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: $U(t) \rightarrow V$ 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
Control the path of the current with laser

left lead

right lead
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

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

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!)

\[
\begin{pmatrix}
H_{LL}^{\text{stat}} & H_{LC}^{\text{stat}} & 0 \\
H_{CL}^{\text{stat}} & H_{CC}^{\text{stat}} & H_{CR}^{\text{stat}} \\
0 & H_{RC}^{\text{stat}} & H_{RR}^{\text{stat}}
\end{pmatrix}
\begin{pmatrix}
\phi_L \\
\phi_C \\
\phi_R
\end{pmatrix}
= E
\begin{pmatrix}
\phi_L \\
\phi_C \\
\phi_R
\end{pmatrix}
\]

Define Green’s functions of the static leads

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

\[
\left( E - H_{RR}^{\text{stat}} \right) G_{R}^{\text{stat}} (E) = \mathbb{1}
\]
Substitute $\varphi_L$ and $\varphi_R$ in equation for central region

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

Effective KS equation for the central region

$$\Sigma_L := H_{CL}G_LH_{LC} \quad \Sigma_R := H_{CR}G_RH_{RC}$$

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

$$\Gamma_L = i(\Sigma_L - \Sigma_L^+) \quad \Gamma_R = i(\Sigma_R - \Sigma_R^+)$$

$$\Gamma = \text{trace}(\Gamma_L g \Gamma_R g^+)$$

### Chrysazine

Relative Total Energies and HOMO-LUMO Gaps

<table>
<thead>
<tr>
<th>Chrysazine</th>
<th>Relative Total Energy</th>
<th>HOMO-LUMO Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrysazine 1</td>
<td>0.0 eV</td>
<td>3.35 eV</td>
</tr>
<tr>
<td>Chrysazine 2</td>
<td>0.54 eV</td>
<td>3.41 eV</td>
</tr>
<tr>
<td>Chrysazine 3</td>
<td>1.19 eV</td>
<td>3.77 eV</td>
</tr>
</tbody>
</table>
Relative Total Energies and HOMO-LUMO Gaps

Chrysazine 1
0.0 eV  1.93 eV

Chrysazine 2a
0.70 eV  1.67 eV

Chrysazine 2b
0.57 eV  1.79 eV

Energy (eV)
Transmission Function (1/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.
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?

<table>
<thead>
<tr>
<th>Atom</th>
<th>Experimental Excitation Energies $^1S \rightarrow ^1P$ (in Ry)</th>
<th>KS energy differences $\Delta\varepsilon_{KS}$ (Ry)</th>
<th>TDDFT response (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.388</td>
<td>0.259</td>
<td>0.391</td>
</tr>
<tr>
<td>Mg</td>
<td>0.319</td>
<td>0.234</td>
<td>0.327</td>
</tr>
<tr>
<td>Ca</td>
<td>0.216</td>
<td>0.157</td>
<td>0.234</td>
</tr>
<tr>
<td>Zn</td>
<td>0.426</td>
<td>0.315</td>
<td>0.423</td>
</tr>
<tr>
<td>Sr</td>
<td>0.198</td>
<td>0.141</td>
<td>0.210</td>
</tr>
<tr>
<td>Cd</td>
<td>0.398</td>
<td>0.269</td>
<td>0.391</td>
</tr>
</tbody>
</table>

**Molecular Electronics with TDDFT**

left lead L  central region C  right lead R

**TDKS equation**

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

**Propagate TDKS equation on spatial grid**

- \( \varphi_A(t) = \text{vector}(\varphi(r_1, t), \varphi(r_2, t), \ldots) \) with grid points \( r_1, r_2, \ldots \) in region \( A \) (\( A = L, C, R \))

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

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

\[
H_{CL}, H_{LC}, H_{CR}, H_{RC} \text{ are time-independent}
\]

\[
H_{LR} = H_{RL} = 0
\]
\[
\begin{align*}
\mathbf{H}(t) &= \begin{pmatrix}
H_{LL}(t) & H_{LC} & H_{LR}(t) \\
H_{CL} & H_{CC}(t) & H_{CR}(t) \\
H_{RL}(t) & H_{RC} & H_{RR}(t)
\end{pmatrix}
\end{align*}
\]

Hence:

\[
\begin{align*}
\left( i \frac{\partial}{\partial t} - H_{LL}(t) \right) \varphi_L(t) &= H_{LC} \varphi_C(t) \\
i \frac{\partial}{\partial t} \varphi_C(t) &= H_{CL} \varphi_L(t) + H_{CC}(t) \varphi_C(t) + H_{CR} \varphi_R(t) \\
\left( i \frac{\partial}{\partial t} - H_{RR}(t) \right) \varphi_R(t) &= H_{RC} \varphi_C(t)
\end{align*}
\]

Next step: Solve inhomogeneous Schrödinger equations for \( \varphi_L, \varphi_R \) using Green’s functions of L, R, leads

Define Green’s Functions of left and right leads:

\[
\begin{align*}
\left( i \frac{\partial}{\partial t} - H_{LL}(t) \right) G_L(t, t') &= \delta(t - t') \\
i \frac{\partial}{\partial t} G_R(t, t') &= \delta(t - t')
\end{align*}
\]

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

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

Explicitly:

\[
\begin{align*}
\varphi_L(t) &= \int_0^t dt' G_L(t, t') H_{LC} \varphi_C(t') + i G_L(t, 0) \varphi_L(0) \\
\varphi_R(t) &= \int_0^t dt' G_R(t, t') H_{RC} \varphi_C(t') + i G_R(t, 0) \varphi_R(0)
\end{align*}
\]

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.,

\[
\frac{i}{\partial t} \phi_C(t) = H_{cc}(t)\phi_C(t) + \int_0^t dt' [H_{cl} G_L(t, t')H_{lc} + H_{cr} G_R(t, t')H_{rc}]\phi_C(t') + iH_{cl} G_L(t, 0)\phi_L(0) + iH_{cr} G_R(t, 0)\phi_R(0)
\]

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

Necessary input to start time propagation:

- lead Green’s functions \( G_L, G_R \)
- initial orbitals \( \phi_C(0) \) in central region as initial condition for time propagation
- initial orbitals \( \phi_L(0), \phi_R(0) \) in leads (for source terms)
Calculation of lead Green’s functions:

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

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

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

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

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

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

initial orbitals in C region

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

\[
\begin{pmatrix}
H_{\text{stat}}^{LL} & H_{\text{stat}}^{LC} & 0 \\
H_{\text{stat}}^{CL} & H_{\text{stat}}^{CC} & H_{\text{stat}}^{CR} \\
0 & H_{\text{stat}}^{RC} & H_{\text{stat}}^{RR}
\end{pmatrix}
\begin{pmatrix}
\phi_L^{(0)} \\
\phi_C^{(0)} \\
\phi_R^{(0)}
\end{pmatrix}
= E
\begin{pmatrix}
\phi_L^{(0)} \\
\phi_C^{(0)} \\
\phi_R^{(0)}
\end{pmatrix}
\]
Define Green’s functions of the static leads

\[
\begin{align*}
(E - H_{LL}^{stat})G_L^{stat}(E) &= 1 \\
(E - H_{RR}^{stat})G_R^{stat}(E) &= 1
\end{align*}
\]

Effective static KS equation for central region

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

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 \(\epsilon_F = 0.3\) a.u.  
Steady state coincides with Landauer formula and is reached after a few femtoseconds
**Charge accumulation in device**

- Time evolution of current
- Time evolution of total number of electrons in central region

- Left lead
- Central region
- Right lead

**Barrier height**: 0.5 a.u.

**$\epsilon_{F} = 0.3$ a.u.**

**Transients**

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

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

- Solid lines:
- Same steady state!
**Time-dependent bias**

Current through square potential barrier for AC bias

![Graph](image)

U\(_L\)(t) = U\(_0\) \sin(\omega t)

with \(\omega = 1.0\) 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 $U(x,t) = U_0 \sin(kx - \omega t)$
(k = 1.6 a.u., $\omega = 0.2$ a.u.
Fermi energy = 0.3 a.u.)

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 $|x|<6$:
$U(x,t) = U_0 \sin(qx - \omega t)$ ($U_0 = 0.5$ 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**


![Graph showing current vs. Fermi energy](image1)

**Experimental result:**

![Graph showing current vs. gate voltage](image2)

**Bound state oscillations and memory effects**


**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

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

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: \( V(x) = -1.4 \text{ a.u. for } |x|<1.2 \text{ a.u., } 0 \text{ otherwise} \) \( \rightarrow \) two bound states
At \( t=0 \) switch on static bias \( U_R=0.1 \text{ a.u.} \) in right lead, also the biased Hamiltonian has two bound states \( \rightarrow \) current oscillations

**Time-Frequency Analysis of Time-Dependent Current**
Fourier transform of TD current for finite time interval with \( T_0=800 \text{ a.u.} \) and \( (t_p, t_p+T_0), t_p=(2+p)\times100 \text{ a.u.} \)

![Graph showing the amplitude of oscillation with frequency of transition between bound states is independent of \( t_p \).](image)

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

![Graph showing the amplitude of bound-continuum transitions decay slowly (~1/t) with time](image)

Amplitude of bound-continuum transitions decay slowly (~1/t) with time
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?
Pumping by travelling wave: Fourier Analysis of Time-Dependent Current
Frequency decomposition of current for different amplitudes, $U_1$, of pump wave

![Graph showing the frequency decomposition of current for different amplitudes of the pump wave.](image)

Fourier Analysis of Time-Dependent Current (with Pumping)
Oscillations originating from transitions between bound states:
Dependence on amplitude of pump wave

![Graph showing the oscillations originating from transitions between bound states.](image)
Thanks to

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Network of Excellence

EXCiTiNG
Research & Training Network

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

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
  --Molecular proximity effect