Controlling current and noise through molecular wires

Peter Hänggi
Universität Augsburg

in collaboration with

- Michael Strass, Jörg Lehmann, Sigmund Kohler, Gert-Ludwig Ingold (Augsburg)
- Sébastien Camalet (Lyon)
- Abraham Nitzan (Tel Aviv)
- Volkard May (Berlin)
- Elmar G. Petrov (Kiev)
- experiments
- Floquet transport theory
- applications:
  - resonant excitations
  - current and noise control
  - ratchets, pumps, rectification
We investigate electronic transport through two types of conjugated molecules. Mechanically controlled break junctions are used to couple thiol end groups of single molecules to two gold electrodes. Current-voltage characteristics ($I-V$) of the metal-molecule-metal system are observed. These reduce the spatial symmetry of the molecules with respect to the direction of current flow. We hereby unambiguously detect an intrinsic property of the molecule and are able to distinguish the influence of both the molecule and the contact to the metal electrodes on the transport properties of the compound system.

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The length of both molecules is 1.7 nm. To obtain a contact to a single molecule from both electrodes, an electrode pair with a distance matching exactly this length is required. We have chosen a lithographically fabricated mechanically controlled break junction (MCB) to provide an electrode pair with tunable distance. The same technique is required which target current through a single molecule while the connection to both electrodes is symmetrically realized by a well defined chemical bond, which allows mechanical stability of the junction even at room temperature [8,9]. However, to identify the molecule's sulfur-to-sulfur axis, in the nitro acetylamine derivative ("asymmetric molecule"), the mirror symmetry is absent. For the symmetric molecule the $I-V$ may be expected to be symmetric with respect to voltage inversion; for the asymmetric molecule a current owing in the positive direction or in the negative direction will not necessarily result in the same magnitude of the voltage drop.

The setup is mounted in a three-point bending mechanism driven by a threaded rod. To prepare the experiment, we bend the substrate in order to elongate the bridge and generally it breaks. Then the two open ends form an electrode pair with a distance matching exactly this length. The same technique is required concerning the conductance amplitude, the transport mechanisms, and the electrochemical potential of the sample. The experiment described in this Letter demonstrates clearly and without the necessity of any assumptions that we observe electronic transport through a single molecule (or at most very few) and not a large ensemble of molecules. This is achieved by comparing the data given in this Letter with some theoretical assumptions on this technique, see Ref. [10]. A scanning electron microscope picture of a freshly prepared junction consisting essentially of a freestanding Au bridge is shown in Fig. 2.

Further, an analysis of the data gives new qualitative insight concerning the crucial role of the molecule-metal contact.

The two types of organic molecules were designed specifically for the present experiment (cf. Fig. 1). Both consist of a rigid rodlike central section with additional thiol functions on both ends to form stable covalent bonds to gold electrodes. Details of the synthesis will be published later. Further, an analysis of the data gives new qualitative insight concerning the crucial role of the molecule-metal contact.

[M. A. Reed et al., Science 278, 252 (1997)]

[X. D. Cui et al., Science 294, 571 (2001)]

molecular wires

- molecular electronics: miniaturization, sensors, self-assembly, ...
- effect of Coulomb interaction
- coherent current control by laser light
Driving Current through Single Organic Molecules

J. Reichert, M. Mayor, Forschungszentrum Karlsruhe, Institut für Nanotechnologie, D-76021 Karlsruhe, Germany
Forschungszentrum Karlsruhe, Institut für Festkörperphysik, D-76021 Karlsruhe, Germany
Physikalisches Institut, Universität Karlsruhe, D-76128 Karlsruhe, Germany

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Controlled break junctions are used to couple thiol end groups of single molecules to two gold electrodes. This reproducibly detects an intrinsic property of the molecule and is able to distinguish the influence of both the molecule and the contact to the metal electrodes on the transport properties of the compound system.

The length of both molecules is 10 nm. To obtain a measurement of the current-voltage characteristics for single molecules, we have chosen a lithographically fabricated molecular wire with a small constriction (smallest diameter 10 nm). To prepare the experiment, we bend the substrate in order to elongate the bridge and finally it breaks. Then the two open ends form an electrode pair with a distance matching exactly this length.

The molecules with acetyl protection groups at the ends were used in a previous experiment [9]. For more details on the synthesis, see [J. Reichert, et al., Phys. Rev. Lett. 88, 176804 (2002)].

The current-voltage characteristics for the present experiment (cf. Fig. 1) are clearly nonlinear, displaying some rounded steplike structures.

Figure 3a displays a data set recorded for a single molecule after the junction in Fig. 3a had become unstable. Figure 3b displays a data set obtained for a subsequently prepared junction.


molecular wires

- reproducible measurement of the current-voltage characteristics for single molecules
- asymmetry

Figure 1. Scheme of the experimental setup: a spatially symmetric and asymmetric but otherwise similar molecules. Further, an analysis of the functions on both ends to form stable covalent bonds to gold electrodes. Details of the synthesis will be published elsewhere. As the molecules are very similar, comparable reproducible as long as the junction remains stable. The coverage of a completed monolayer, which would be formed only after hours. This is in contrast to previous experiments experimentally identified for the present experiment (cf. Fig. 1). Both configurations are interpreted as arising from a current through indeed a single sample molecule.
coupled quantum dots in microwaves

interesting questions

- conductance under laser excitation
- ratchet and pump effects
- current control
- noise properties
- ...

...
molecule: Hückel model of a „molecular bridge“ (electron transfer reaction), neglect Coulomb interaction, hopping matrix elements $\Delta$,

- metallic contacts: ideal Fermi gases with chem. potential $\mu$
- effective coupling to metal contacts: $\Gamma$
- laser field: $H_{\text{mol}} \longrightarrow H_{\text{mol}}(t)$, periodically time-dependent
- experiments
- Floquet transport theory
- applications:
  - resonant excitations
  - current and noise control
  - ratchets, pumps, rectification
**static case: scattering formula**

- **Landauer (1957):** „conductance is transmission“

\[
I = \frac{e}{2\pi\hbar} \int dE \ T(E, V) \left[ f(E + eV) - f(E) \right]
\]

- **current**

- **transmission** of an electron with energy \( E \)

\[
T(E, V) = \Gamma_L \Gamma_R |\langle 1 | G(E, V) | N \rangle|^2
\]

- **Green function** \( G(E, V) = \sum_{\alpha} \frac{|\phi_\alpha \rangle \langle \phi_\alpha|}{E - E_\alpha + i\hbar\gamma_\alpha} \)
**static case: current noise**

- **zero-frequency noise:** static component of the current-current correlation function

\[
\tilde{S} = S(\omega = 0) = \int_{-\infty}^{+\infty} d\tau \langle \Delta I(t) \Delta I(t + \tau) \rangle
\]

\[
\tilde{S} = \frac{e^2}{2\pi\hbar} \int dE \ T(E) \left\{ \left[ 1 - T(E) \right] \left[ f(E + eV) - f(E) \right]^2 + f(E + eV)[1 - f(E + eV)] + f(E)[1 - f(E)] \right\}
\]

- **shot noise** (remains for \( k_B T = 0 \))
- **equilibrium noise** (remains for \( eV = 0 \))

- depends only on transmission probability \( T(E) \)
current noise: Fano factor

- relative noise strength: Fano factor $F = \bar{S}/e\bar{I}$
- role of discreteness of charge carriers
- single transport channel
  - open channel $F = 0$
  - tunnel barrier $F \approx 1$ (Poisson process)
  - double barrier $F \approx 1/2$
driven systems

- **problem:** \[ U(t, t') = \overleftarrow{T} \exp \left( - \frac{i}{\hbar} \int_{t'}^{t} dt'' H(t'') \right) \]

\( \overleftarrow{T} \): time-ordering operator

- **periodic time-dependence:** „Bloch theory in time“ (Floquet 1883)
Floquet theory

- Floquet theorem: time-periodic Schrödinger equation has complete solution of the form

\[ |\psi_\alpha(t)\rangle = e^{-i\epsilon_\alpha t/\hbar} |\phi_\alpha(t)\rangle, \text{ where } |\phi_\alpha(t)\rangle = |\phi_\alpha(t + T)\rangle \]

- quasienergies \( \epsilon_\alpha \), Brillouin zones
  - Floquet states \( |\phi_\alpha(t)\rangle = \sum_k e^{-ik\Omega t} |\phi_{\alpha,k}\rangle \)

- Floquet-Schrödinger equation

\[
\left( H(t) - i\hbar \frac{d}{dt} \right) |\phi_\alpha(t)\rangle = \epsilon_\alpha |\phi_\alpha(t)\rangle
\]

Hilbert space extended by periodic time coordinate

non-linear response
transport and driving: computation of the Green function and scattering formula for time-dependent situation
transport and driving: computation of the Green function and scattering formula for time-dependent situation

Heisenberg equations of motion for wire electrons

\[ \dot{c}_{1/N} = - \frac{i}{\hbar} \sum_{n'} H_{1/N,n'}(t) c_{n'} - \frac{\Gamma_{L/R}}{2\hbar} c_{1/N} + \xi_{L/R}(t), \]
\[ \dot{c}_n = - \frac{i}{\hbar} \sum_{n'} H_{nn'}(t) c_{n'} \quad n = 2, \ldots, N - 1 \]

with Gaussian noise operators defined by

\[ \langle \xi_\ell(t) \rangle = 0, \]
\[ \langle \xi_\ell^\dagger(t) \xi_{\ell'}(t') \rangle = \frac{\delta_{\ell\ell'}}{2\pi\hbar^2} \int d\epsilon \Gamma_\ell(\epsilon) e^{i\epsilon(t-t')/\hbar} f_\ell(\epsilon) \]
Floquet transport theory

- Floquet equation with self-energy \( \Sigma = |1\rangle \frac{\Gamma_L}{2} \langle 1| + |N\rangle \frac{\Gamma_R}{2} \langle N| \)

\[
\left( H(t) - i\Sigma - i\hbar \frac{d}{dt} \right) |\varphi_\alpha(t)\rangle = (\epsilon_\alpha - i\hbar \gamma_\alpha) |\varphi_\alpha(t)\rangle
\]

- Propagator in the presence of the contacts

\[
G(t, t - \tau) = \sum_{k=-\infty}^{\infty} e^{ik\Omega t} \int d\epsilon e^{-i\epsilon \tau} \sum_{\alpha, k'} \frac{|\varphi_\alpha, k + k'\rangle \langle \varphi_\alpha, k'|}{\epsilon - (\epsilon_\alpha + k'\Omega - i\hbar \gamma_\alpha)}
\]

propagation under absorption/emission of \(|k|\) photons
**Floquet transport theory: current**

- **time-dependent current**: change of electron number in, e.g., left lead ($\times$ electron charge $e$)

$$ I(t) = e \frac{d}{dt} \langle N_L(t) \rangle $$

- **two periodically time-dependent contributions**
  - transport between contacts
  - periodic charging/discharging of the conductor
**Floquet transport theory: current**

- dc current [note: no blocking factors $1 - f_\ell$]

\[
\bar{I} = \frac{e}{2\pi \hbar} \sum_{k=-\infty}^{\infty} \int d\epsilon \left\{ T_{LR}^{(k)}(\epsilon) f_R(\epsilon) - T_{RL}^{(k)}(\epsilon) f_L(\epsilon) \right\}
\]

- transmission under absorption of $k$ photons

\[
T_{LR}^{(k)}(\epsilon) = \Gamma_L \Gamma_R \left| \langle 1 | G^{(k)}(\epsilon) | N \rangle \right|^2 \neq T_{RL}^{(\pm k)}(\epsilon \pm k \hbar \Omega)
\]

**Floquet scattering theory — current noise**

**time-averaged zero-frequency noise**

\[
\bar{S} = \frac{1}{T} \int_{0}^{T} dt \int_{-\infty}^{+\infty} d\tau \left\langle \Delta I(t) \Delta I(t + \tau) \right\rangle \\
= \frac{e^2}{\hbar} \sum_{k} \int d\epsilon \left\{ \Gamma_R \Gamma_R \left| \sum_{k'} \Gamma_L(\epsilon_{k'}) G_{1N}^{(k'-k)}(\epsilon_k)^* G_{1N}^{(k')}(\epsilon) \right|^2 f_R(\epsilon) \bar{f}_R(\epsilon_k) \right. \\
+ \Gamma_R \Gamma_L \left| \sum_{k'} \Gamma_L G_{1N}^{(k'-k)}(\epsilon_k)^* - iG_{1N}^{(-k)}(\epsilon_k) \right|^2 f_L(\epsilon) \bar{f}_R(\epsilon_k) \\
+ \text{same terms with the replacement } (L, 1) \leftrightarrow (R, N) \left\} \right.
\]

where \( \epsilon_k = \epsilon + k\hbar\Omega \)

depends on transmission amplitudes \( G_{1N}^{(k)} \)
reminder: noise for static case

\[ \bar{S} = \frac{e^2}{2\pi\hbar} \int dE \ T(E) \left\{ \left[ 1 - T(E) \right] \left[ f_L(E) - f_R(E) \right]^2 \right. \\
+ \left. f_L(E)\left[ 1 - f_L(E) \right] + f_R(E)\left[ 1 - f_R(E) \right] \right\} \]

depends only on transmission probability \( T(E) \)
- experiments
- Floquet transport theory
- applications:
  - resonant excitations
  - current and noise control
  - ratchets, pumps, rectification
resonant excitations

\[ H_{nn'}(t) = -\Delta (\delta_{n,n'+1} + \delta_{n+1,n'}) + (E_n + A x_n \cos(\Omega t)) \delta_{nn'} \]

undriven \( (A = 0) \), high barrier

- \( \bar{I} \propto \exp(-\kappa N) \) where \( \kappa = 2 \ln(E_B/\Delta) \)
  (cf. reaction rate in super-exchange)
- Fano factor \( F \approx 1 \)
resonant excitations

dc current

\[ I_{\text{peak}} \propto \frac{A^2}{(N - 1)\Gamma} \]

- drastic current enhancement for long wires

\[ \hbar \Omega = 10\Delta, \ V = 5\Delta, \ \Gamma = 0.1\Delta \]

resonant excitations

\[ \langle N \rangle = \begin{cases} 5, & N = 5 \\ 10, & N = 10 \\ 15, & N = 15 \end{cases} \]

\[ \tilde{I}(N-1) \times 10^{-3} \text{eV}/\hbar \]

\[ \hbar \Omega = 10\Delta, \ V = 5\Delta, \ \Gamma = 0.1\Delta \]

\[ \text{dc current} \]

\[ I_{\text{peak}} \propto \frac{A^2}{(N - 1)\Gamma} \]

\[ \text{drastic current enhancement for long wires} \]

\[ \text{Fano factor} \ F = \frac{\bar{S}}{e\bar{I}} \]

\[ \text{noise reduced, channel “more open”} \]

- experiments
- Floquet transport theory
- **applications:**
  - resonant excitations
  - *current and noise control*
  - ratchets, pumps, rectification
current and noise control

- current control by driving field
- current noise for time-dependent transport

**Motivation:** Coherent suppression of tunneling

- Relevant time-scale for tunneling: \[ \frac{\hbar}{E_1 - E_0} = \frac{\hbar}{\Delta} \]

- Driven tunneling: energies replaced by quasienergies

- Divergent time-scale at exact crossings (\( \Delta \ll \hbar \Omega \)) \( \longrightarrow \) **Coherent destruction of tunnelling (CDT)**


- High-frequency approximation: \( \Delta \longrightarrow \Delta_{\text{eff}} = J_0(\frac{A}{\hbar \Omega}) \Delta \)
motivation: coherent suppression of tunneling

Does a related transport phenomenon exist?
transport through three-level system

dc current, noise

- current and noise suppressed if $\Delta_{\text{eff}} = 0$

Fano factor $F = \bar{S}/e\bar{I}$

- control of relative noise strength
- current suppression accompanied by maximum and two minima of the Fano factor

$N = 3$, $\hbar\Omega = 5\Delta$, $V = 50\Delta$, $\Gamma_L = \Gamma_R = 0.2\Delta$
**high-frequency approximation**

expansion of transport equations in $1/\Omega$

- **effective static problem with**
  - electron distribution $f_{\text{eff}}(\epsilon) = \sum_k J_k^2(A/2\hbar\Omega)f(\epsilon + k\hbar\Omega)$
  - tunnel matrix element $\Delta \longrightarrow \Delta_{\text{eff}} = J_0(A/\hbar\Omega)\Delta$

- **switching between weak and strong lead-wire coupling**

  - $\Delta_{\text{eff}} \gg \Gamma$
  - “barriers”

  - $\Delta_{\text{eff}} \ll \Gamma$
  - “barriers”

- **both are double barrier situations** (Fano factor $\approx 1/2$)
optical current router

- three-terminal geometry with $\mu_E = -\mu_{C_1} = -\mu_{C_2}$
- linearly polarized laser field: polarization angle $\vartheta$

![Diagram showing three-terminal geometry with linearly polarized laser field and corresponding polarization angles $\vartheta$]
experiments

Floquet transport theory

applications:
  ▶ resonant excitations
  ▶ current and noise control
  ▶ ratchets, pumps, rectification
coherent quantum ratchet: motivation

- Brownian motion in a periodic but asymmetric potential

- thermal equilibrium
  → no directed transport from noise: $\bar{I} = 0$
  
  no perpetuum mobile of the second kind

- here: coherent quantum dynamics, non-adiabatic driving
coherent quantum ratchet

no transport voltage

\[ \mu_L = \mu_R \]

finite periodic system consisting of \( N_g \) asymmetric groups

\[ H_{nn'}(t) = -\Delta (\delta_{n,n'+1} + \delta_{n+1,n'}) + \left( E_n + A x_n \cos(\Omega t) \right) \delta_{nn'} \]

ratchet effect due to effective dissipation from leads?

length dependence?

coherent quantum ratchet: length dependence

dc current vs. driving amplitude  dc current vs. driving frequency

\[ I \left( 10^{-3} e \right) \]

\( A [\Delta] \)

\( \Omega [\Delta / \hbar] \)

\( N_g = 1 \)

\( N_g = 2 \)

\( N_g = 3 \)

\( \Delta = 1, \mu_L = \mu_R = 0, \Gamma = 0.1, kT = 0.25, E_D = E_A = 0, E_B = 10, E_S = 1 \)

- ratchet current exhibits resonances \( \longrightarrow \) coherent transport
- e.g. molecule: \( A = e \mathcal{E} d_{\text{site}}, \quad d_{\text{site}} \approx 1 \text{ nm}, \quad \Delta = 0.1 \text{ eV} \)
  \( \longrightarrow \) electric field strength \( \mathcal{E} = 10^6 \text{ V/cm} \)
coherent quantum ratchet

dc current vs. length

- current inversion as a function of $N_g$
- current converges to non-zero value

$\Delta = 1, \hbar \Omega = 3, \Gamma = 0.1,$
$kT = 0.25, \mu = 0, E_B = 10,$
$E_S = 1$
coherent quantum ratchet: symmetries

no ratchet current for parity \( x \rightarrow -x \)

- parity of a time-dependent Hamiltonian
  \[
  H = H_0(x) - x a(t)
  \]
  \([H_0(x) = H_0(-x) \text{ symmetric}]\)

- symmetry of Hamiltonian
  \( \rightarrow \) two different scattering events have equal probability

- harmonic driving \([a(t) = \sin(\Omega t)]\): three symmetries
  - time reversal \( t \rightarrow T/2 - t \) not relevant for \( \bar{I} \)
  - generalized parity \((x, t) \rightarrow (-x, t + T/2) \implies \bar{I} = 0\)
  - time-reversal parity \((x, t) \rightarrow (-x, -t) \implies \bar{I} = \mathcal{O}(\Gamma^2)\)
**harmonic mixing**

symmetry breaking due to driving

- mixing with higher harmonics

\[ a(t) = A_1 \sin(\Omega t) + A_2 \sin(2\Omega t + \phi) \]

harmonic mixing: dc current

dc current vs. coupling strength

▶ influence of the phase $\phi$:

$\bar{I} \propto \Gamma$ für $\phi = \pi/2$

$\bar{I} \propto \Gamma^2$ for $\phi = 0$, e.g. for time-reversal parity
summary

- Floquet theory for driven conductors

- effects
  - current and noise control
  - ratchets, pumps, rectification
  - current amplification by resonant excitations

- actual projects
  - decoherence effects
  - coupling to molecule vibrations
  - spectroscopy during transport
  - noise in electron pumps
thanks to …

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