Time-dependence and control of quantum transport

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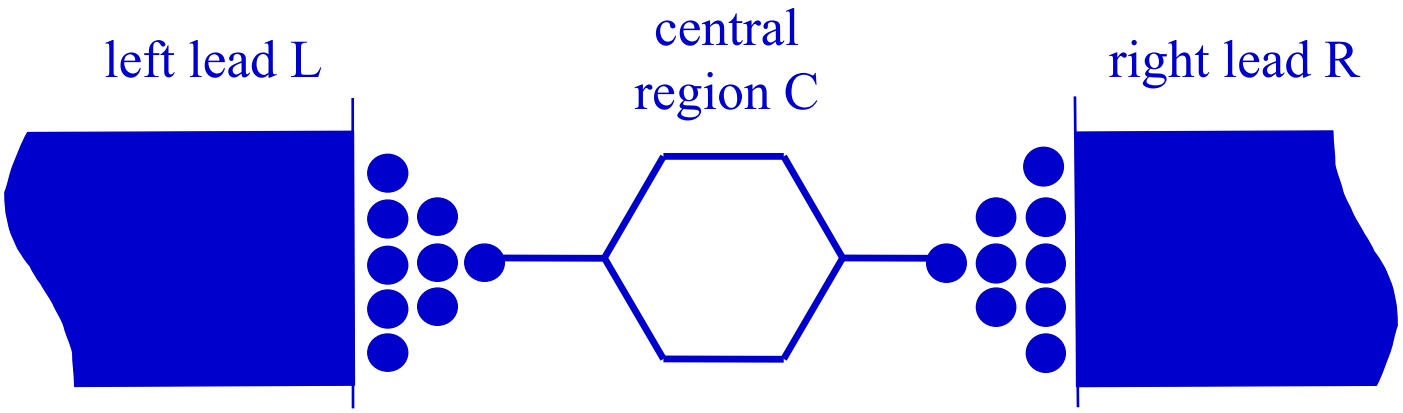
Molecular Electronics

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



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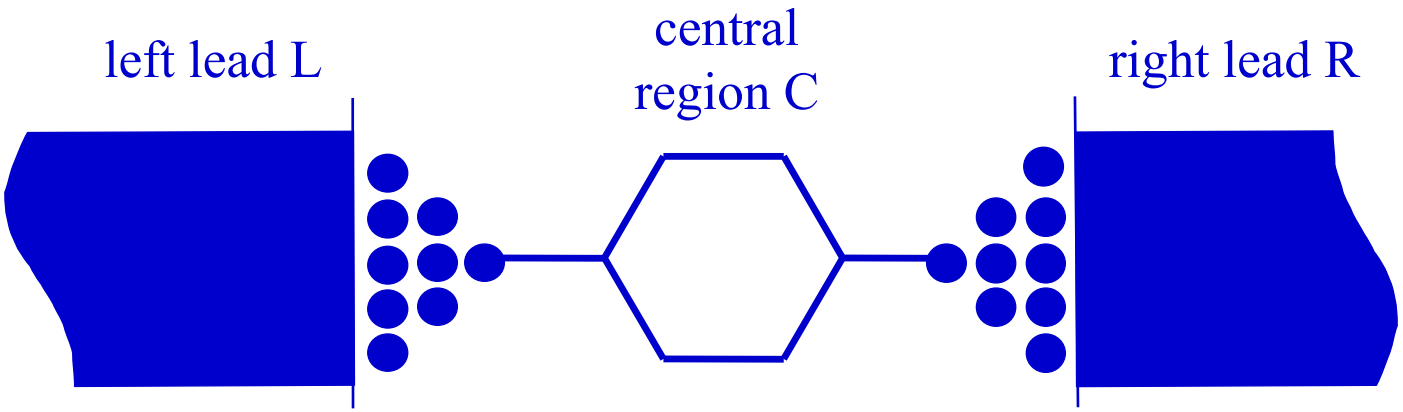

Bias between L and R is turned on: U(t) ⟶ V for large t

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

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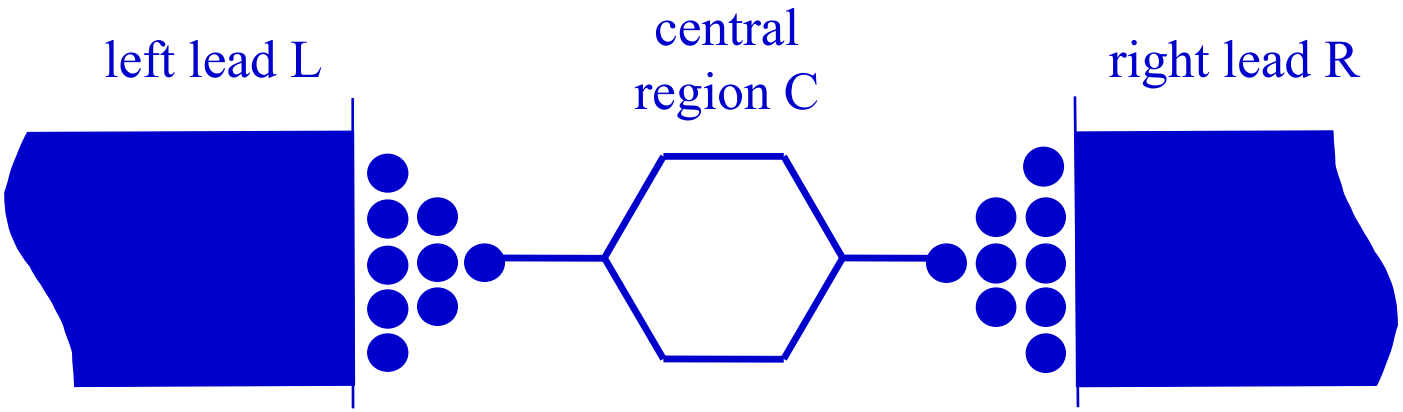

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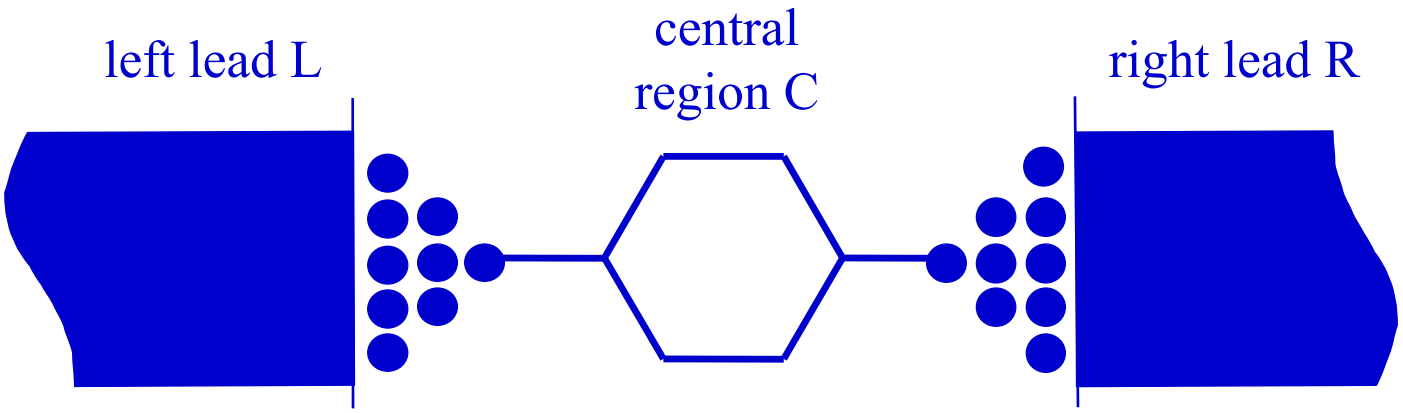

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Goal 2: Analyze how steady state evolves, and whether it evolves at all

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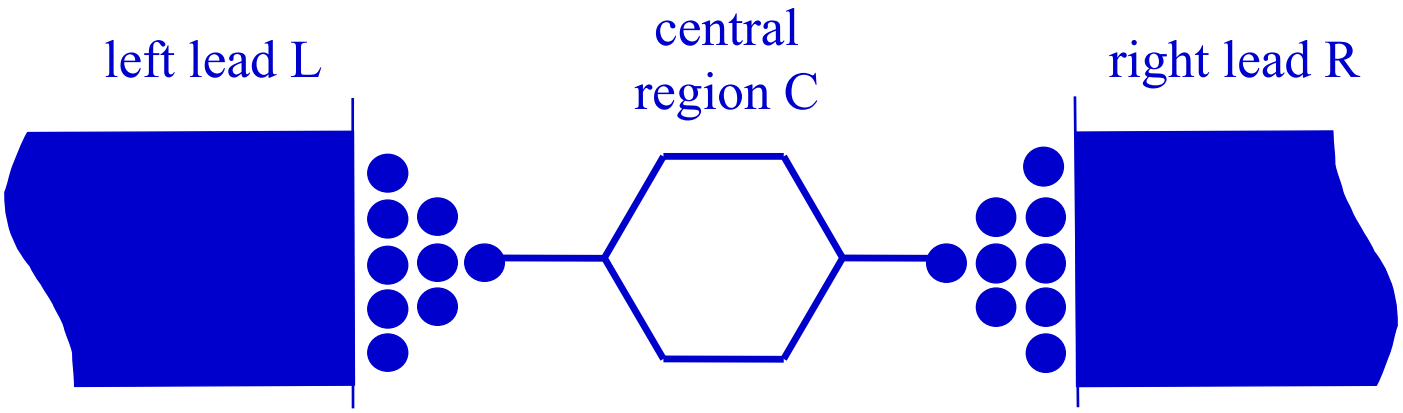

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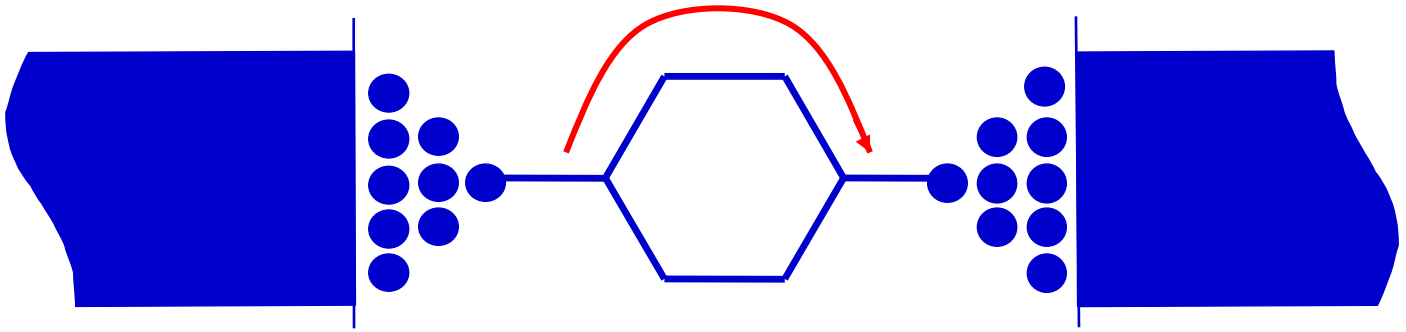
A steady current, I, may develop as a result.

Goal 1: Calculate current-voltage characteristics I(V)
Goal 2: Analyze how steady state evolves, and whether it evolves at all
Goal 3: Control path of current through molecule by laser

Molecular Electronics

Control the path of the current with laser

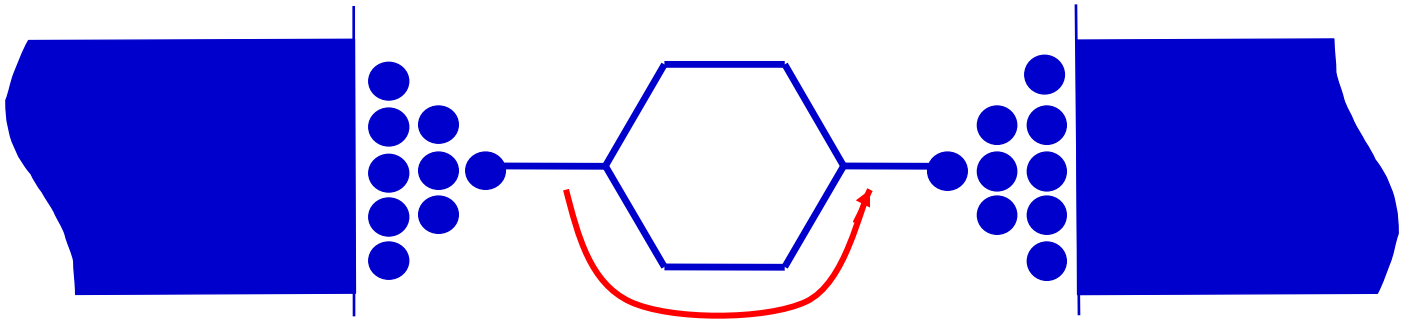


left lead

right lead

Molecular Electronics

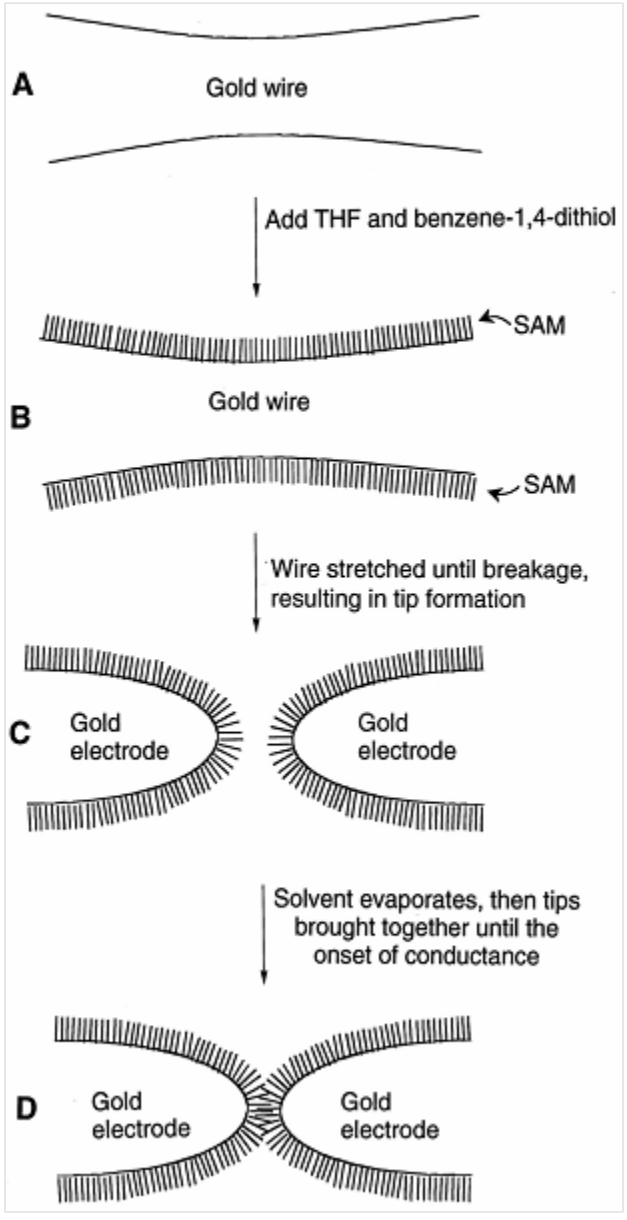
Control the path of the current with laser

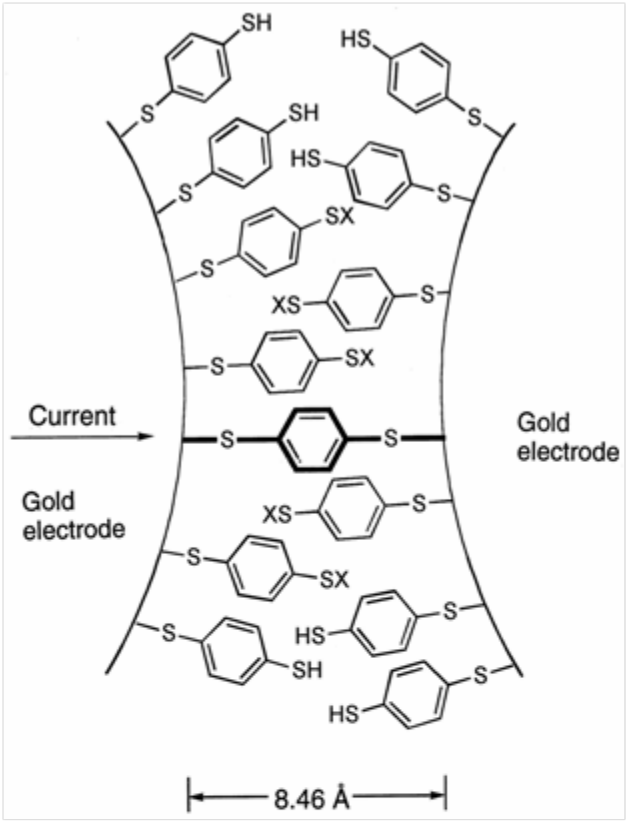


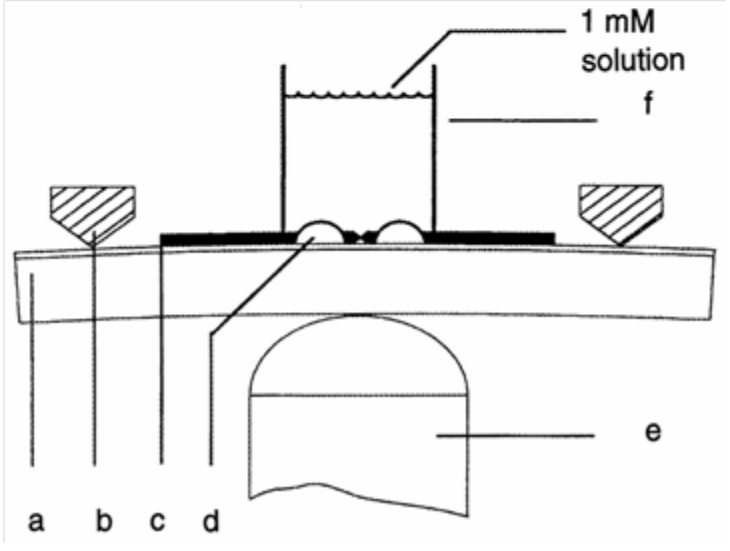
left lead

right lead

Break junction experiment

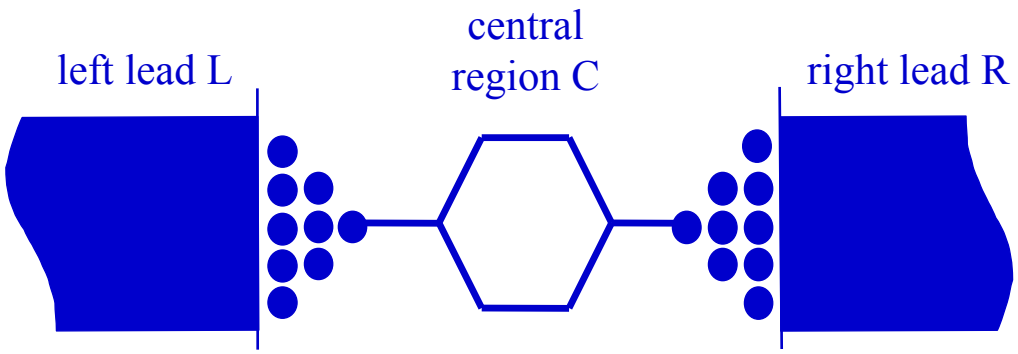






Outline

- Standard Landauer approach (using static DFT)
- Why time-dependent transport?
- Computational issues (open, nonperiodic system)
- Recovering Landauer steady state within TD framework
- Transients and the time-scale of decoherence
- Electron pumping
- Undamped oscillations associated with bound states
- Optimal control of current



Standard approach: Landauer formalism plus static DFT

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

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

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

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

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

$$(H_{CL} G_L H_{LC} + H_{CC} + H_{CR} G_R H_{RC})\, \varphi_C = E\, \varphi_C$$

Effective KS equation for the central region

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

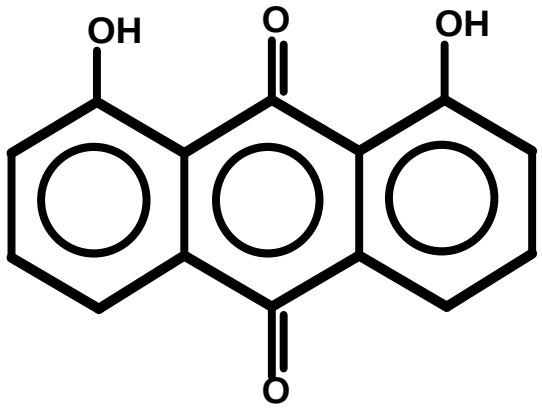
$$g = (E - H_{CC} - \Sigma_L - \Sigma_R)^{-1}$$

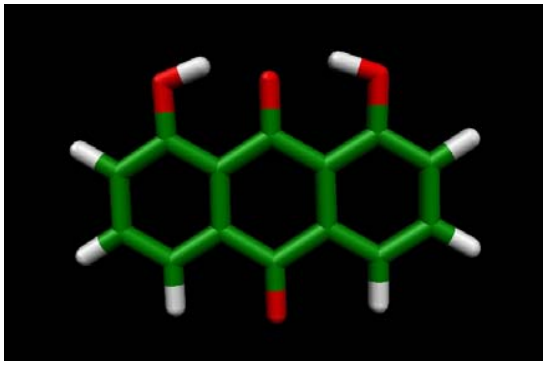
$$\Gamma_L = -i\left(\Sigma_L - \Sigma_L^{+}\right) \qquad \Gamma_R = -i\left(\Sigma_R - \Sigma_R^{+}\right)$$

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

Chrysazine

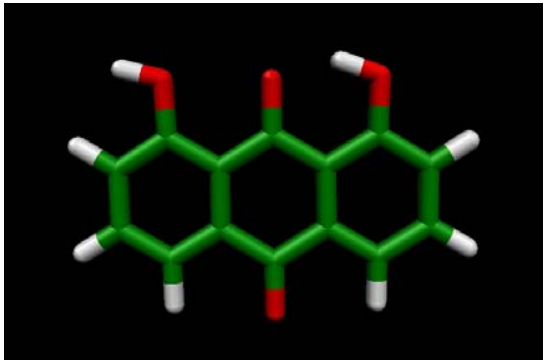
Relative Total Energies and HOMO-LUMO Gaps





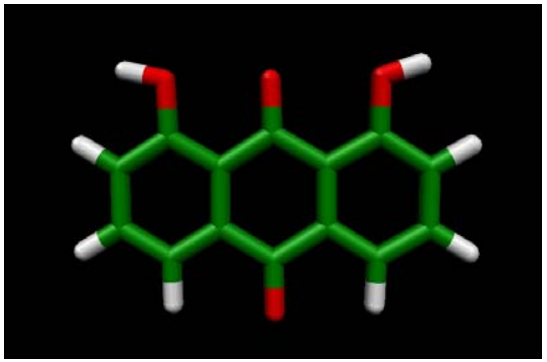
Chrysazine (a)

0.0 eV 3.35 eV



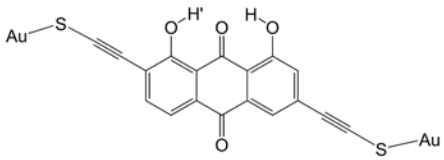
Chrysazine (b)

0.54 eV 3.41 eV

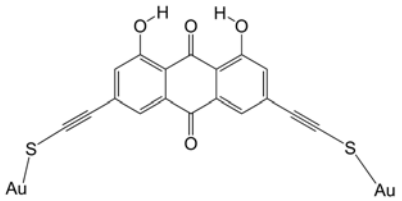


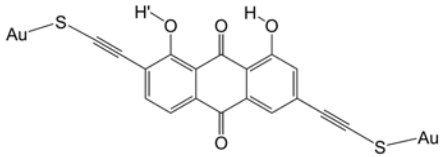
Chrysazine (c)

1.19 eV 3.77 eV

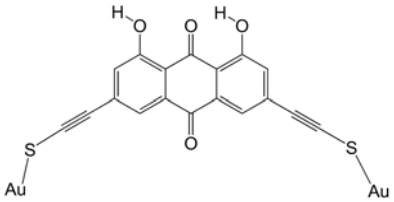

Au
S
O
H'
H
O
O
O
S
Au

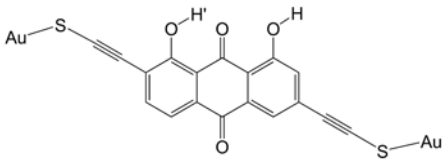
(a)


O
H
H
O
O
O
S
S
Au
Au

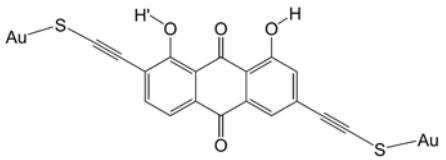

H'
O
H
O
Au
S
O
O
S
Au

(b)

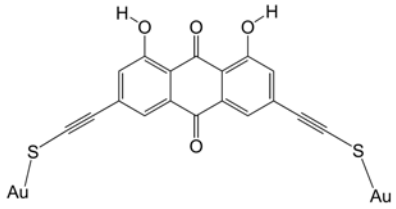

H
O
H
O
O
S
S
Au
Au


O
H'
O
H
Au
S
O
S
Au

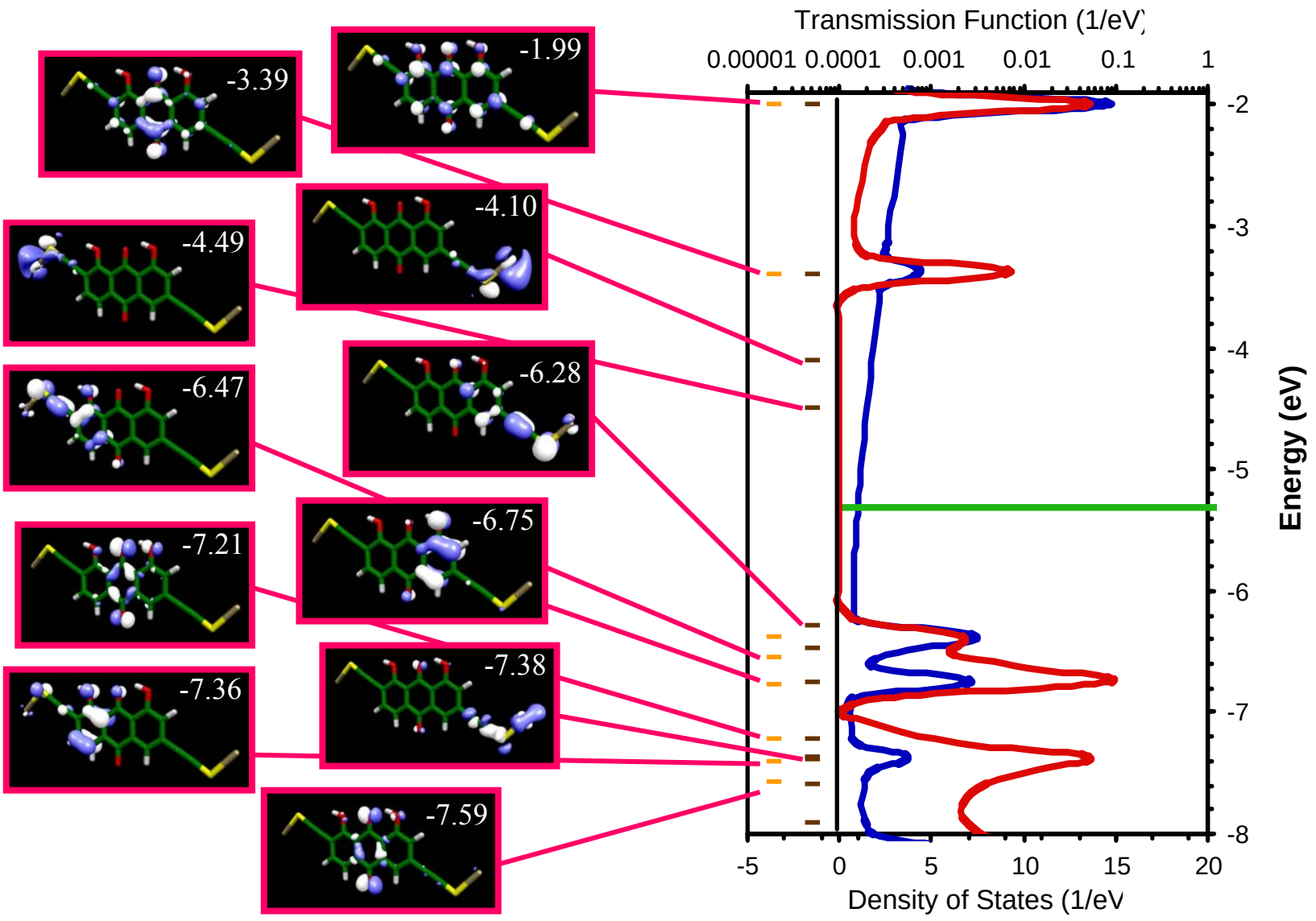
(b’)

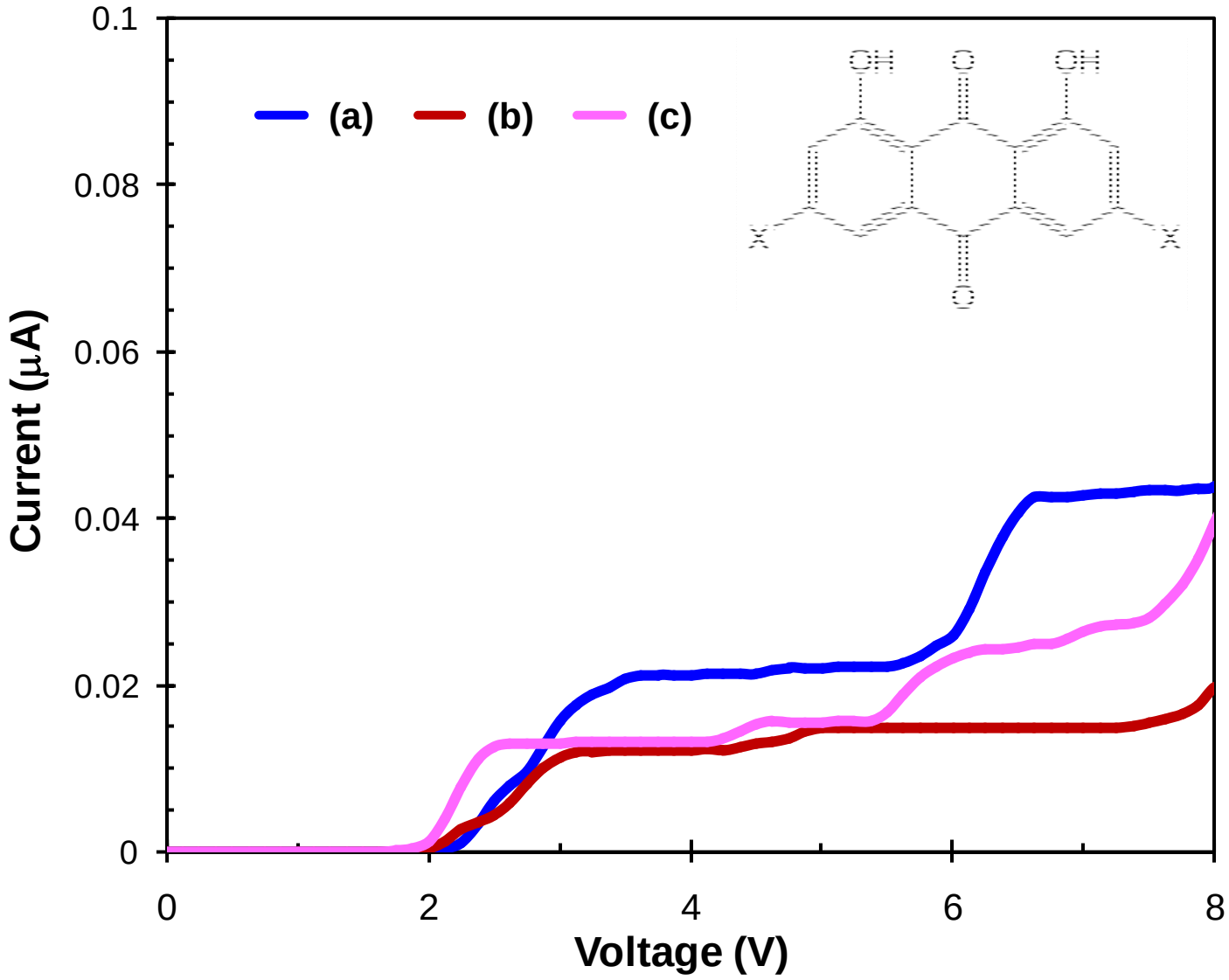

H'
O
O
O
H
Au
S
O
S
Au

(c)


H
O
O
O
H
S
S
Au
Au

Chrysazine (b)




0.1
0.08
0.06
0.04
0.02
0
Current (μA)
0
2
4
6
8
Voltage (V)
(a)
(b)
(c)
OH
O
OH
O

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

Two conceptual issues:

- Assumption that upon switching-on the bias a steady state evolves

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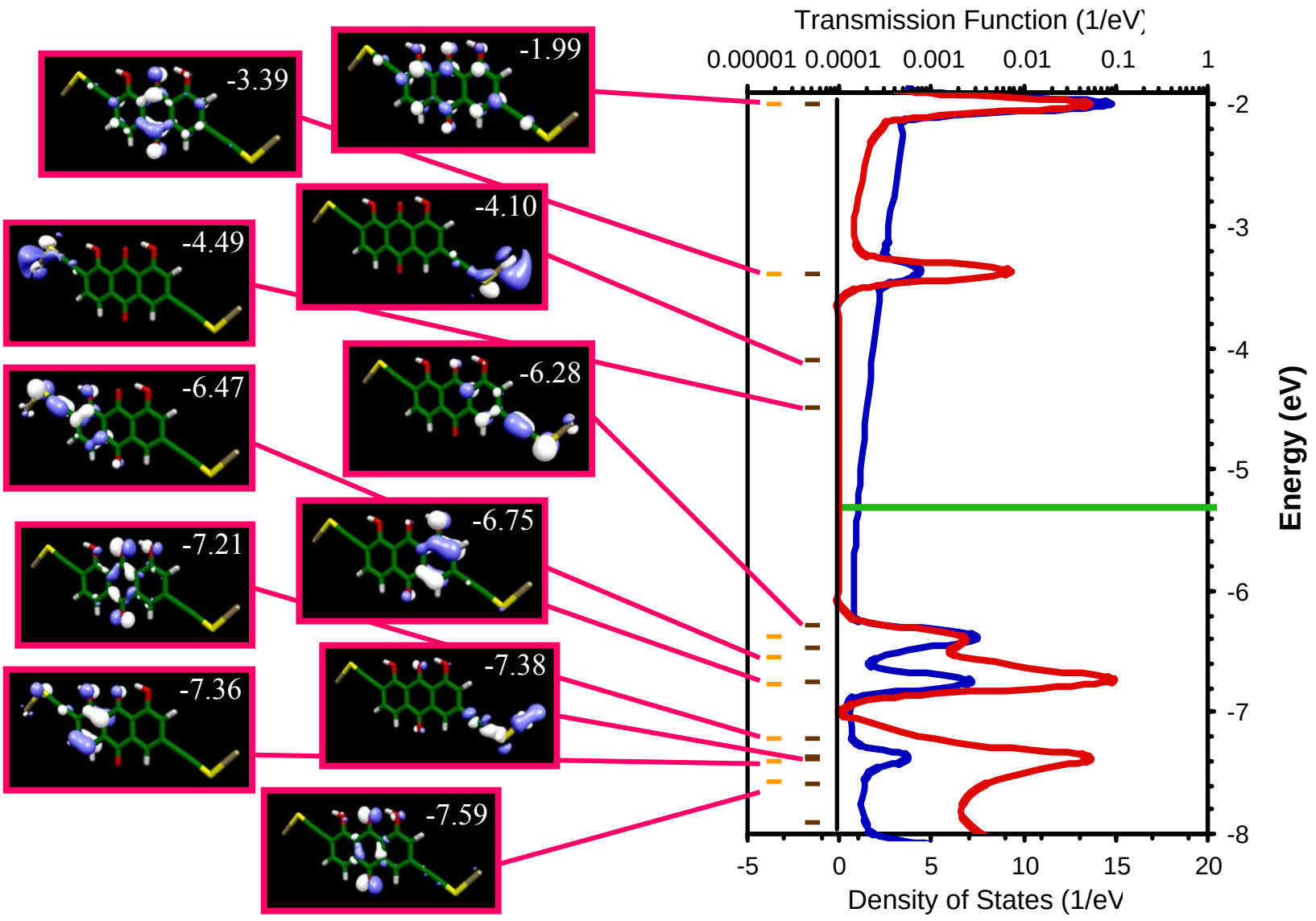
- Steady state is treated with ground-state DFT
  In particular, transmission function has peaks at the excitation energies of the gs KS potential.
  Hence, resonant tunneling occurs at wrong energies (even with the exact xc functional of gs DFT).

Chrysazine (b)



How serious is this problem?

Atom	Experimental Excitation Energies $^1S \rightarrow {}^1P$ (in Ry)	KS energy differences $\Delta \in_{KS}$ (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)

Two conceptual issues:

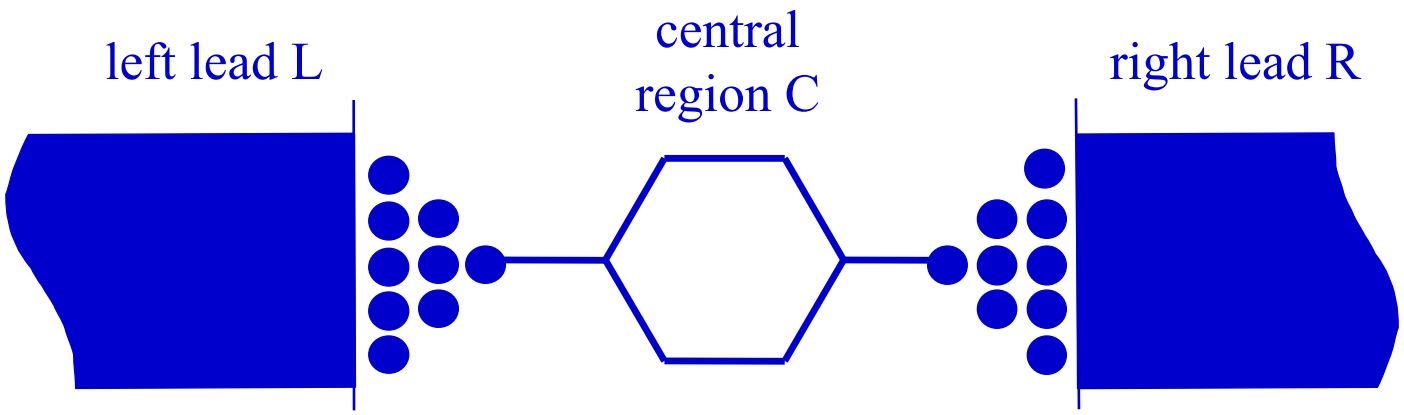
- Assumption that upon switching-on the bias a steady state evolves

- Steady state is treated with ground-state DFT
  In particular, transmission function has peaks at the excitation energies of the gs KS potential.
  Hence, resonant tunneling occurs at wrong energies (even with the exact xc functional of gs DFT).

One practical issue:

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

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)
- $H_{AB}(t) =$ corresponding grid - blocks of TDKS Hamiltonian

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

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

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

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

Hence:

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

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

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

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

Define Green's Functions of left and right leads:

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

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

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

explicity:

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

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

insert this in equation (C)

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)

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

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

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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

Note: This is a formally exact way of treating the decoherence coming from the coupling to the semi-infinite leads!

Necessary input to start time propagation:

- lead Green's functions G_L, G_R
- initial orbitals $\varphi_C(0)$ in central region as initial condition for time propagation

Calculation of lead Green's functions:

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

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

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

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

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

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

initial orbitals in C region

eigenstates of static KS Hamiltonian of the complete system

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

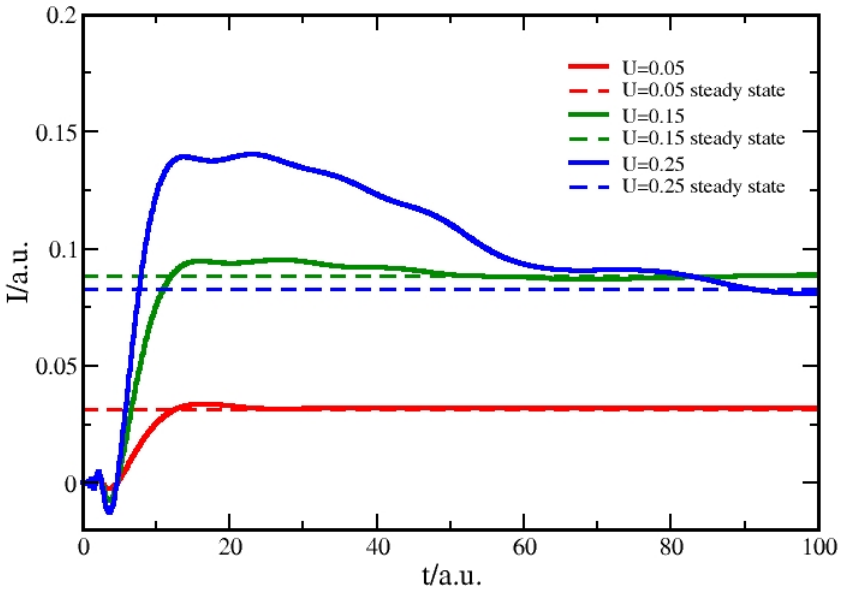
Gives effective static KS equation for central region

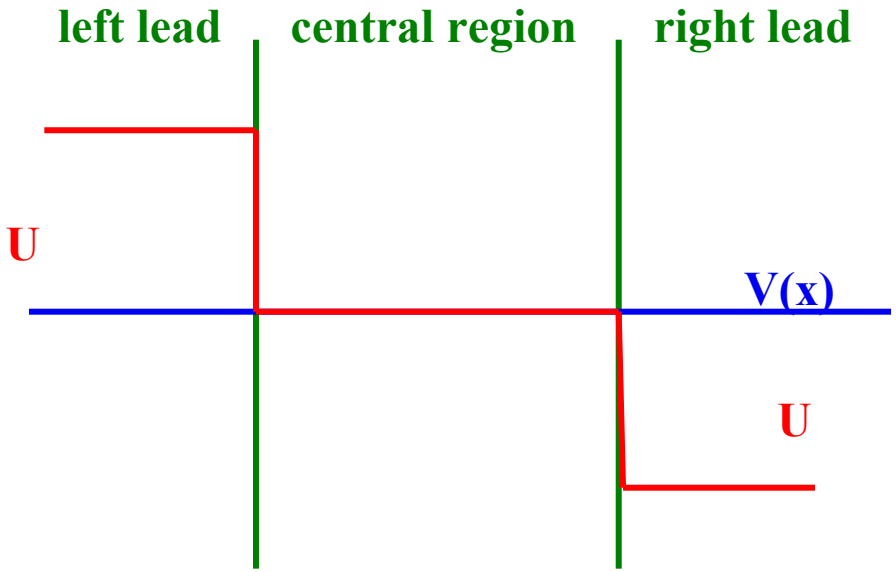
$$\left(H_{CC}^{stat} + H_{CL}^{stat} G_L^{stat}(E) H_{LC}^{stat} + H_{CR}^{stat} G_R^{stat}(E) H_{RC}^{stat} \right) \varphi_C^{(0)} = E \varphi_C^{(0)}$$

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.

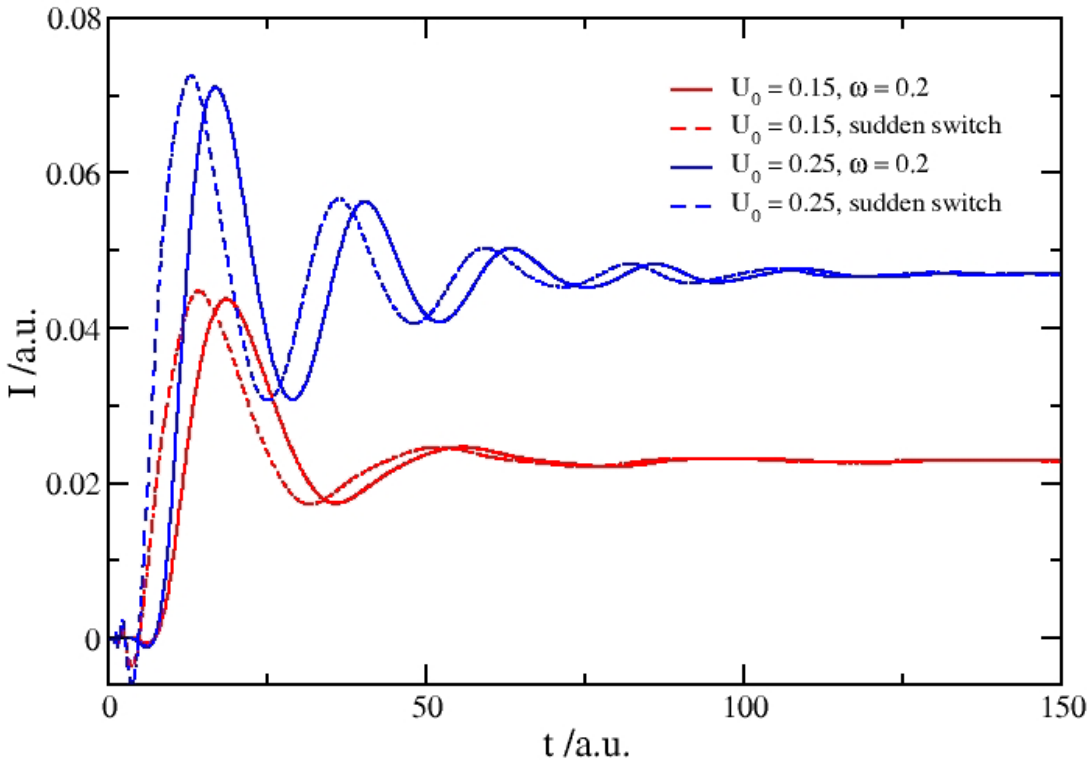
Steady state coincides with Landauer formula

and is reached after a few femtoseconds

Transients

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

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

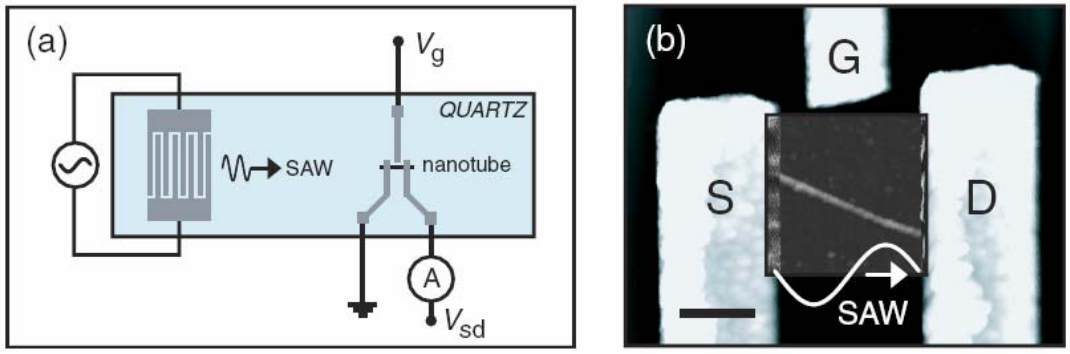


same steady state!

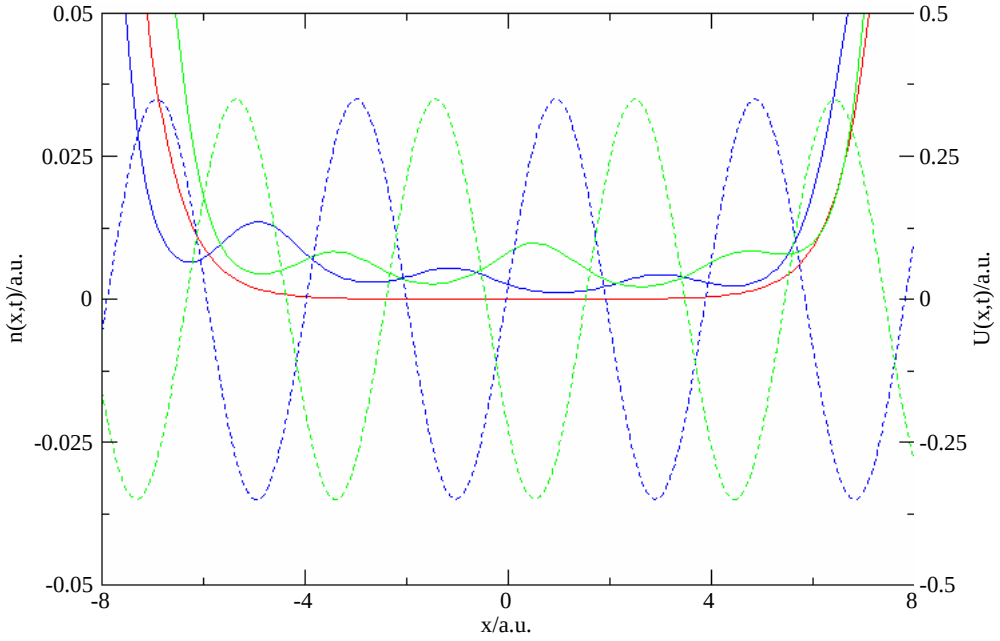
ELECTRON PUMP

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))

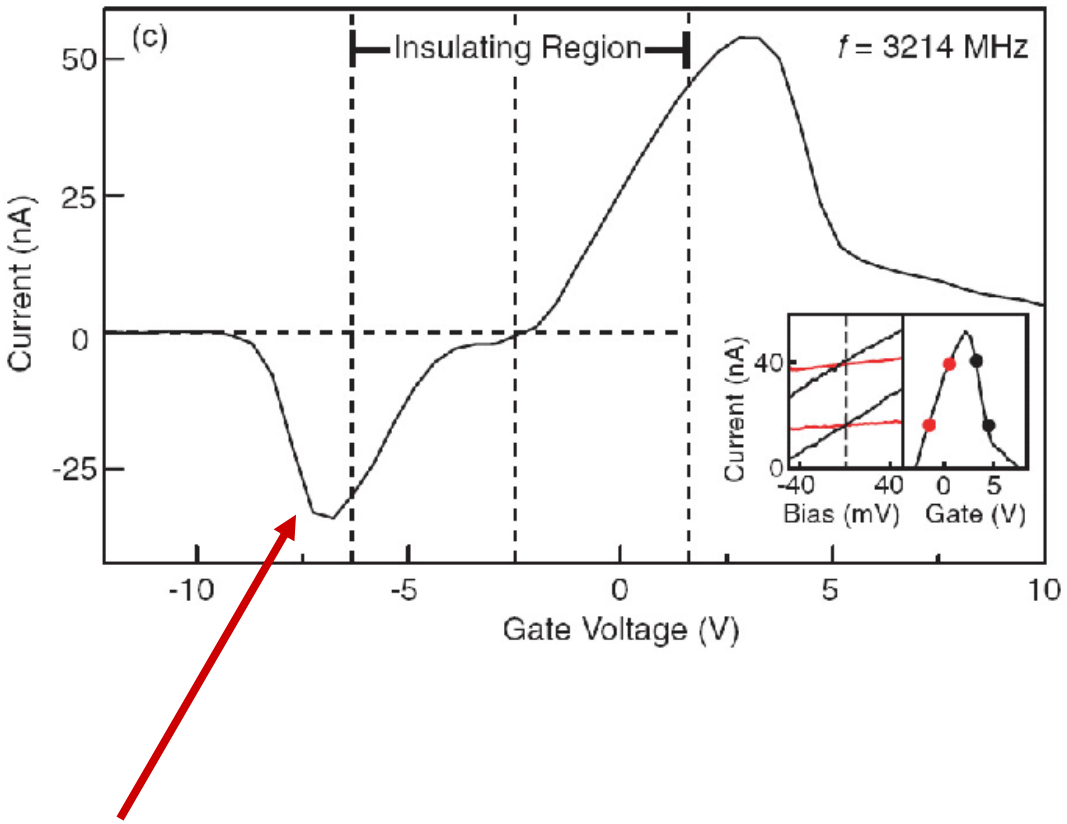


Pumping through a square barrier (of height 0.5 a.u.) using a travelling wave in device region $U(x,t) = U_o \sin(kx-\omega t)$ ($k = 1.6$ a.u., $\omega = 0.2$ a.u. Fermi energy = 0.3 a.u.)

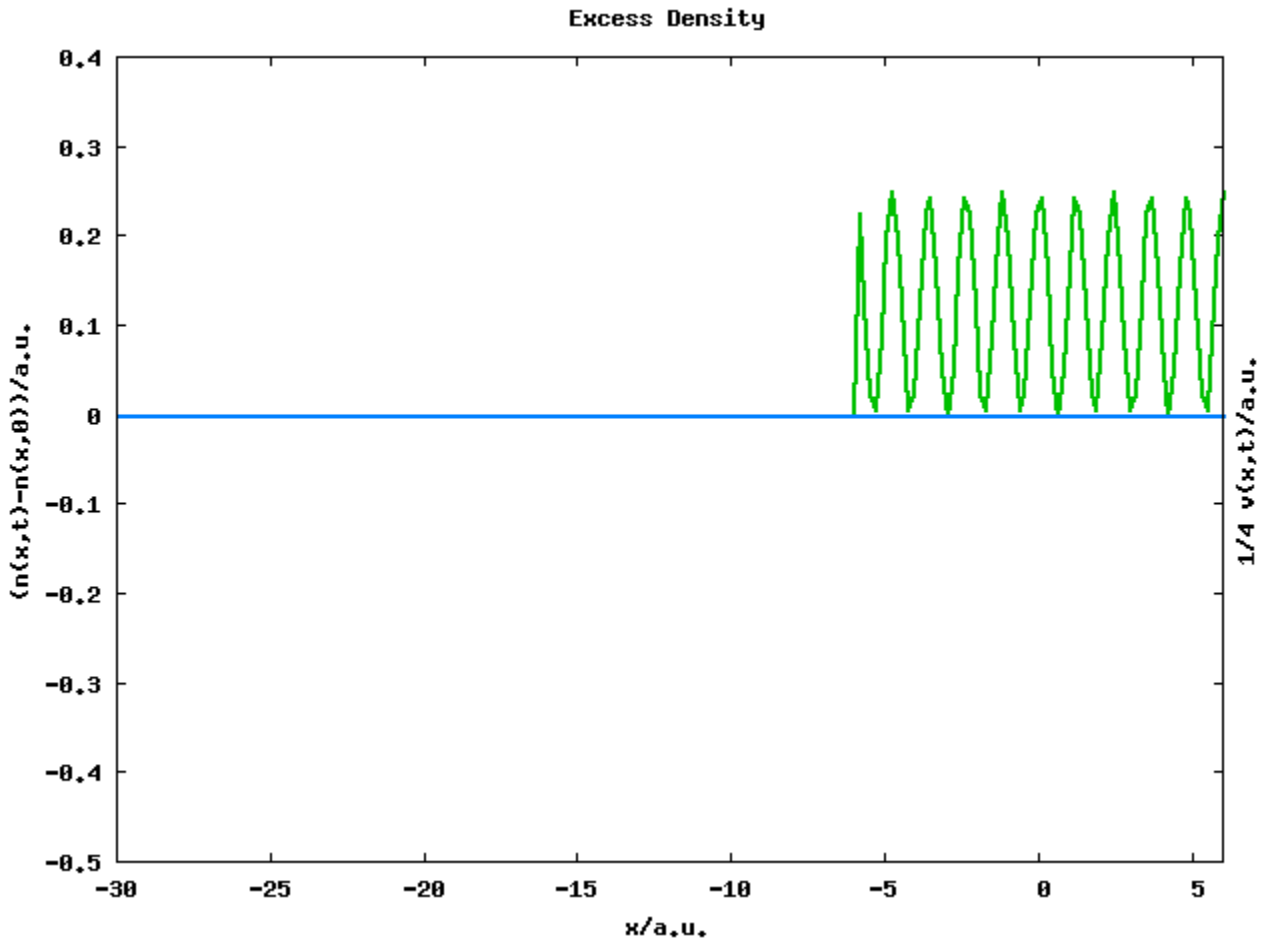


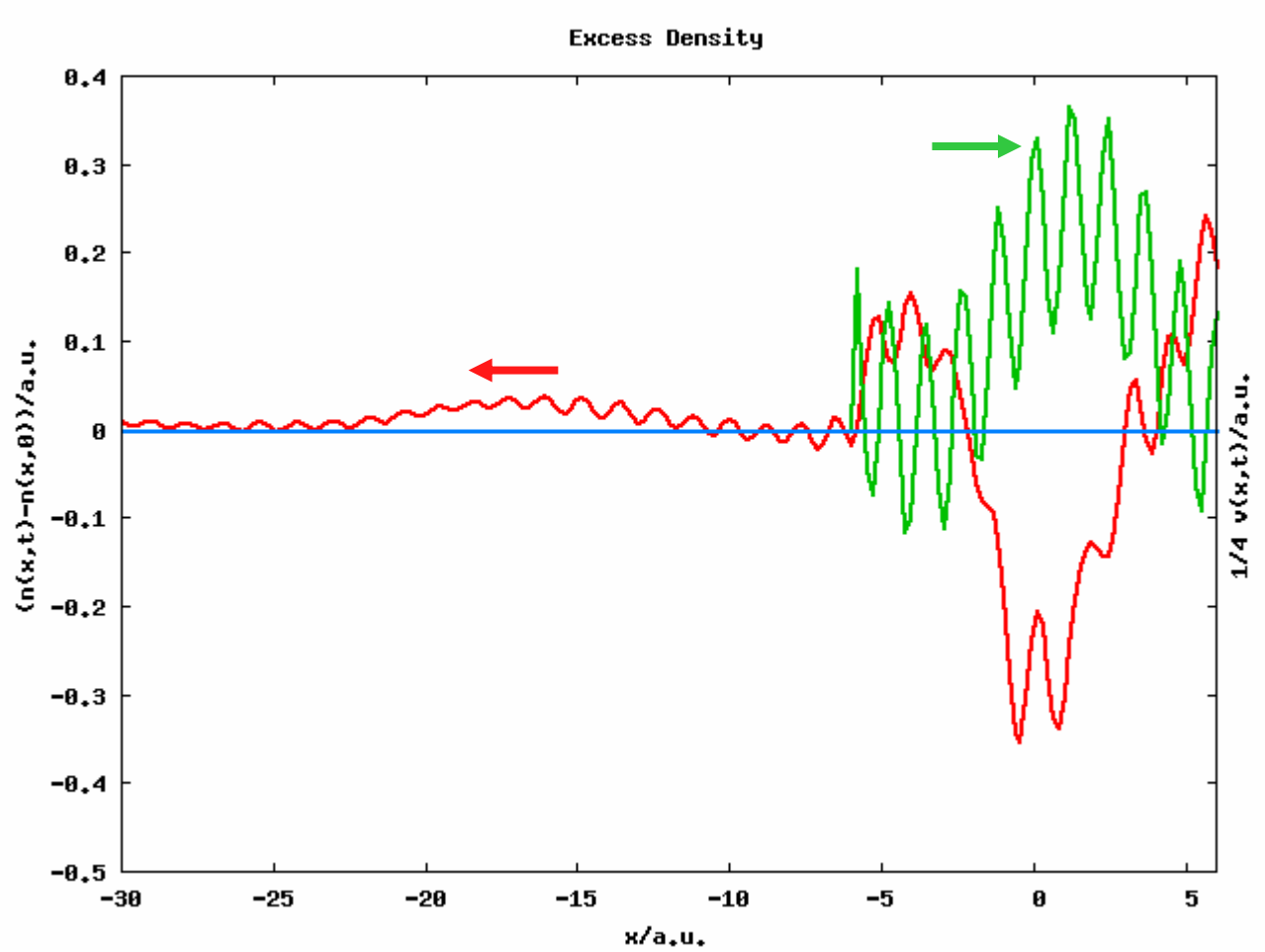
Archimedes' screw: patent 200 b.c.

Experimental result:



Current flows in direction opposite to sound wave

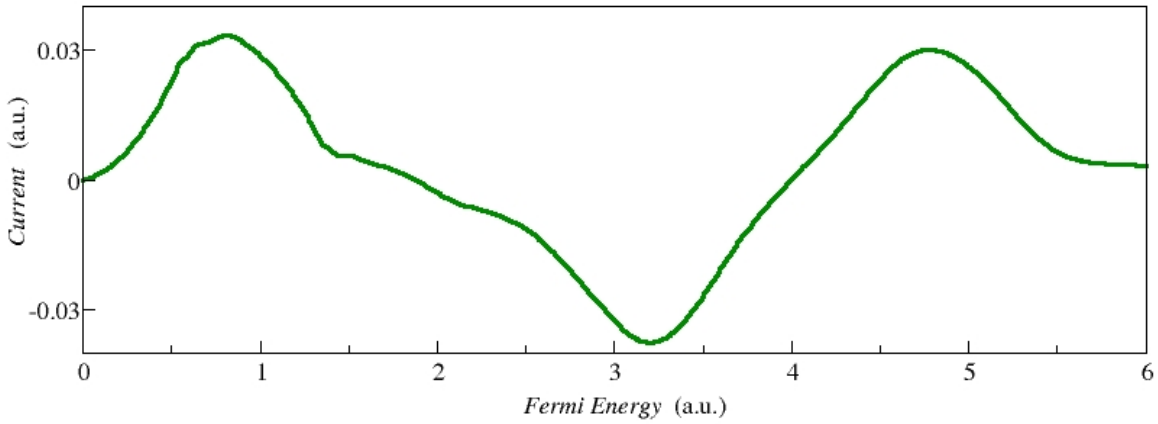

Excess Density
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
(n(x,t)-n(x,0))/a.u.
-30
-25
-20
-15
-10
-5
0
5
x/a.u.
1/4 v(x,t)/a.u.



Current goes in direction opposite to the external field !!

G. Stefanucci, S. Kurth, A. Rubio, E.K.U. Gross, Phys. Rev. B 77, 075339 (2008)

Time-averaged current



G. Stefanucci, S. Kurth, A. Rubio, E.K.U. Gross, Phys. Rev. B 77, 075339 (2008)

Bound state oscillations and memory effects

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

Numerical: E. Khosravi, S. Kurth, G. Stefanucci, E.K.U. Gross, 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 → 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

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

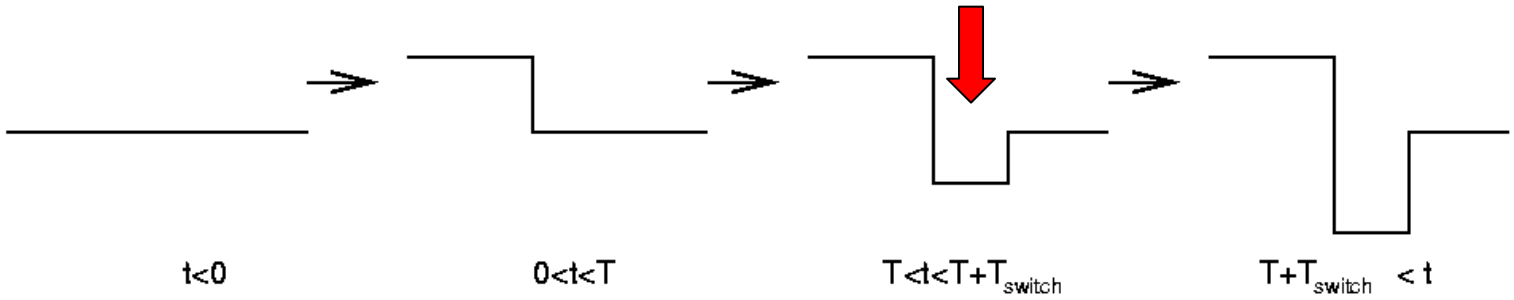
sum runs over the bound states of the biased Hamiltonian in the long-time limit.

Note: - Λ_{bb}, depends on history of time-dependent Hamiltonian (memory!)

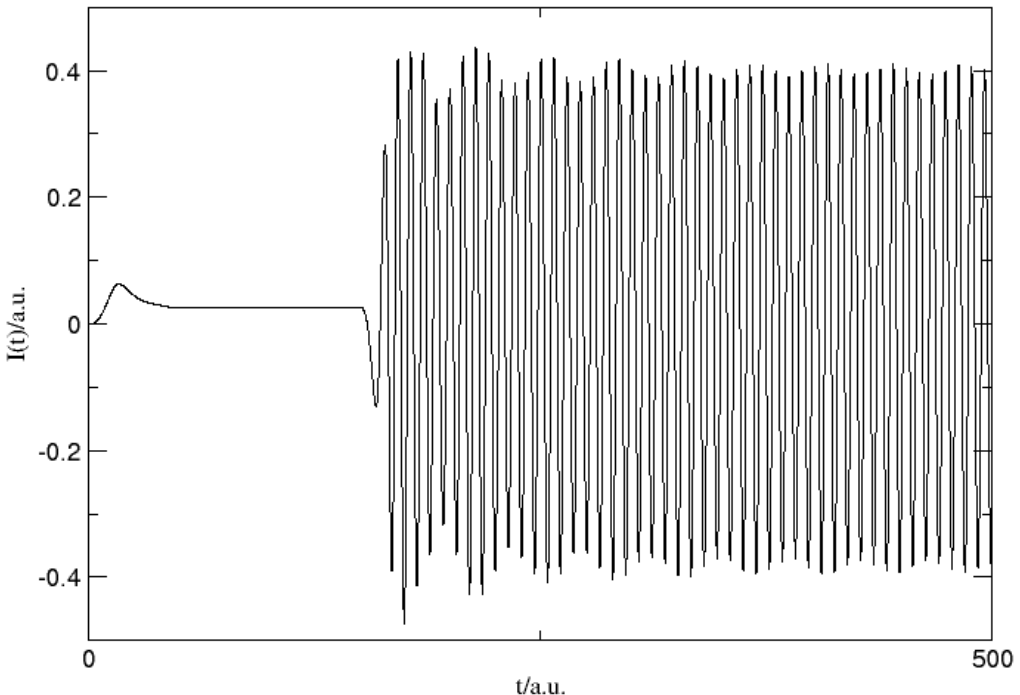
History dependence of undamped oscillations

1-D model:

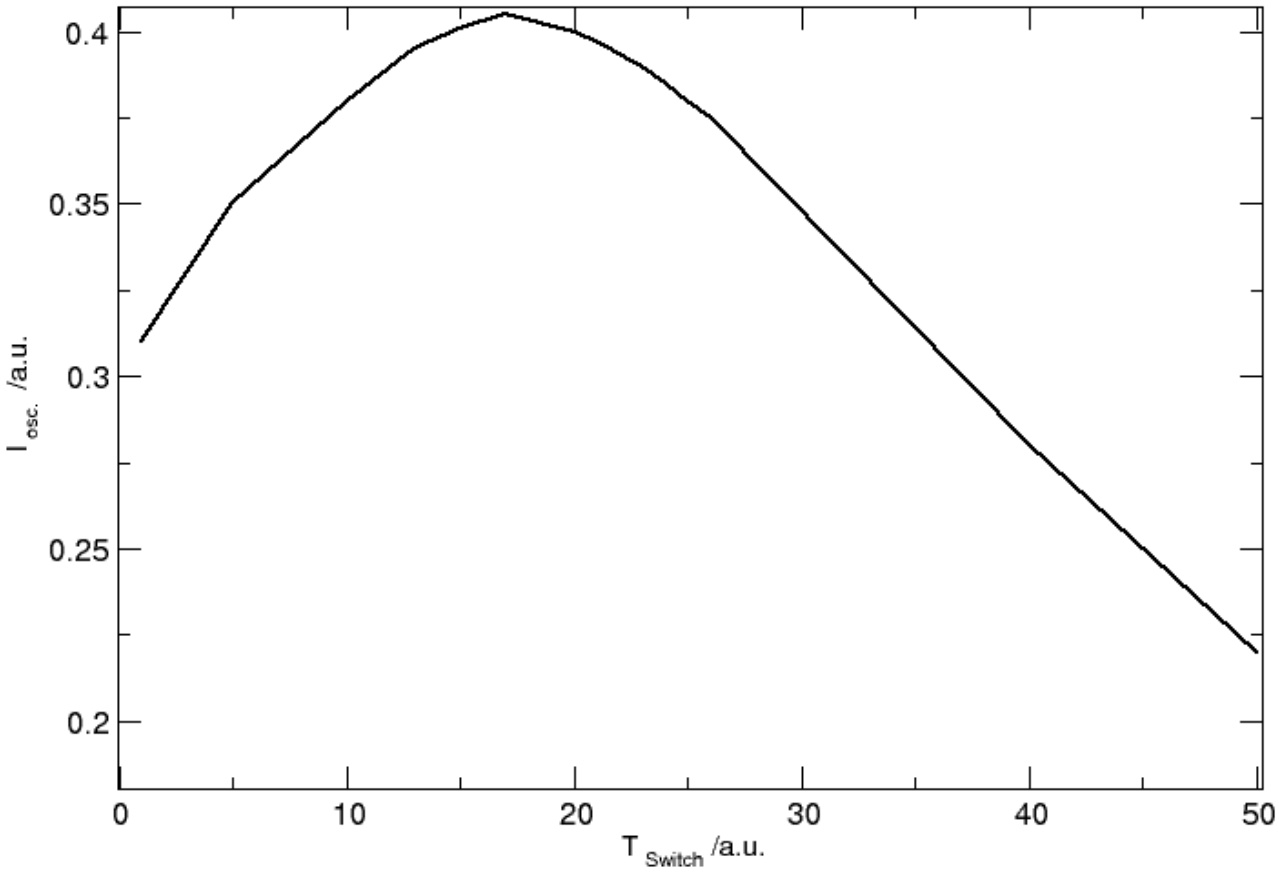
start with flat potential, switch on constant bias, wait until transients die out, switch on gate potential with different switching times to create two bound states



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



amplitude of current oscillations as function of switching time of gate



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

OPTIMAL CONTROL OF TIME-DEPENDENT TARGETS

Maximize $J = J_1 + J_2 + J_3$

$$J_1[\Psi] = \frac{1}{T}\int_0^T dt \left\langle \Psi(t) \middle| \hat{O}(t) \middle| \Psi(t) \right\rangle$$

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

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

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

Control equations

1. Schrödinger equation with initial condition:

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

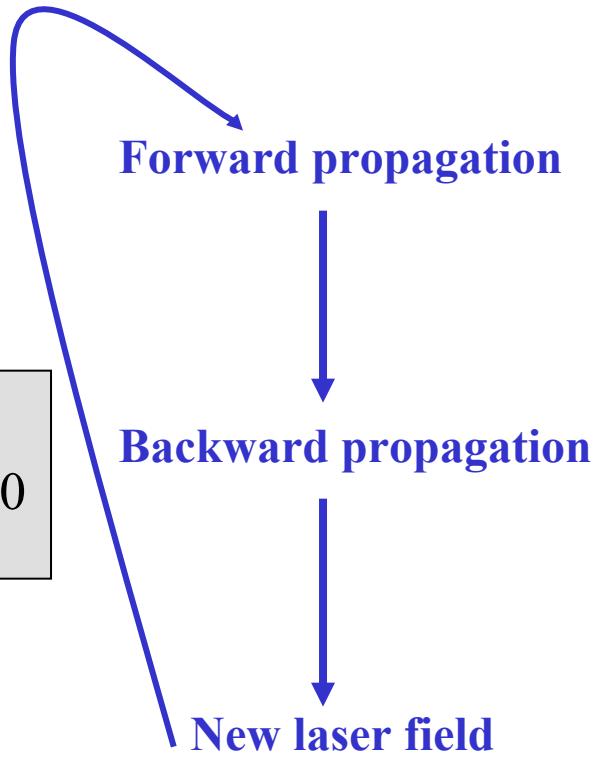
2. Schrödinger equation with final condition:

$$\delta_\psi J = 0 \rightarrow \boxed{\text{Inhomogenous TDSE}: \left[i\partial_t - \hat{H}(t)\right]\chi(t) = -\frac{i}{T}\hat{O}(t)\psi(t), \quad \chi(T) = 0}$$

3. Field equation:

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

Algorithm



Y. Ohtsuki, G. Turinici, H. Rabitz, JCP 120, 5509 (2004)
I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

Control of path in Hilbert space

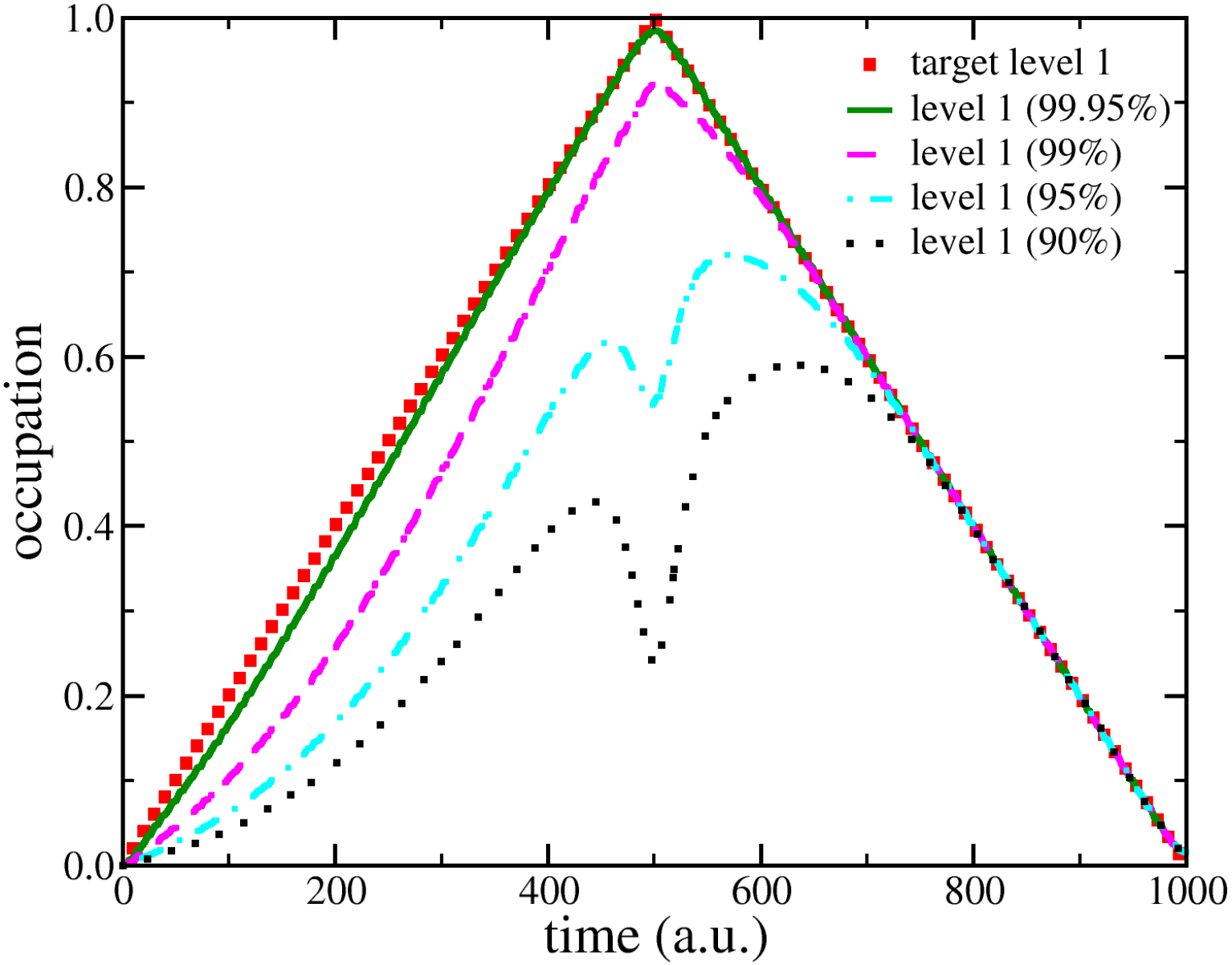
I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

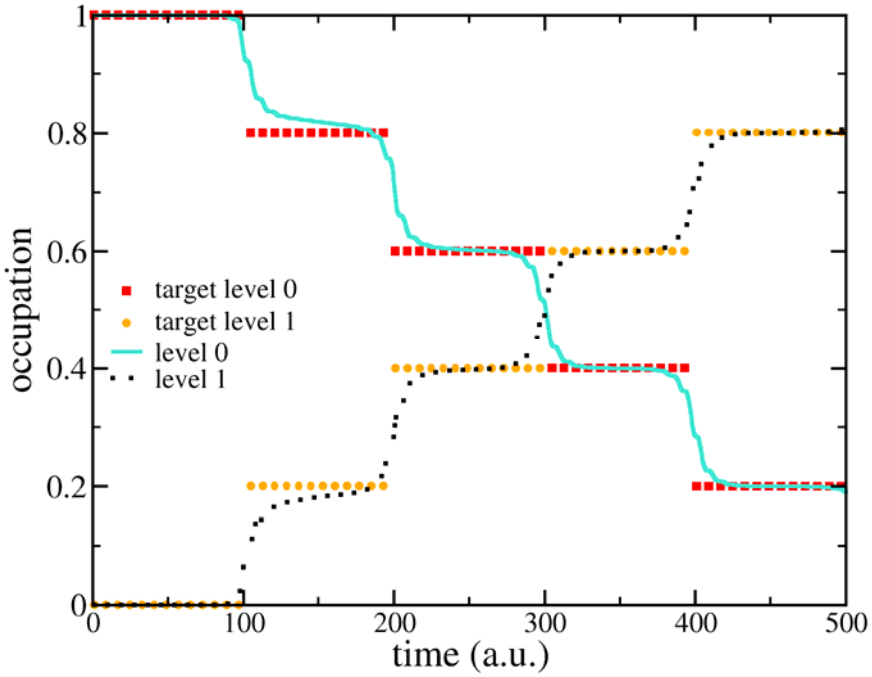
$$\hat{O}(t) = |\Phi(t)\rangle\langle\Phi(t)|$$

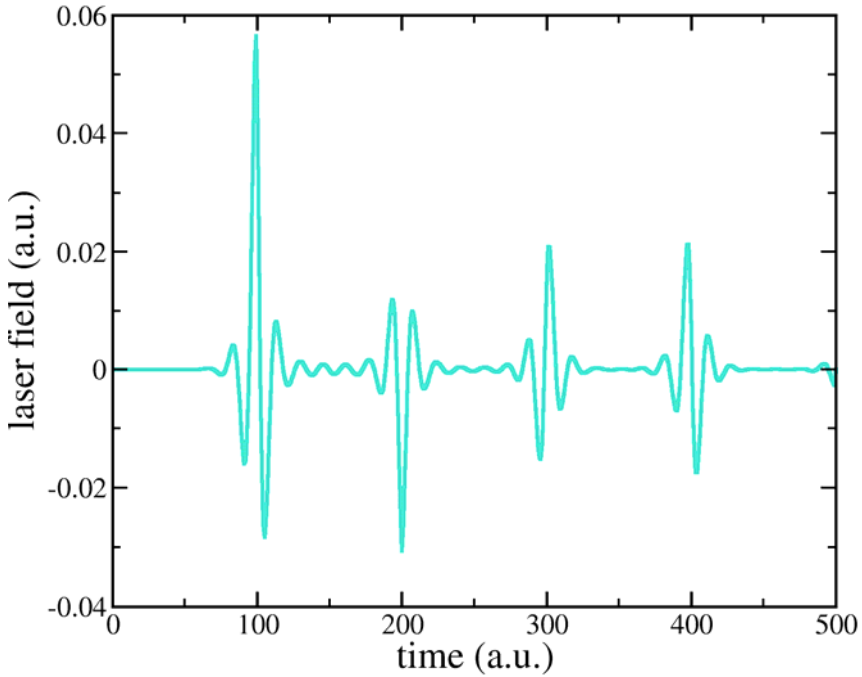
with $$|\Phi(t)\rangle = \alpha_0(t)e^{-i\varepsilon_o t}|0\rangle + \alpha_1(t)e^{-i\varepsilon_1 t}|1\rangle$$

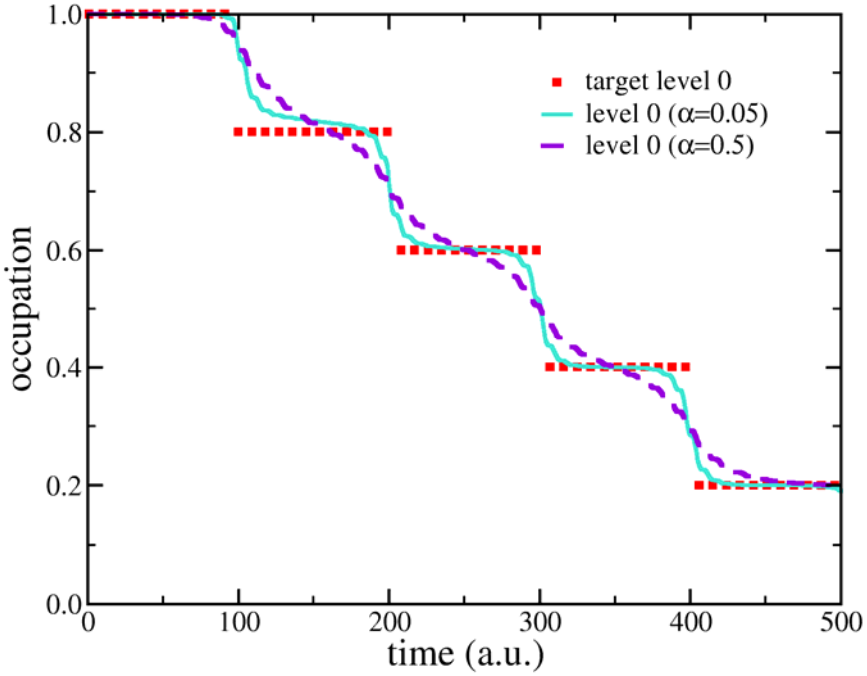
$|\alpha_0(t)|^2$ **given target occupation, and** $|\alpha_1(t)|^2 = 1 - |\alpha_0(t)|^2$

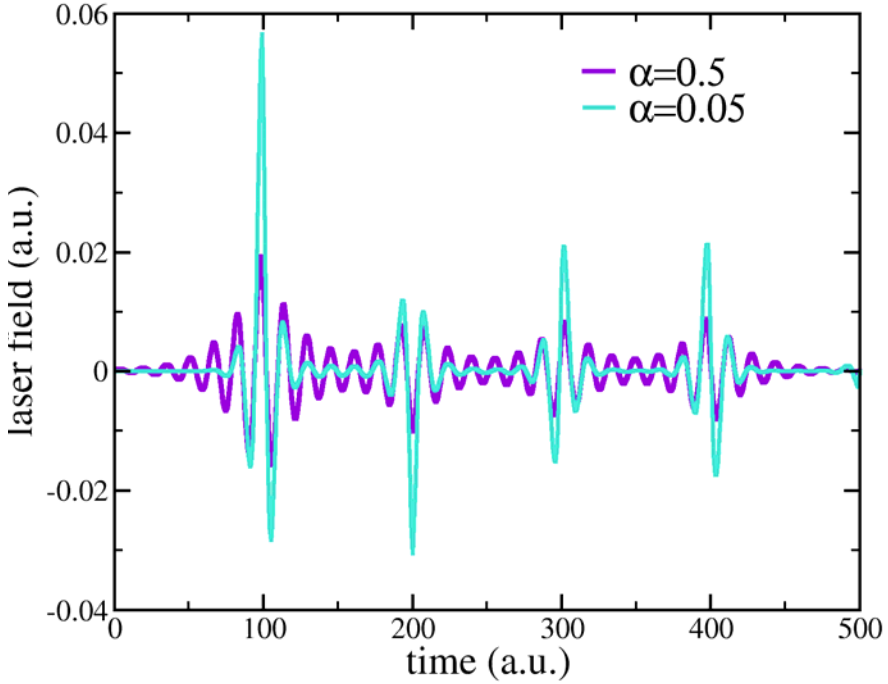
Goal: Find laser pulse that reproduces $|\alpha_o(t)|^2$


target level 1
level 1 (99.95%)
level 1 (99%)
level 1 (95%)
level 1 (90%)
occupation
time (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
0
200
400
600
800
1000


occupation
time (a.u.)
target level 0
target level 1
level 0
level 1
0
0.2
0.4
0.6
0.8
1
0
100
200
300
400
500


laser field (a.u.)
time (a.u.)
0.06
0.04
0.02
0
-0.02
-0.04
0
100
200
300
400
500


target level 0
level 0 (α=0.05)
level 0 (α=0.5)
occupation
time (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500


α=0.5
α=0.05
laser field (a.u.)
time (a.u.)
-0.04
-0.02
0
0.02
0.04
0.06
0
100
200
300
400
500

Control path in real space

$$\hat{O}(t) = \delta(r - r_0(t)) \approx \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(r-r_0(t))^2/2\sigma^2}$$

with <u>given</u> trajectory $r_0(t)$**.**

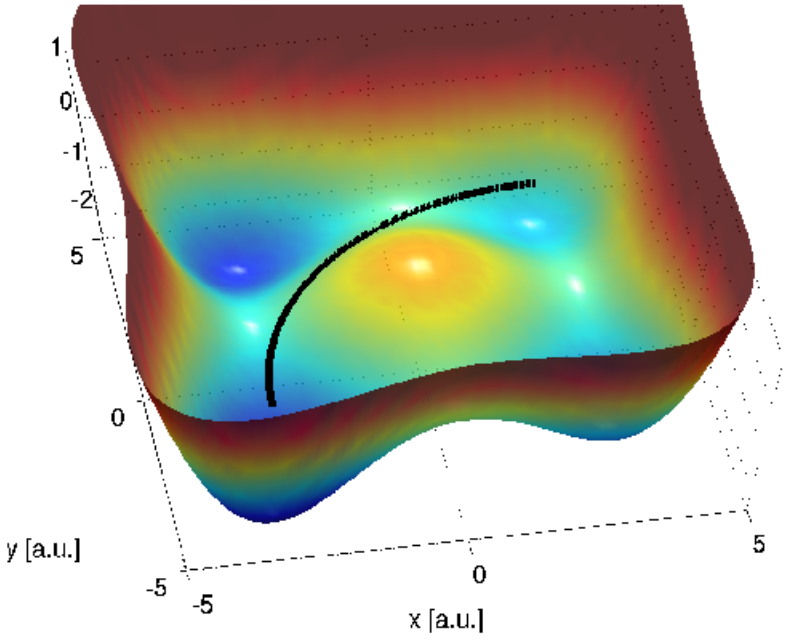
Algorithm maximizes the density along the path $r_0(t)$:

I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

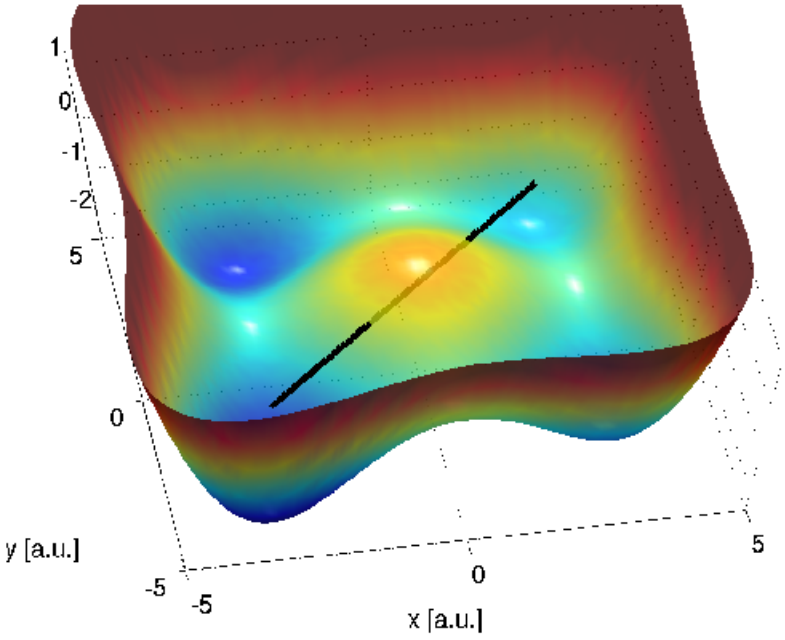
J. Werschnik and E.K.U.G., in: Physical Chemistry of Interfaces and Nanomaterials V, M. Spitler and F. Willig, eds, Proc. SPIE 6325, 63250Q(1-13) (doi: 10.1117/12.680065)

Control of charge transfer along selected pathways

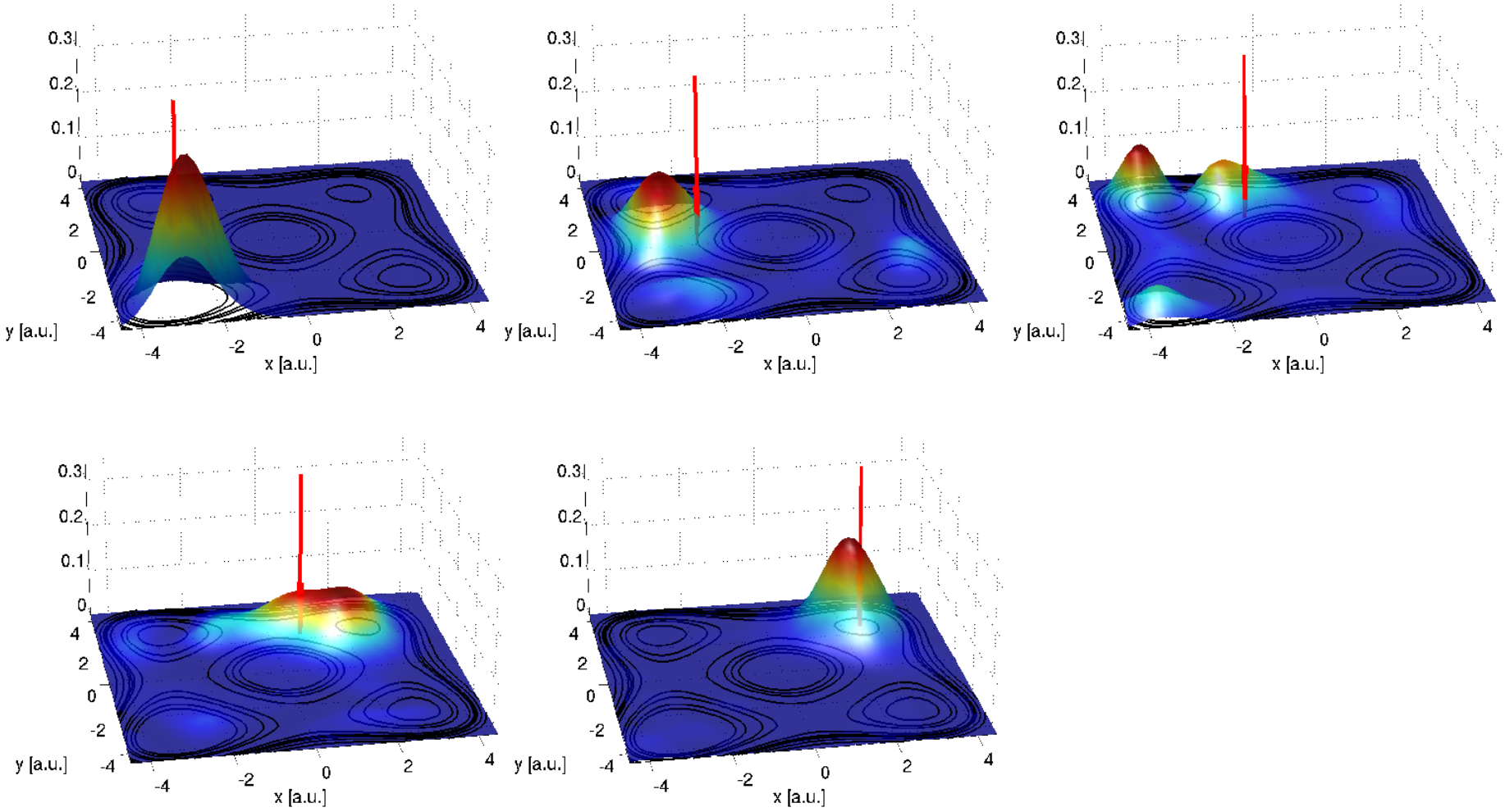
Trajectory 1



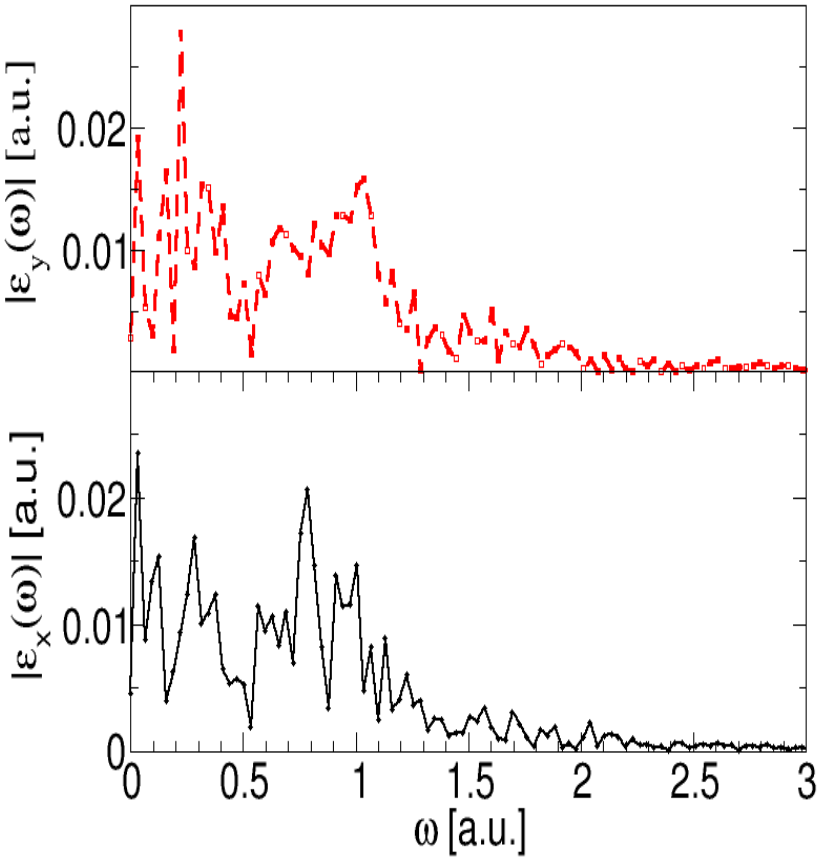
Trajectory 2



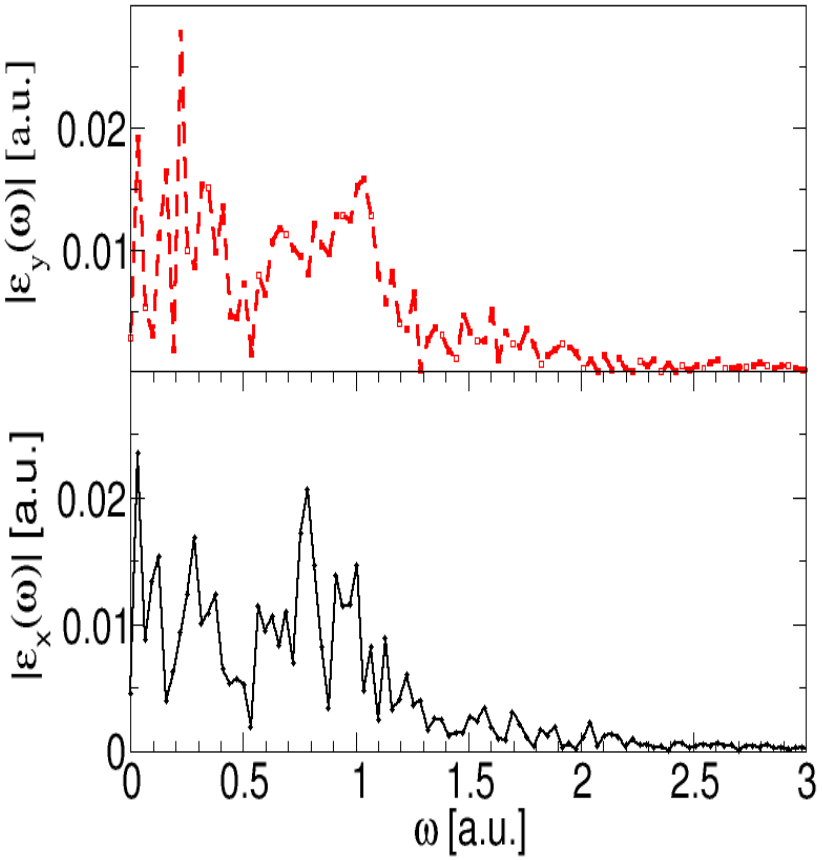
Time-evolution of wavepacket with the optimal laser pulse for trajectory 1



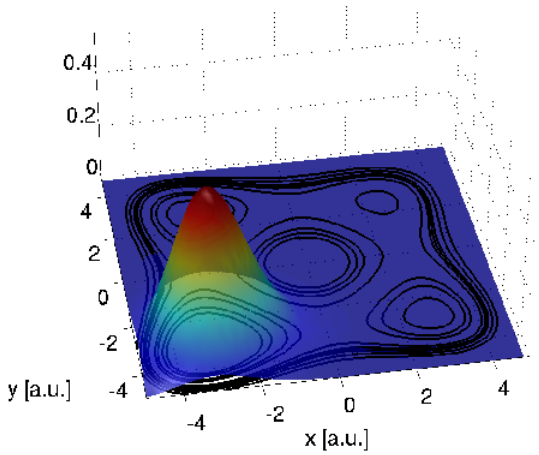
Optimal pulse

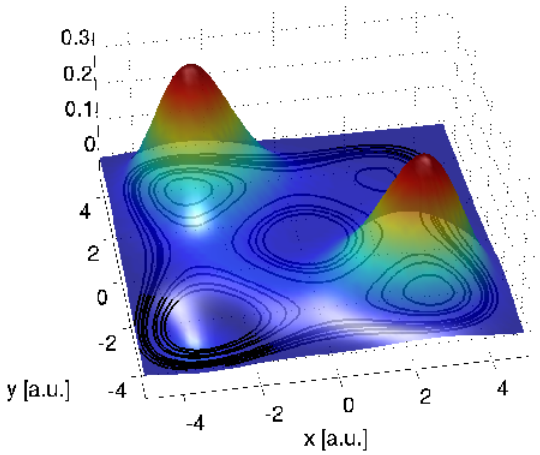


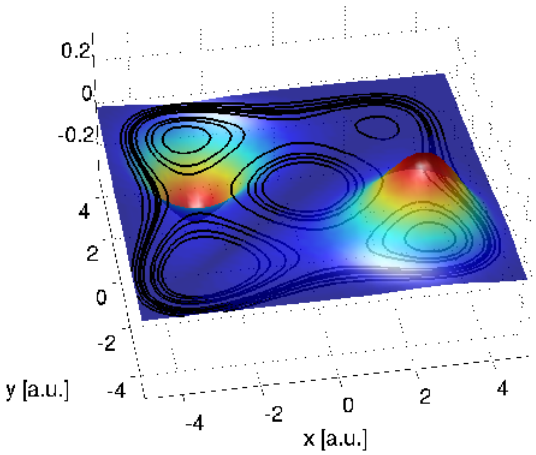
Optimal pulse

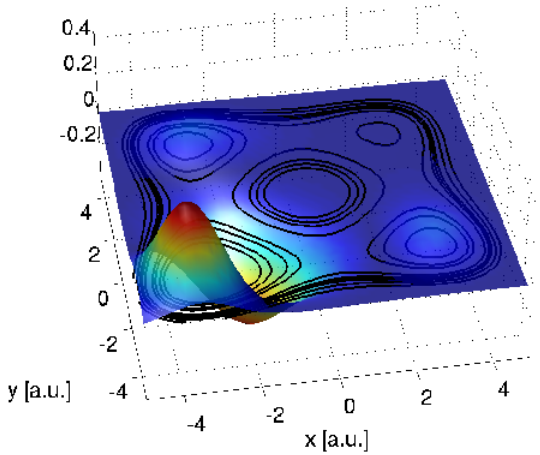


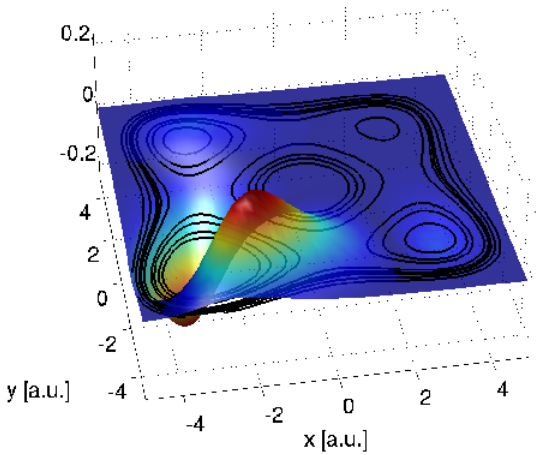
Lowest six eigenstates

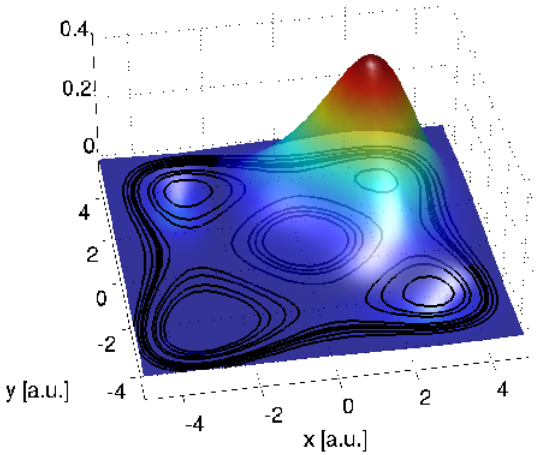




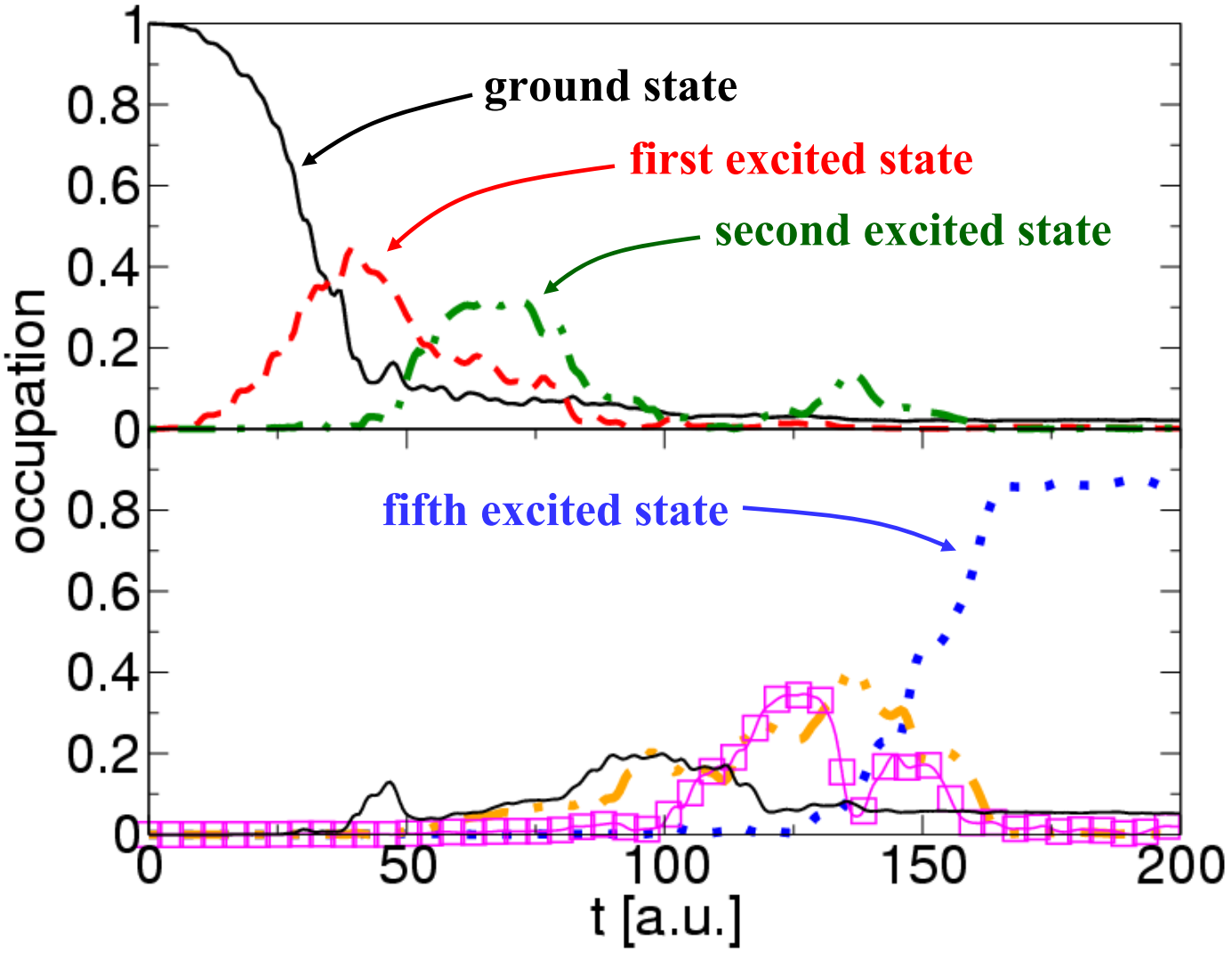




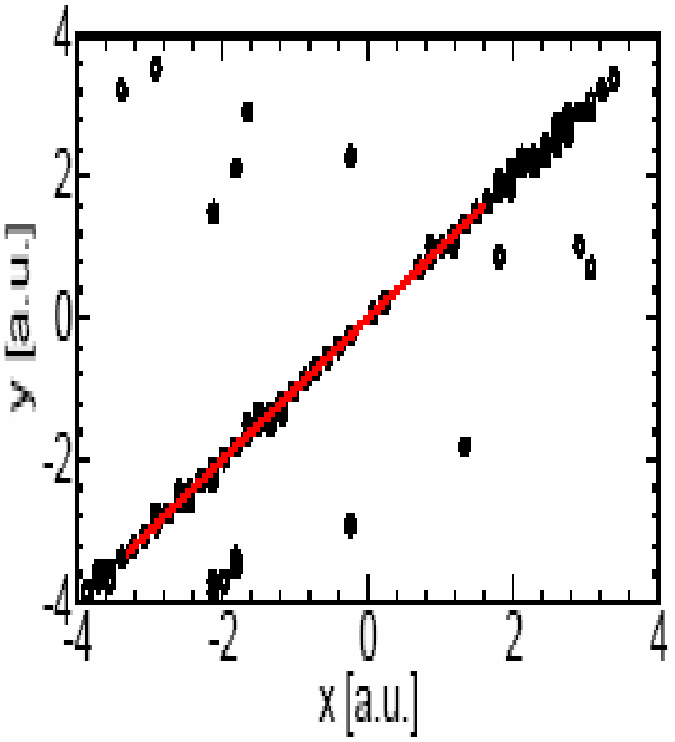


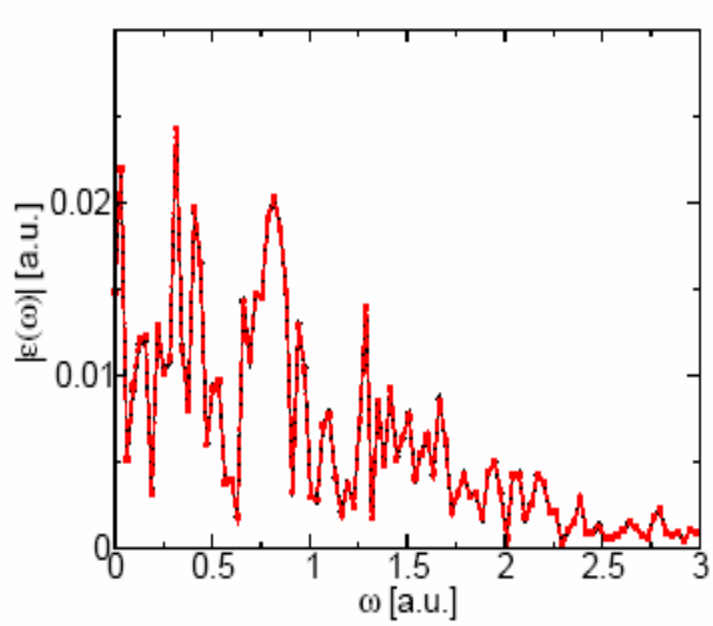


Populations of eigenstates



Trajectory 2





Red: <r>(t)

Black: position of maximum of density

Optimal pulse

Thanks to

S. Kurth
G.L. Stefanucci
H. Appel
A. Zacarias
D. Nitsche
E. Khosravi
I. Serban
J. Werschnik

} FU Berlin

A. Rubio (San Sebastian)
C. O. Almbladh (Lund)

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SFB 450
SFB 658

Outlook

- **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
- **OCT with leads**