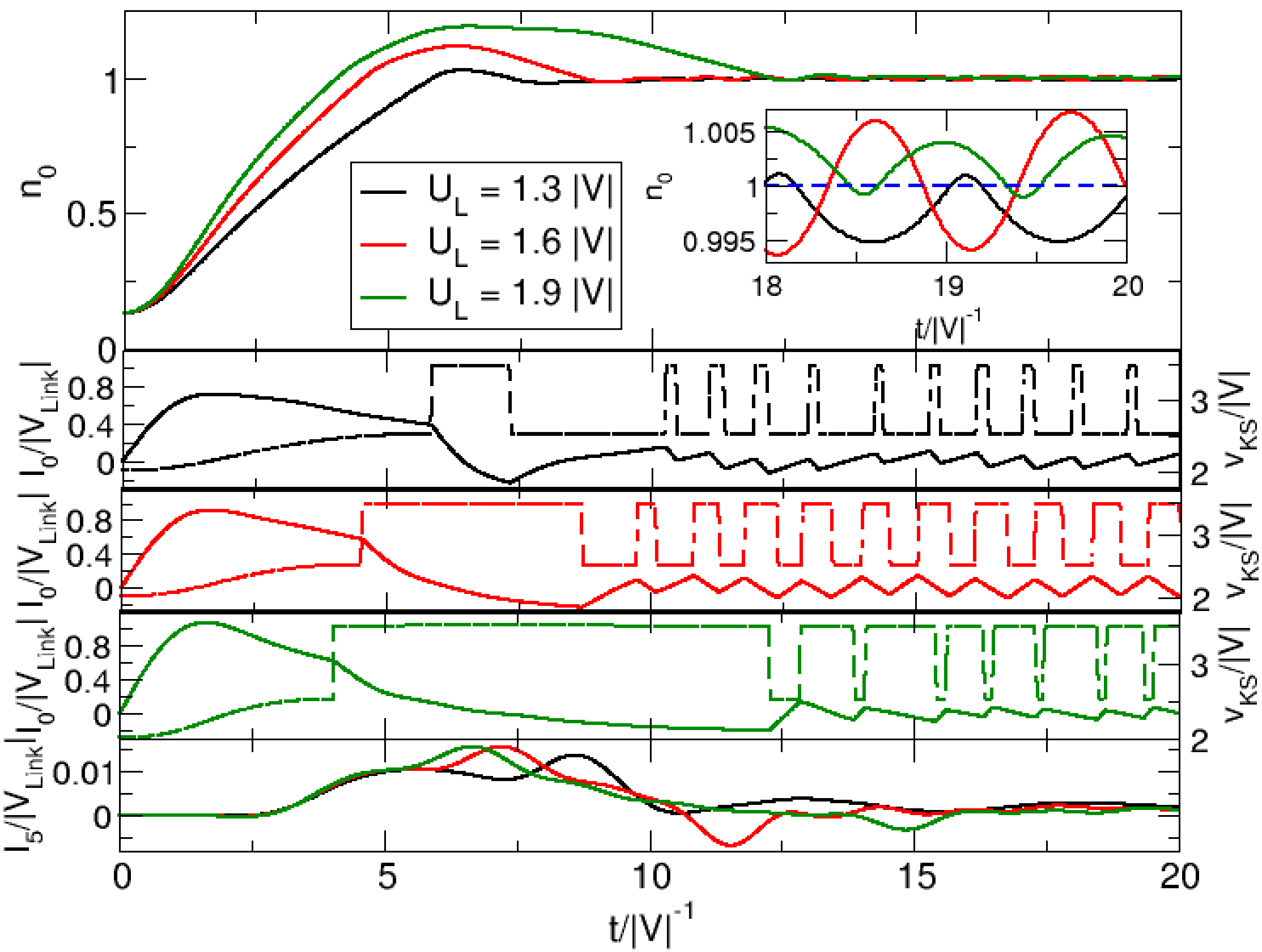
N.A. Lima, M.F. Silva, L.N. Oliveira, K. Capelle, PRL 90, 146402 (2003)

$$v_{xc}^{LDA}[n] = \theta(1-n)\, v_{xc}^{(1)}[n] - \theta(n-1)\, v_{xc}^{(1)}[2-n]$$

$$v_{xc}^{(1)}[n] = -\frac{1}{2}Un - 2V_{link}\left[\cos\left(\frac{\pi n}{2}\right) - \cos\left(\frac{\pi n}{\beta}\right)\right]$$

We use this functional as Adiabatic LDA (ALDA) in the TD simulations.

<u>Note:</u> $v_{xc}^{LDA}[n]$ has a discontinuity at n = 1



n_0
$U_L = 1.3\ |V|$
$U_L = 1.6\ |V|$
$U_L = 1.9\ |V|$
1.005
1
0.995
18
19
20
$t/|V|^{-1}$
$I_0/|V_{Link}|$
$v_{KS}/|V|$
$I_5/|V_{Link}|$
0
0.5
1
0.4
0.8
0.01
2
3
5
10
15
$t/|V|^{-1}$

Is this Coulomb blockade??

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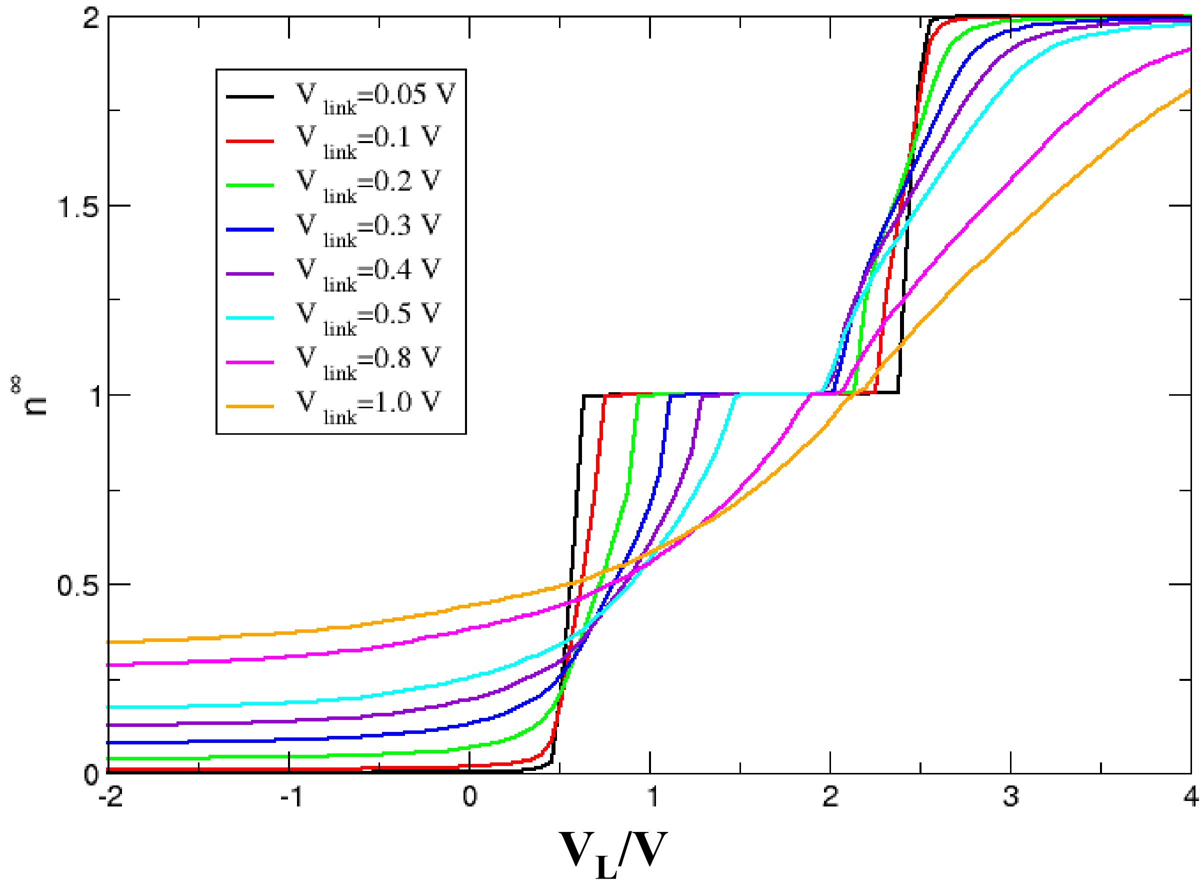
Steady-state equation has no solution in this parameter regime (if v_{KS} has sharp discontinuity) !!



Steady-state density as function of applied bias for KS potential with smoothened discontinuity

Optimal Control Theory (OCT)

Normal question:

What happens if a system is exposed to a given laser pulse?

Inverse question (solved by OCT):

Which is the laser pulse that achieves a prescribed goal?

possible goals:

a) **system should end up in a given final state ϕ_f at the end of the pulse**

b) **density should follow a given classical trajectory r(t)**

Optimal control of static targets (standard formulation)

For <u>given</u> target state Φ_f , maximize the functional:

$$J_1 = \left| \left\langle \Psi(T) \middle| \Phi_f \right\rangle \right|^2 = \left\langle \Psi(T) \middle| \Phi_f \right\rangle \left\langle \Phi_f \middle| \Psi(T) \right\rangle = \left\langle \Psi(T) \middle| \hat{O} \middle| \Psi(T) \right\rangle$$

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$\hat{O}$

with the constraints:

$$J_2 = -\alpha \left[\int_0^T dt\, \varepsilon^2(t) - E_0 \right]$$

E_0 = given fluence

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$\hat{O}$

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E_0 = given fluence

$$J_3[\varepsilon, \Psi, \chi] = -2\, \mathrm{Im} \int_0^T dt \left\langle \chi(t) \middle| -i\partial_t - \left[\hat{T} + \hat{V} - \mu\varepsilon(t) \right] \middle| \Psi(t) \right\rangle$$

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TDSE

Optimal control of static targets (standard formulation)

For given target state Φ_f , maximize the functional:

$$J_1 = \left|\left\langle \Psi(T) \middle| \Phi_f \right\rangle\right|^2 = \left\langle \Psi(T) \middle| \Phi_f \right\rangle\left\langle \Phi_f \middle| \Psi(T) \right\rangle = \left\langle \Psi(T) \middle| \hat{O} \middle| \Psi(T) \right\rangle$$

$\hat{O}$

with the constraints:

$$J_2 = -\alpha\left[\int_0^T dt\, \varepsilon^2(t) - E_0\right]$$

E_0 = given fluence

$$J_3[\varepsilon, \Psi, \chi] = -2\,\mathrm{Im}\int_0^T dt \left\langle \chi(t) \middle| -i\partial_t - \left[\hat{T} + \hat{V} - \mu\varepsilon(t)\right] \middle| \Psi(t) \right\rangle$$

TDSE

GOAL: Maximize $J = J_1 + J_2 + J_3$

Set the total variation of $J = J_1 + J_2 + J_3$ equal to zero:

Control equations

1. Schrödinger equation with initial condition:

$$\delta_\chi J = 0 \rightarrow \boxed{i\partial_t \psi(t) = \hat{H}(t)\psi(t), \quad \psi(0) = \phi}$$

2. Schrödinger equation with final condition:

$$\delta_\psi J = 0 \rightarrow \boxed{i\partial_t \chi(t) = \hat{H}(t)\chi(t), \quad \chi(T) = \hat{O}\psi(T)}$$

3. Field equation:

$$\delta_\varepsilon J = 0 \rightarrow \boxed{\varepsilon(t) = \frac{1}{\alpha} \operatorname{Im}\left\langle \chi(t) \middle| \hat{\mu} \middle| \psi(t) \right\rangle}$$

Set the total variation of $J = J_1 + J_2 + J_3$ equal to zero:

Control equations

Algorithm

1. Schrödinger equation with initial condition:

$$\delta_\chi J = 0 \rightarrow \boxed{i\partial_t \psi(t) = \hat{H}(t)\psi(t), \quad \psi(0) = \phi}$$

Forward propagation

$\downarrow$

2. Schrödinger equation with final condition:

$$\delta_\psi J = 0 \rightarrow \boxed{i\partial_t \chi(t) = \hat{H}(t)\chi(t), \quad \chi(T) = \hat{O}\psi(T)}$$

Backward propagation

$\downarrow$

3. Field equation:

$$\delta_\varepsilon J = 0 \rightarrow \boxed{\varepsilon(t) = \frac{1}{\alpha}\mathrm{Im}\left\langle \chi(t) \middle| \hat{\mu} \middle| \psi(t) \right\rangle}$$

New laser field

Algorithm monotonically convergent: W. Zhu, J. Botina, H. Rabitz, J. Chem. Phys. 108, 1953 (1998))

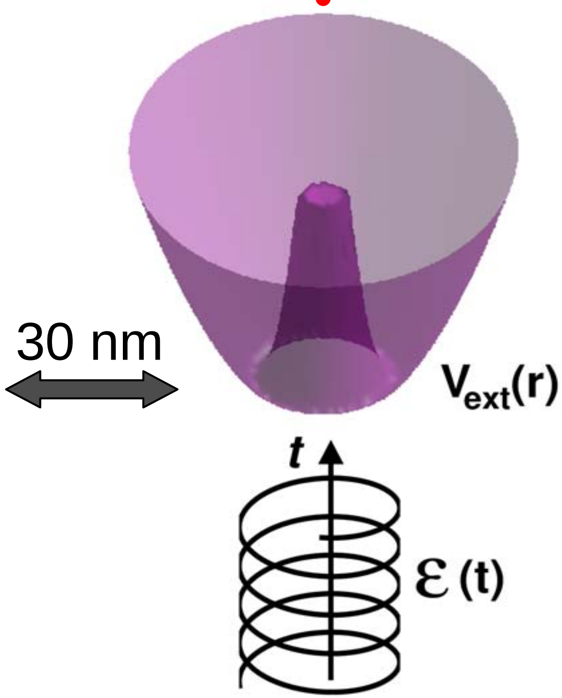
Time-dependent targets: I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

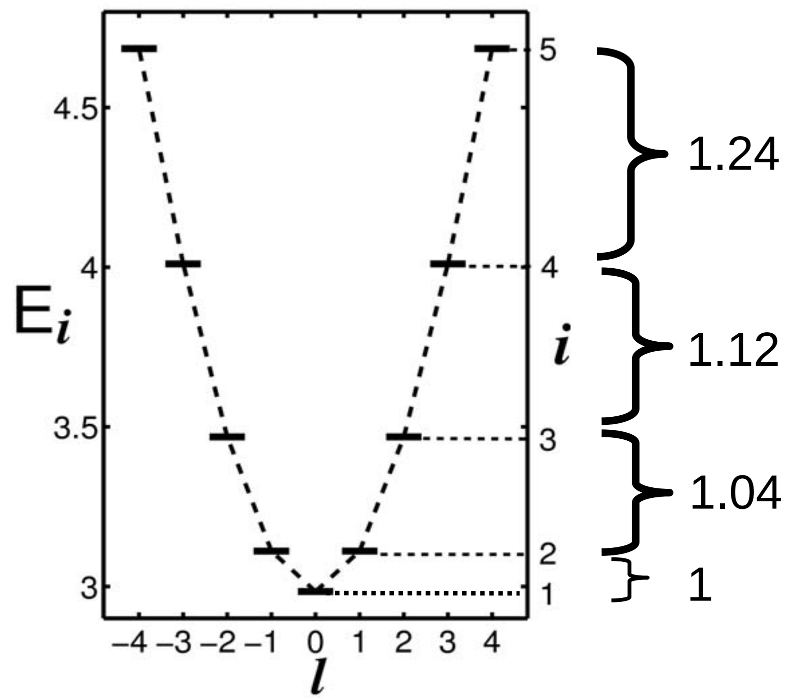
Quantum ring: Control of circular current

- TD-SE: $$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\hat{H}_0 + e\,\mathbf{r}\,\epsilon(t)\right]\Psi(\mathbf{r},t)$$

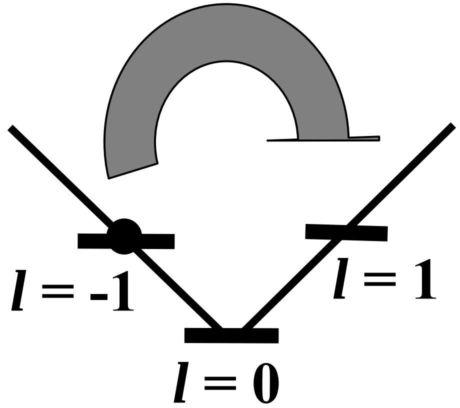
$$\hat{H}_0 = -\frac{\hbar^2}{2m^*}\nabla^2 + \frac{1}{2}m^*\omega_0^2 r^2 + V_0 e^{-r^2/d^2}$$

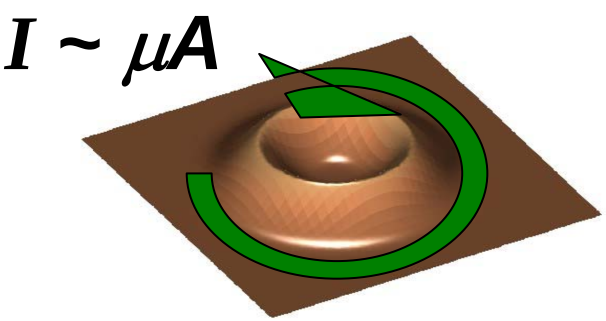
$$\epsilon(t) = (\epsilon_x(t), \epsilon_y(t))$$



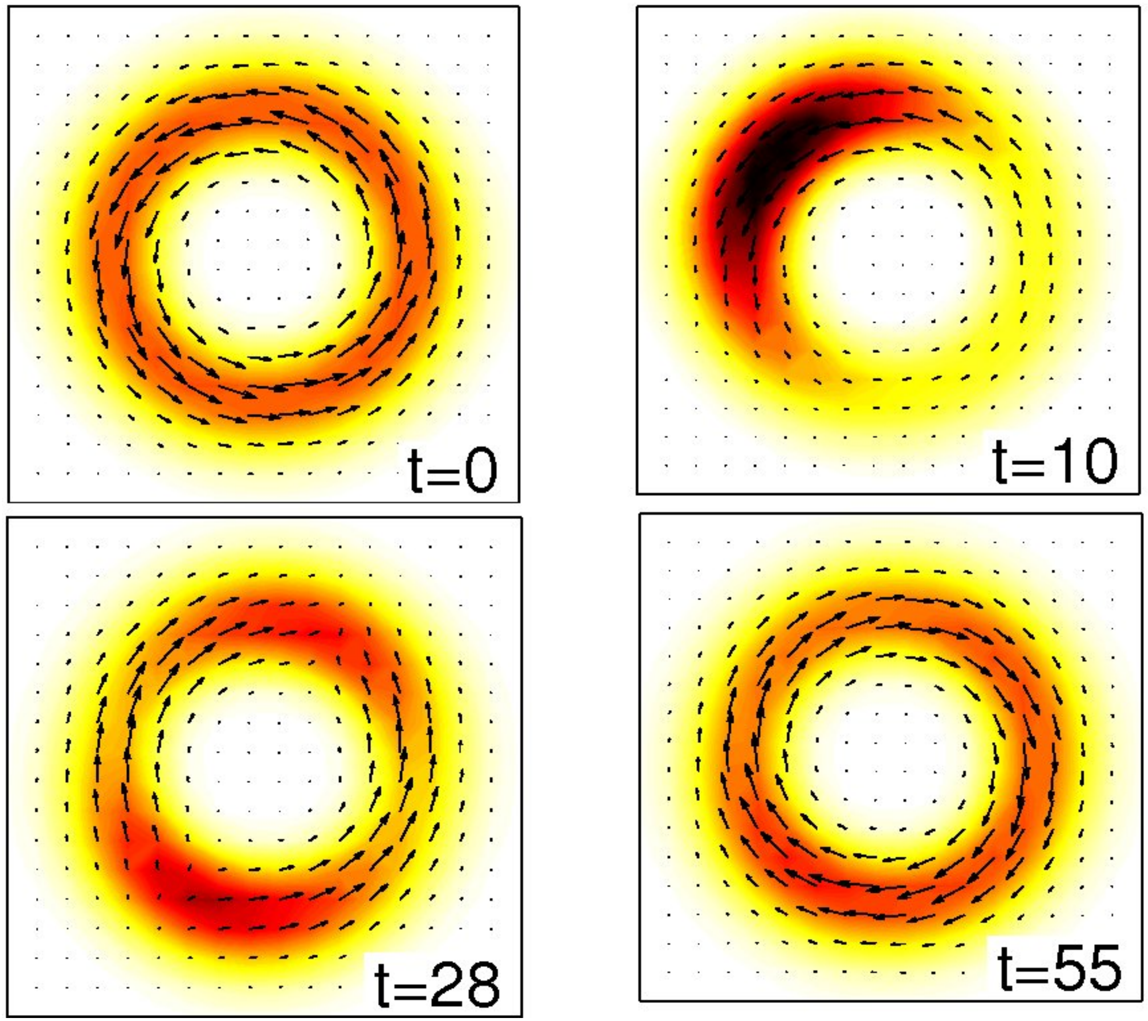


Control of currents





$|\psi(t)|^2$ and **j (t)**



E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U.G., PRL 98, 157404 (2007)

SUMMARY

- **Standard static DFT + Landauer approach**: **Chrysazine as optical switch**

- **TDDFT approach to transport properties**

  -- Electron pumping

  -- Persistent current oscillations from transitions between bound states

  -- Memory effect: amplitude of oscillations depends on history

  -- TD picture of Coulomb blockade

  -- Discontiuity of xc potential of crucial importance

- **Optimal laser control of**

  -- Chirality of current in quantum rings

Thanks !

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