Controlling current and noise through molecular wires

Peter Hänggi

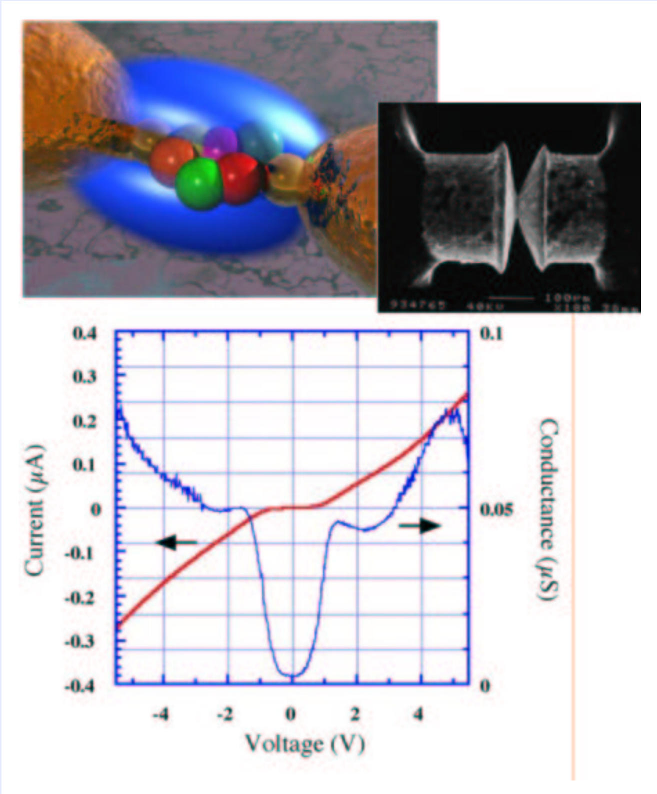
Universität Augsburg

in collaboration with

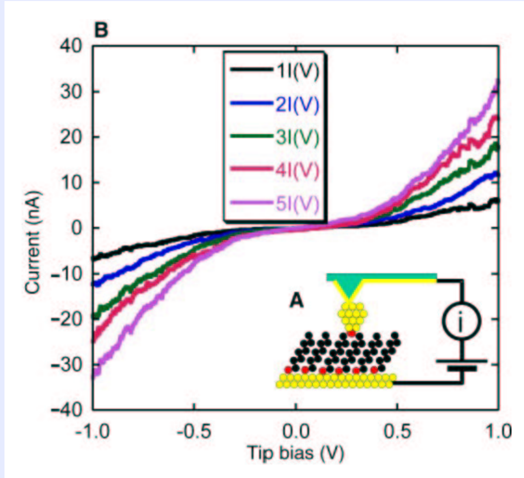
- Michael Strass, Jörg Lehmann, Sigmund Kohler, Gert-Ludwig Ingold (Augsburg)
- Sébastien Camalet (Lyon)
- Abraham Nitzan (Tel Aviv)
- Volkard May (Berlin)
- Elmar G. Petrov (Kiev)

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

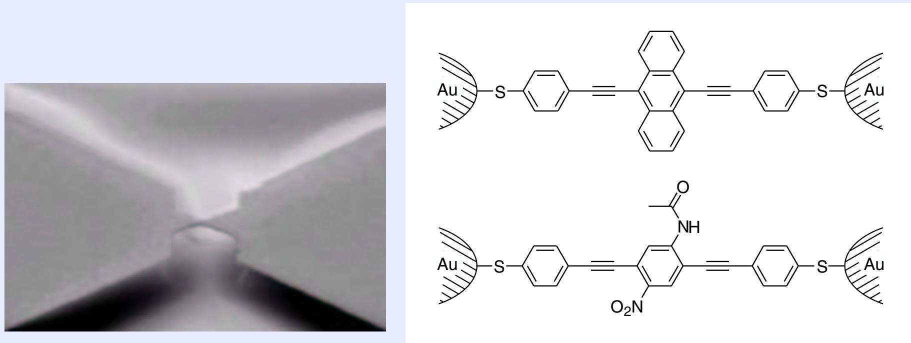
single-molecule conduction



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

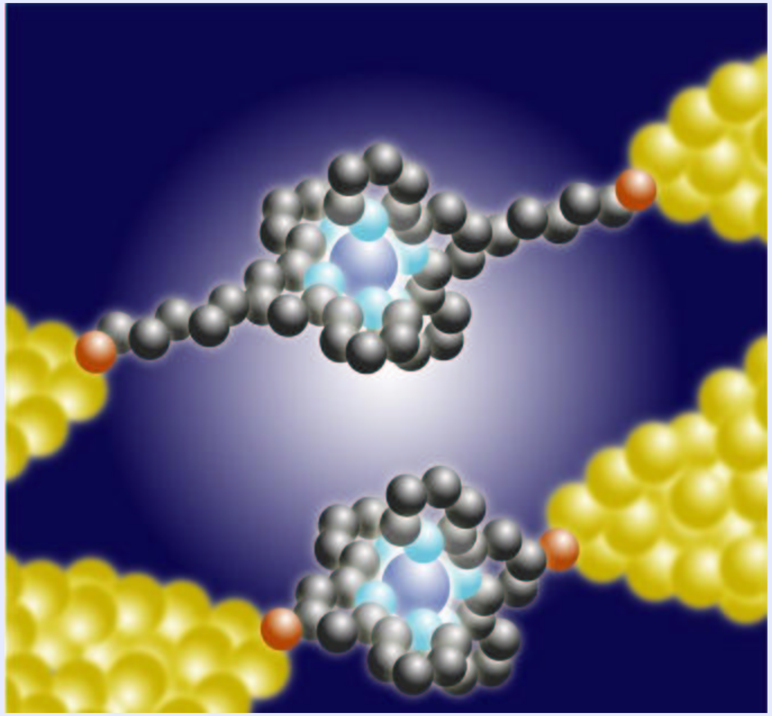


[X. D. Cui *et al.*, Science **294**, 571 (2001)]



[J. Reichert *et al.*, Phys. Rev. Lett. **88**, 176804 (2002)]

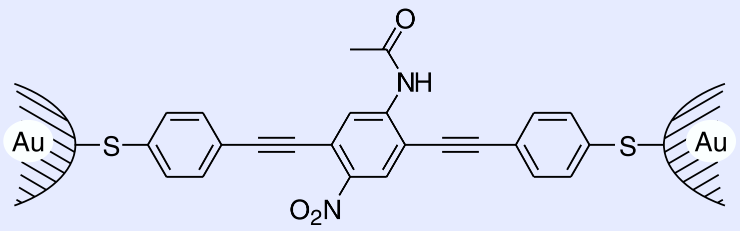
molecular wires

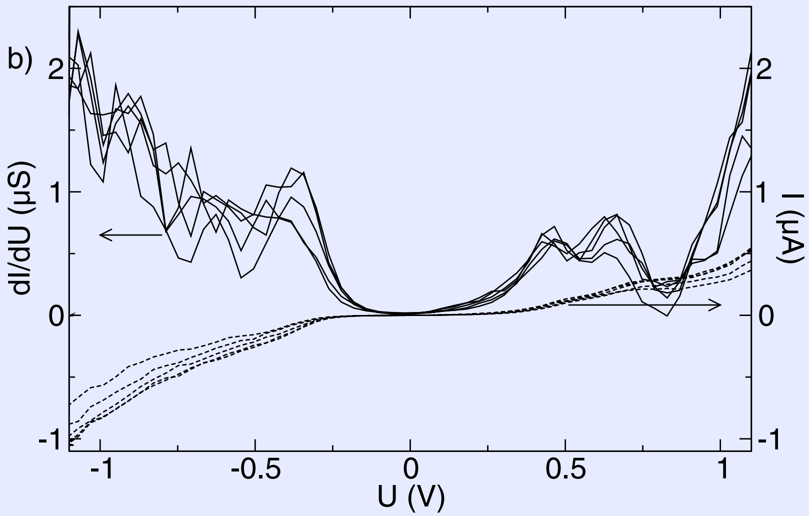


- molecular electronics:
  miniaturization, sensors, self-assembly, . . .
- effect of Coulomb interaction
- coherent current control by laser light

molecular wires

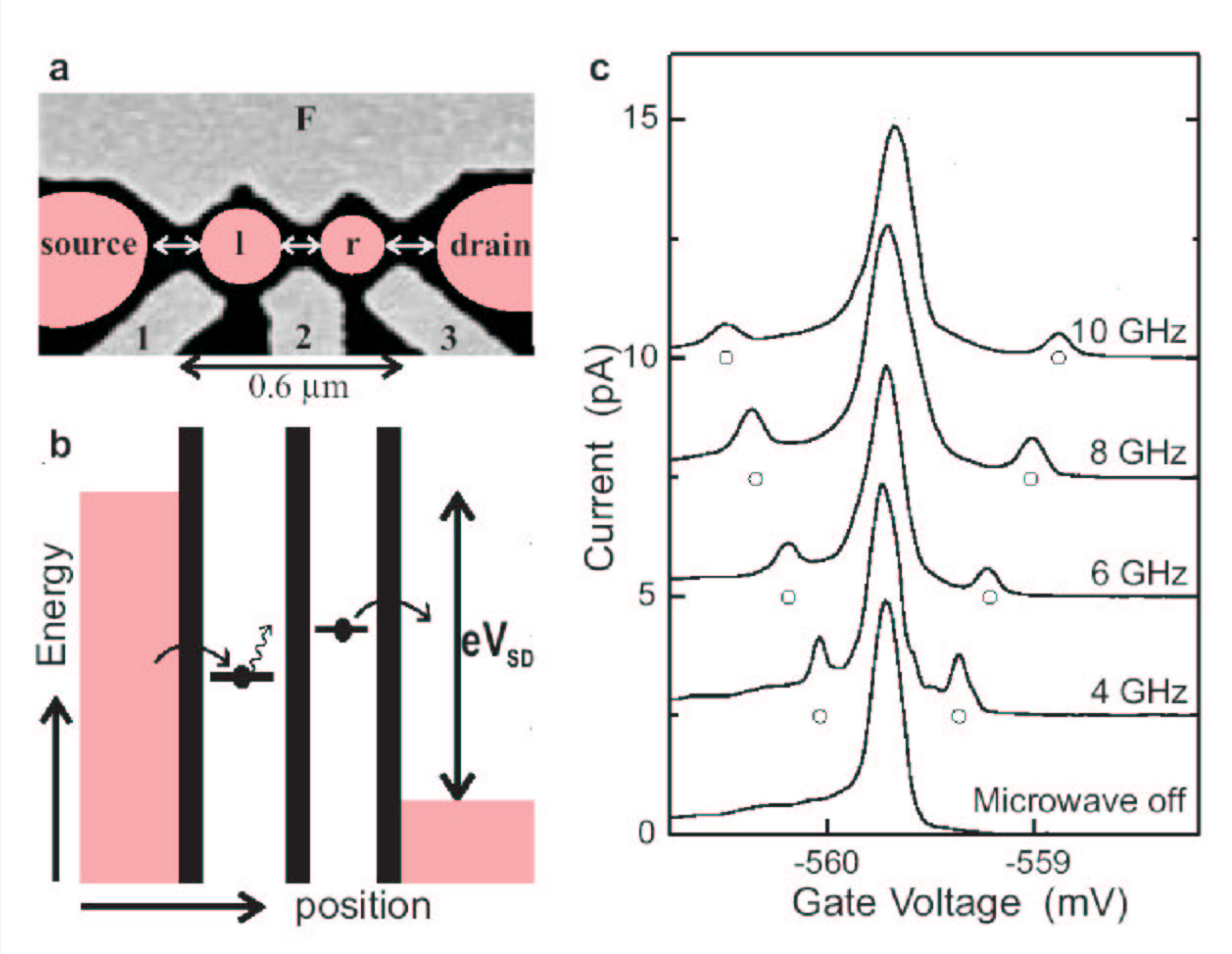
- reproducible measurement of the current-voltage characteristics for single molecules
- asymmetry





[J. Reichert, *et al.*, Phys. Rev. Lett. **88**, 176804 (2002)]

coupled quantum dots in microwaves

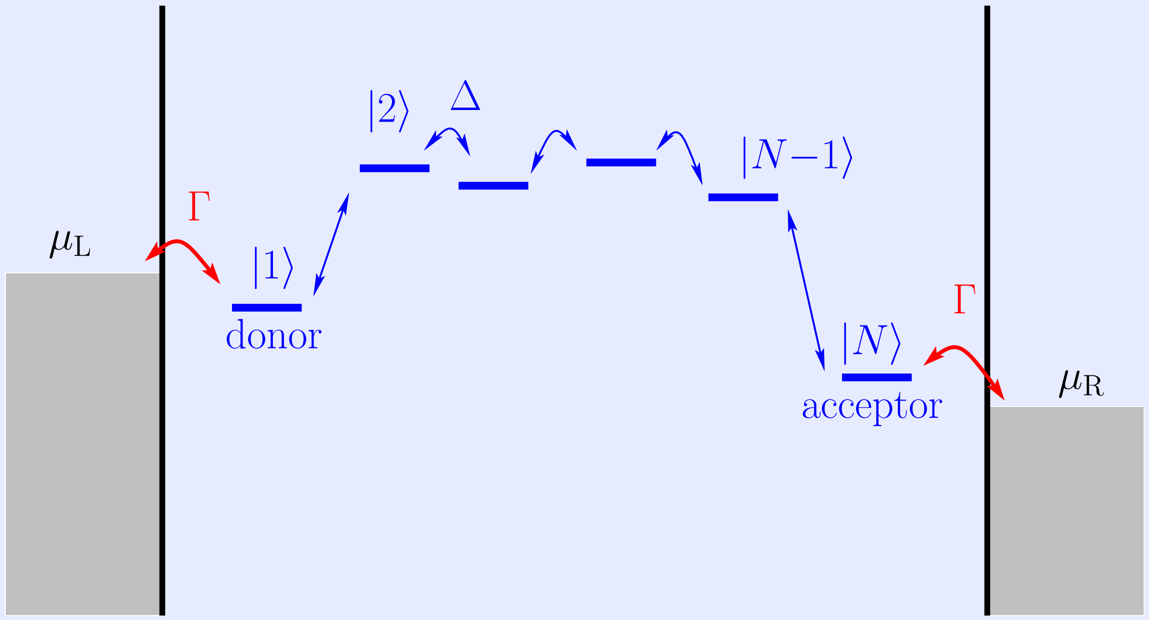


[T. H. Oosterkamp, *et al.*, Nature **395**, 873 (1998)]

interesting questions

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

model

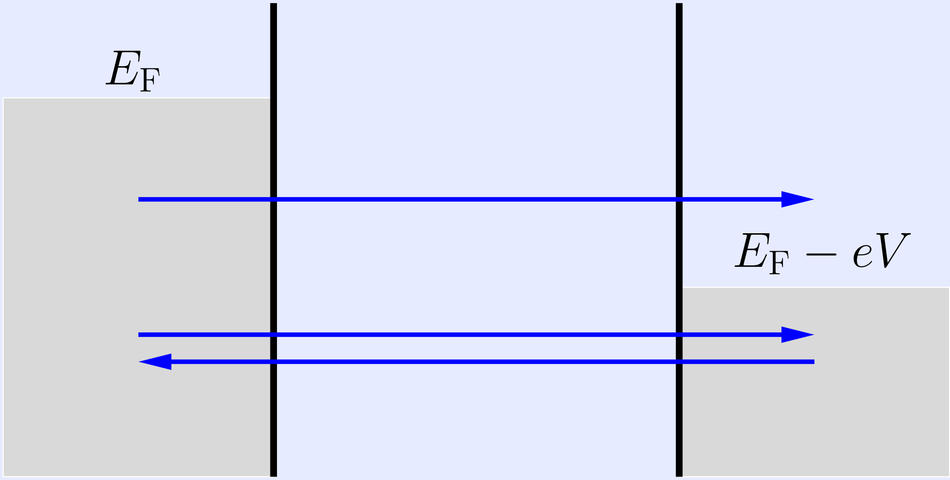


- molecule: Hückel model of a „molecular bridge“ (electron transfer reaction), neglect Coublomb interaction, hopping matrix elements Δ,
- metalic contacts: ideal Fermi gases with chem. potential μ
- effective coupling to metal contacts: Γ
- laser field: $H_{\mathrm{mol}} \longrightarrow H_{\mathrm{mol}}(t)$, 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"



- current $$\boxed{I = \frac{e}{2\pi\hbar} \int \mathrm{d}E \; T(E,V) \big[f(E+eV) - f(E) \big]}$$

- transmission of an electron with energy E

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

- Green function $G(E,V) = \sum_\alpha \frac{|\phi_\alpha\rangle\langle\phi_\alpha|}{E - E_\alpha + \mathrm{i}\hbar\gamma_\alpha}$

static case: current noise

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

$$\bar{S} = S(\omega = 0) = \int_{-\infty}^{+\infty} \mathrm{d}\tau \, \langle \Delta I(t) \, \Delta I(t+\tau) \rangle$$

$$\bar{S} = \frac{e^2}{2\pi\hbar} \int \mathrm{d}E \, T(E) \Big\{ \big[1 - T(E)\big] \big[f(E+eV) - f(E) \big]^2 + f(E+eV)[1 - f(E+eV)] + f(E)[1 - f(E)] \Big\}$$

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

$\boxed{\text{depends only on transmission probability } T(E)}$

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: $U(t,t') = \overleftarrow{T} \exp\left(-\frac{\mathrm{i}}{\hbar} \int_{t'}^{t} \mathrm{d}t'' \, H(t'') \right)$

  $\overleftarrow{T}$: 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

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

- quasienergies ϵ_α, Brillouin zones
  Floquet states $|\phi_\alpha(t)\rangle = \sum_k \mathrm{e}^{-\mathrm{i}k\Omega t}|\phi_{\alpha,k}\rangle$
- Floquet-Schrödinger equation

$$\Big(H(t) - \mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Big)|\phi_\alpha(t)\rangle = \epsilon_\alpha|\phi_\alpha(t)\rangle$$

Hilbert space extended by periodic time coordinate

$\boxed{\text{non-linear response}}$

Floquet transport theory

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

Floquet transport theory

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

Heisenberg equations of motion for wire electrons

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

$$\dot{c}_n = -\frac{i}{\hbar}\sum_{n'} H_{nn'}(t)\, c_{n'} \qquad n = 2, \ldots, N-1$$

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 $\Sigma = |1\rangle \frac{\Gamma_L}{2} \langle 1| + |N\rangle \frac{\Gamma_R}{2} \langle N|$

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

- propagator in the presence of the contacts

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

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)

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

- two periodically time-dependent contributions
  - transport between contacts
  - periodic charging/discharging of the conductor

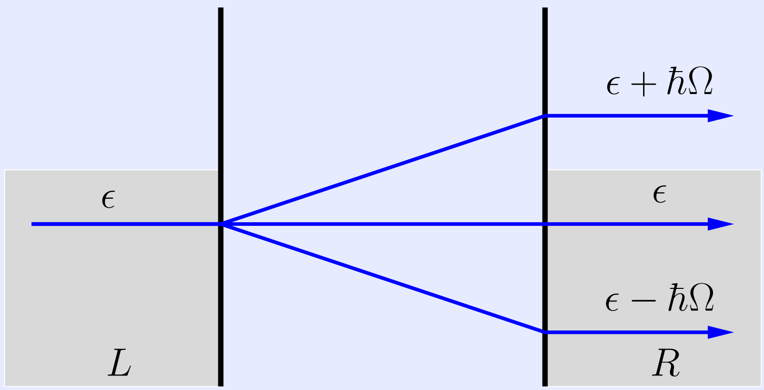
Floquet transport theory: current

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

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

- transmission under absorption of k photons

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



[S. Camalet, J. Lehmann, S. Kohler, and P. Hänggi, Phys. Rev. Lett. **90**, 210602 (2003)]

Floquet scattering theory — current noise

time-averaged zero-frequency noise

$$\bar{S} = \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} \mathrm{d}t \int_{-\infty}^{+\infty} \mathrm{d}\tau \, \langle \Delta I(t) \, \Delta I(t+\tau) \rangle$$

$$= \frac{e^2}{h} \sum_k \int d\epsilon \Big\{ \Gamma_R \Gamma_R \Big| \sum_{k'} \Gamma_L(\epsilon_{k'}) G_{1N}^{(k'-k)}(\epsilon_k) \big[G_{1N}^{(k')}(\epsilon) \big]^* \Big|^2 f_R(\epsilon) \bar{f}_R(\epsilon_k)$$

$$+ \Gamma_R \Gamma_L \Big| \sum_{k'} \Gamma_L G_{1N}^{(k'-k)}(\epsilon_k) \big[G_{11}^{(k')}(\epsilon) \big]^* - \mathrm{i} G_{1N}^{(-k)}(\epsilon_k) \Big|^2 f_L(\epsilon) \bar{f}_R(\epsilon_k)$$

$$+ \text{ same terms with the replacement } (L,1) \leftrightarrow (R,N) \Big\}$$

where $\epsilon_k = \epsilon + k\hbar\Omega$

$\boxed{\text{depends on transmission amplitudes } G_{1N}^{(k)}}$

reminder: noise for static case

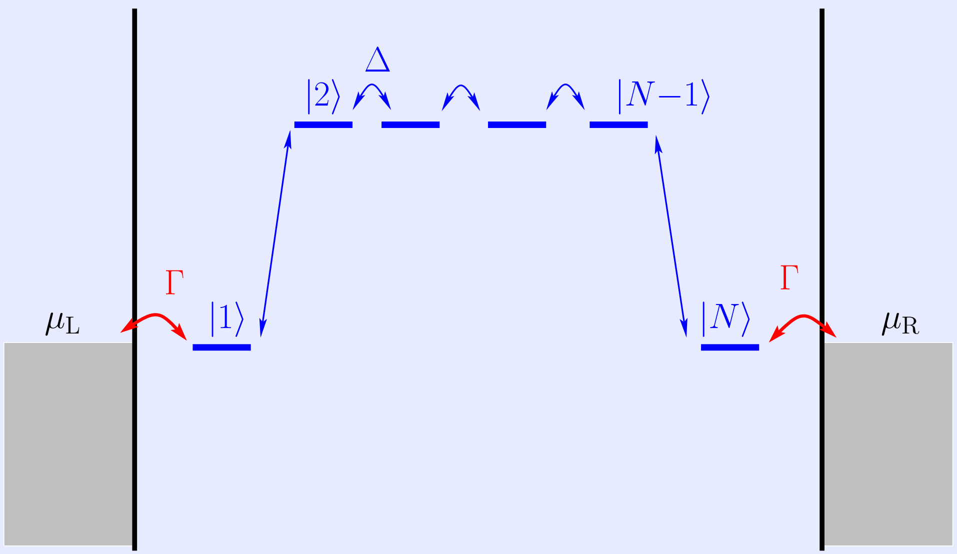
$$\bar{S} = \frac{e^2}{2\pi\hbar} \int \mathrm{d}E\, T(E) \Big\{ \big[1 - T(E)\big] \big[f_L(E) - f_R(E)\big]^2 + f_L(E)[1 - f_L(E)] + f_R(E)[1 - f_R(E)] \Big\}$$

$\boxed{\text{depends only on transmission probability } T(E)}$

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

resonant excitations

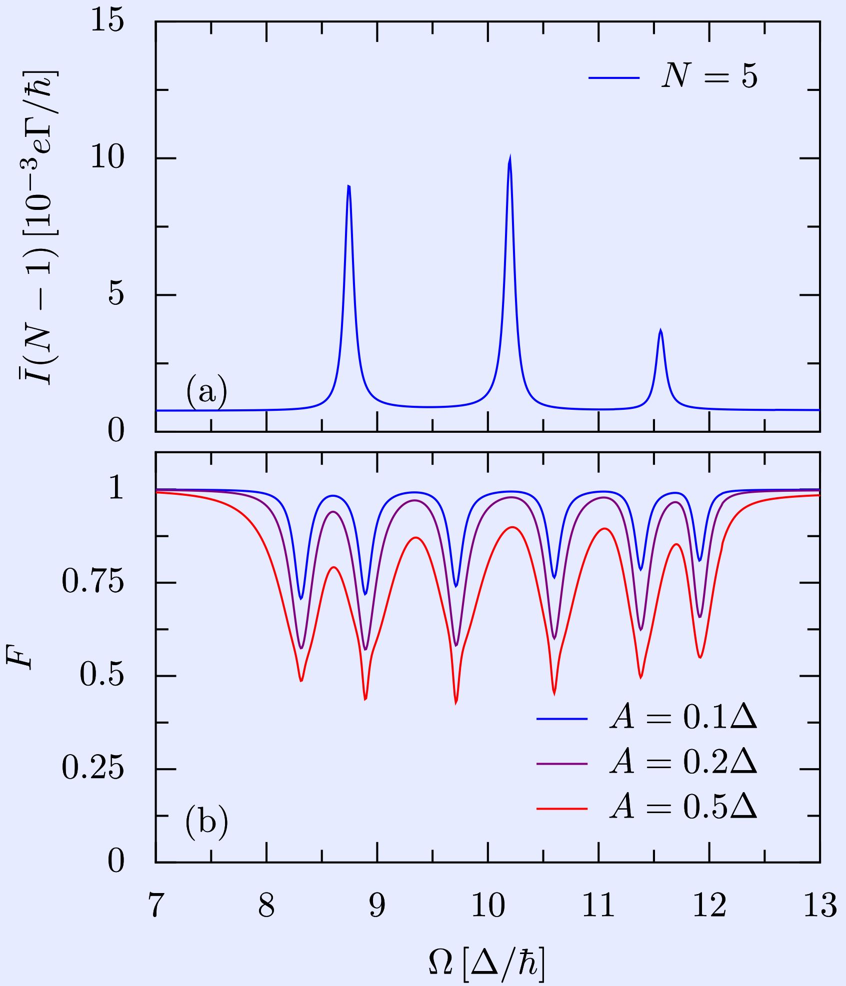
$$H_{nn'}(t) = -\Delta(\delta_{n,n'+1} + \delta_{n+1,n'}) + \big(E_n + A\, x_n \cos(\Omega t)\big)\delta_{nn'}$$



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



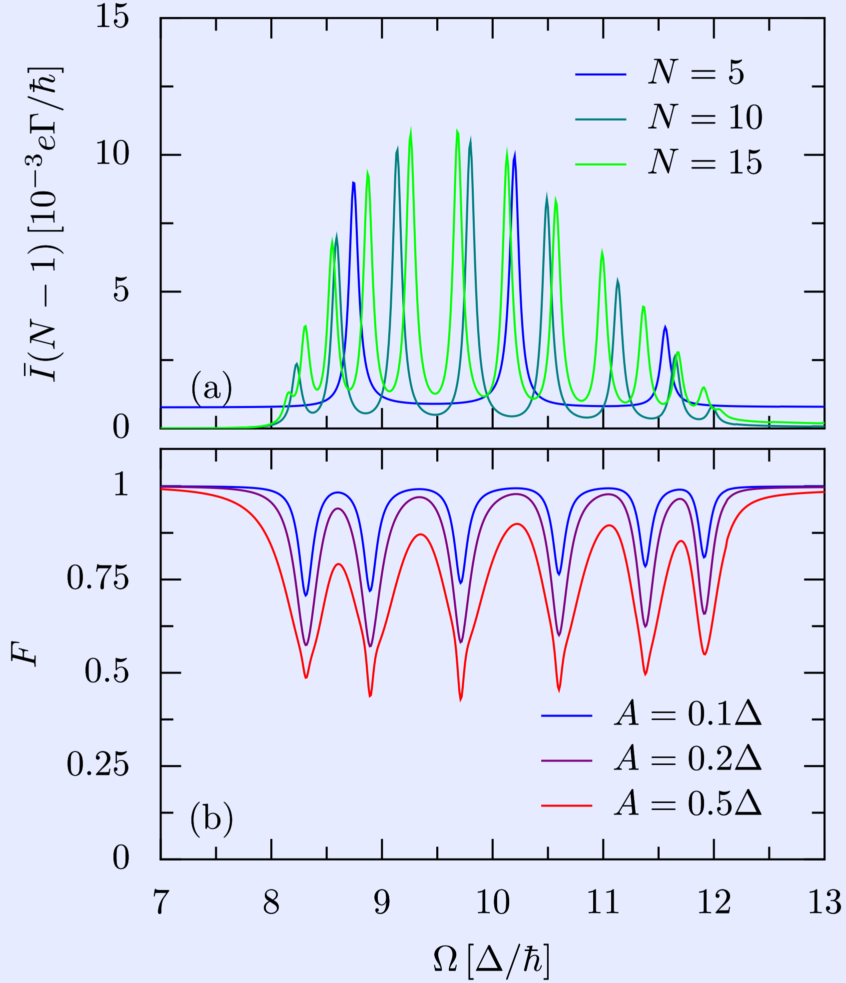
$\hbar\Omega = 10\Delta$, $V = 5\Delta$, $\Gamma = 0.1\Delta$

dc current

- $I_{\text{peak}} \propto \dfrac{A^2}{(N-1)\Gamma}$
- drastic current enhance-ment for long wires

[S. Kohler, J. Lehmann, S. Camalet, and P. Hänggi, Israel J. Chem. **42**, 135 (2003)]

resonant excitations



$\hbar\Omega = 10\Delta$, $V = 5\Delta$, $\Gamma = 0.1\Delta$

dc current

- $I_{\text{peak}} \propto \dfrac{A^2}{(N-1)\Gamma}$
- drastic current enhancement for long wires

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

- noise reduced, channel “more open”

[S. Kohler, J. Lehmann, S. Camalet, and P. Hänggi, Israel J. Chem. **42**, 135 (2003)]

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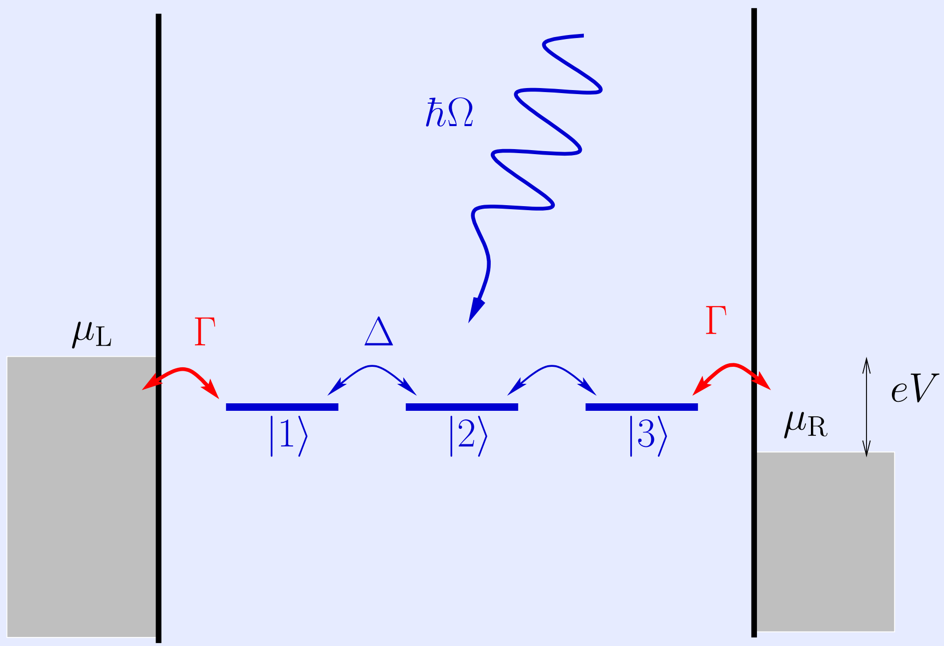
current and noise control



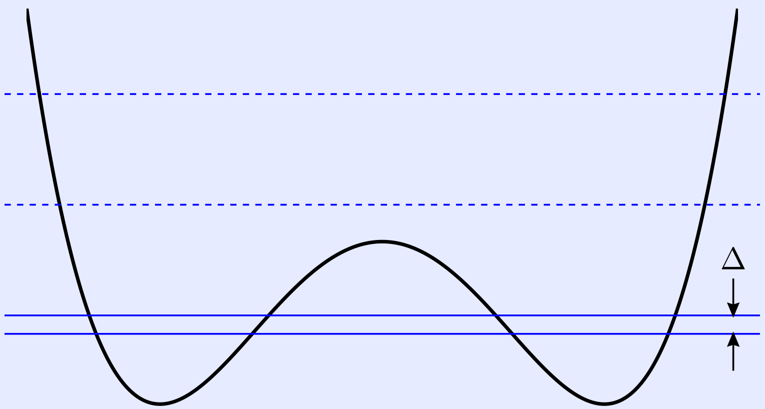
- current control by driving field
- current noise for time-dependent transport

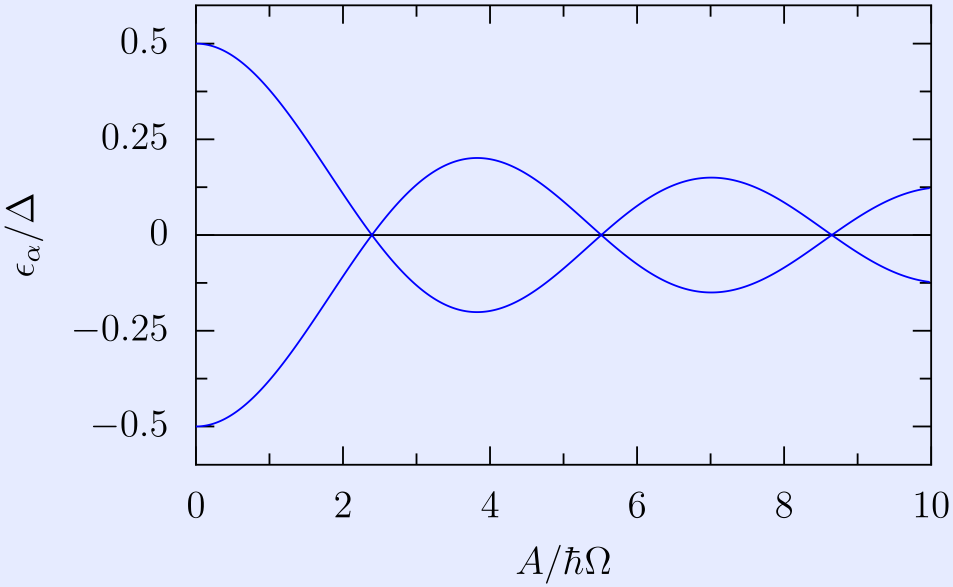
[J. Lehmann, S. Camalet, S. Kohler, and P. Hänggi, Chem. Phys. Lett. **368**, 282 (2003)]

[S. Camalet, J. Lehmann, S. Kohler, and P. Hänggi, Phys. Rev. Lett. **90**, 210602 (2003)]

[S. Kohler, S. Camalet, M. Strass, J. Lehmann, G.-L. Ingold, and PH, Chem. Phys. **296**, 243 (2004)]

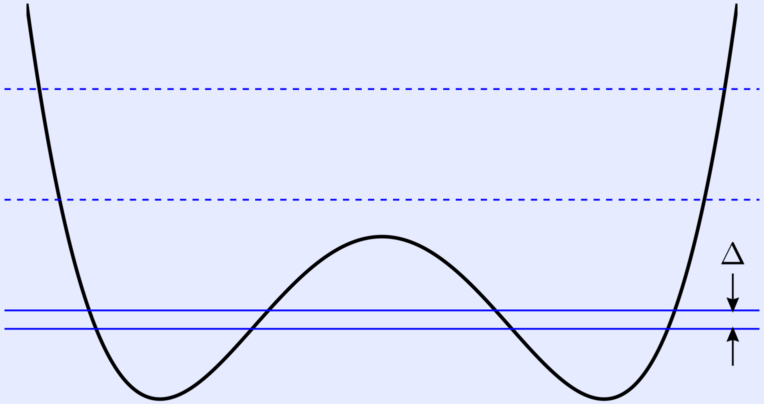
motivation: coherent suppression of tunneling

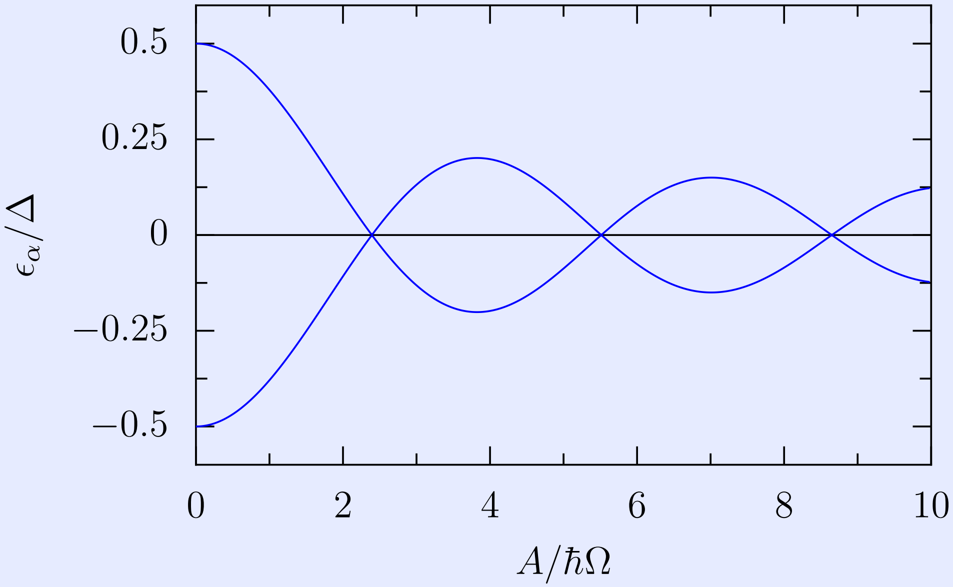




- relevant time-scale for tunneling: $\dfrac{\hbar}{E_1 - E_0} = \dfrac{\hbar}{\Delta}$
- driven tunneling: energies replaced by quasienergies
- divergent time-scale at exact crossings ($\Delta \ll \hbar\Omega$)
  $\longrightarrow$ *coherent destruction of tunnelling (CDT)*
  [F. Grossmann, T. Dittrich, P. Jung, and P. Hänggi, Phys. Rev. Lett. **67**, 516 (1991)]
- high-frequency approximation: $\Delta \longrightarrow \Delta_{\text{eff}} = J_0(A/\hbar\Omega)\Delta$

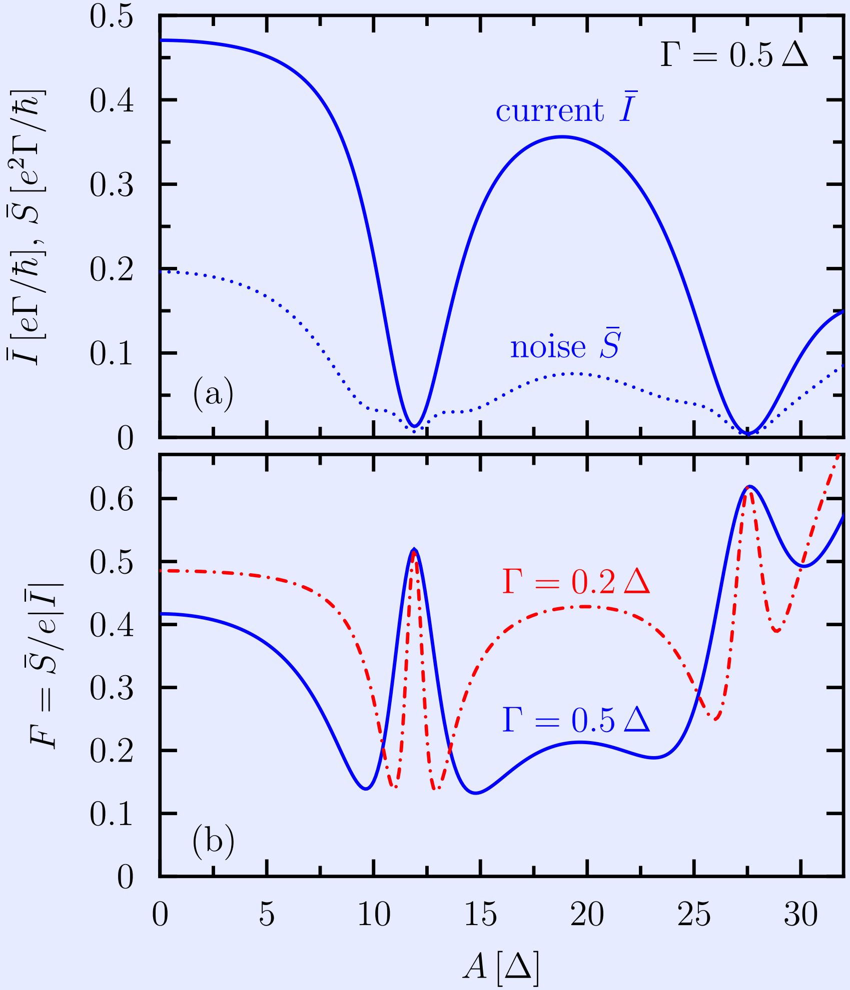
motivation: coherent suppression of tunneling





Does a related transport phenomenon exist?

transport through three-level system



$N = 3$, $\hbar\Omega = 5\Delta$, $V = 50\Delta$,

$\Gamma_L = \Gamma_R = 0.2\Delta$

dc current, noise

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

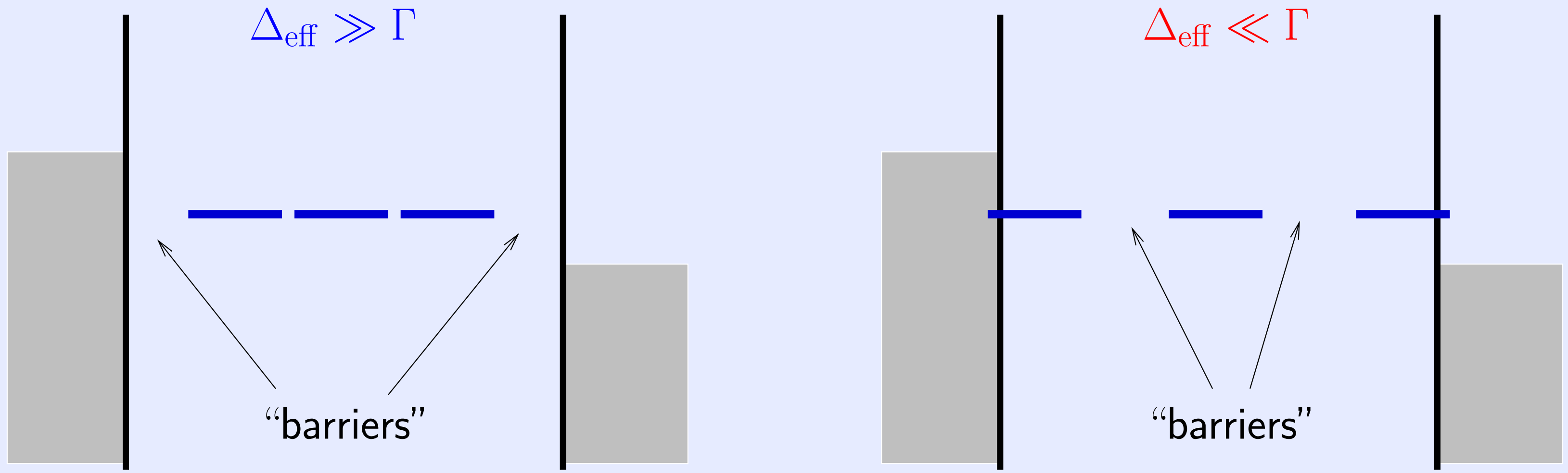
Fano factor $F = \bar{S}/e\bar{I}$

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

high-frequency approximation

expansion of transport equations in $1/\Omega$

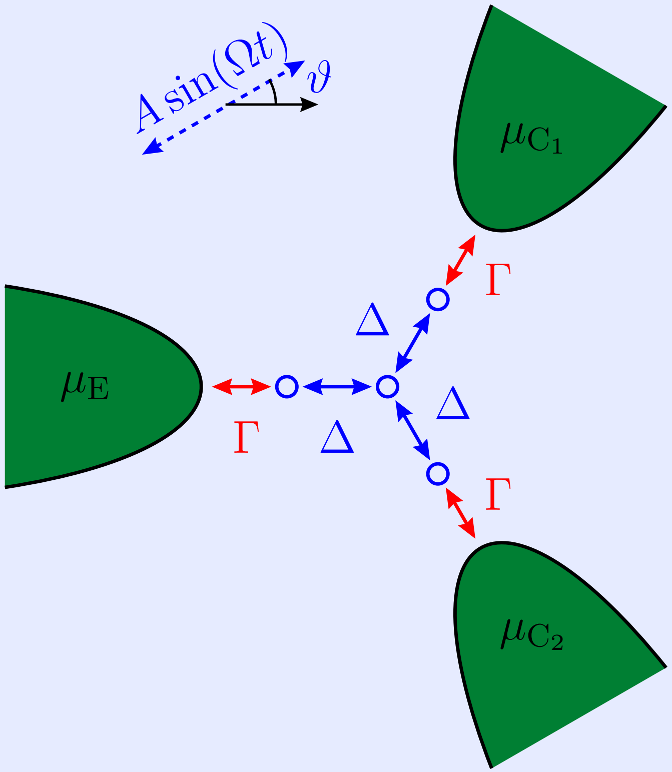
- effective static problem with
  - electron distribution $f_{\text{eff}}(\epsilon) = \sum_k J_k^2(A/2\hbar\Omega) f(\epsilon + k\hbar\Omega)$
  - tunnel matrix element $\Delta \longrightarrow \Delta_{\text{eff}} = J_0(A/\hbar\Omega)\Delta$
- switching between weak and strong lead-wire coupling

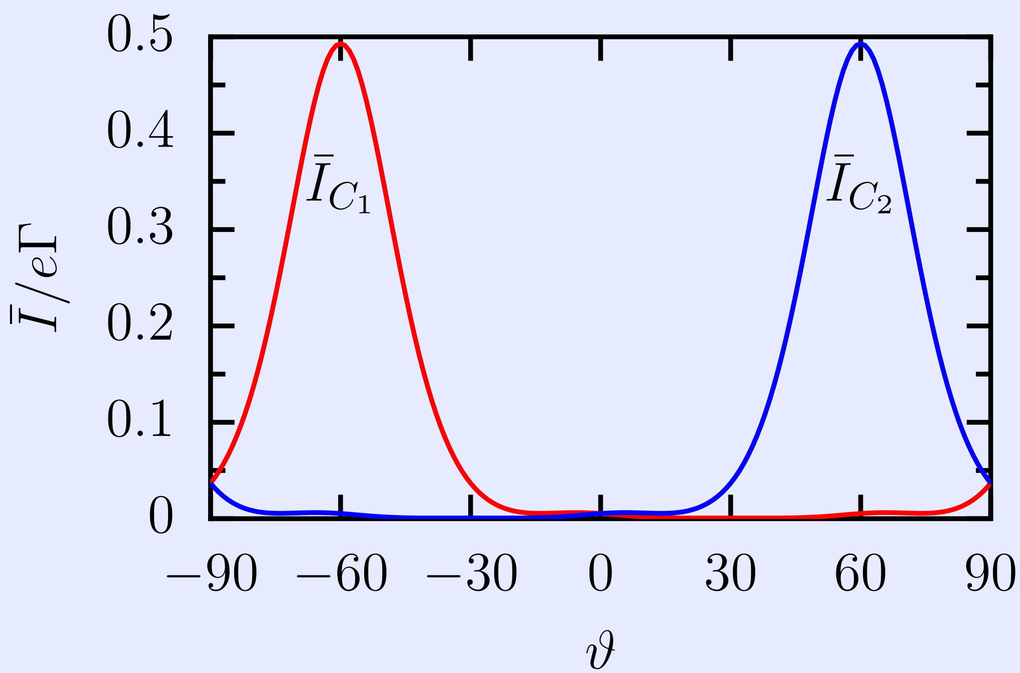


- both are double barrier situations (Fano factor $\approx 1/2$)

optical current router

- three-terminal geometry with $\mu_{\mathrm{E}} = -\mu_{\mathrm{C}_1} = -\mu_{\mathrm{C}_2}$
- linearly polarized laser field: polarization angle ϑ





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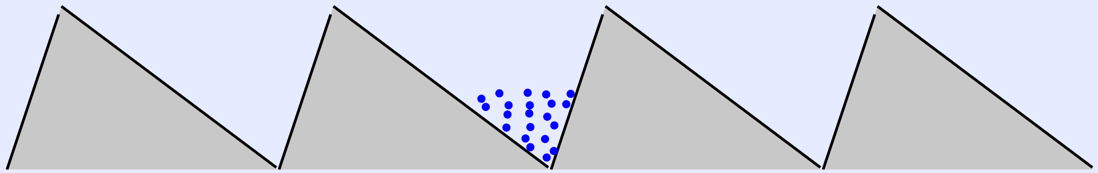
coherent quantum ratchet: motivation

- Brownian motion in a periodic but asymmetric potential



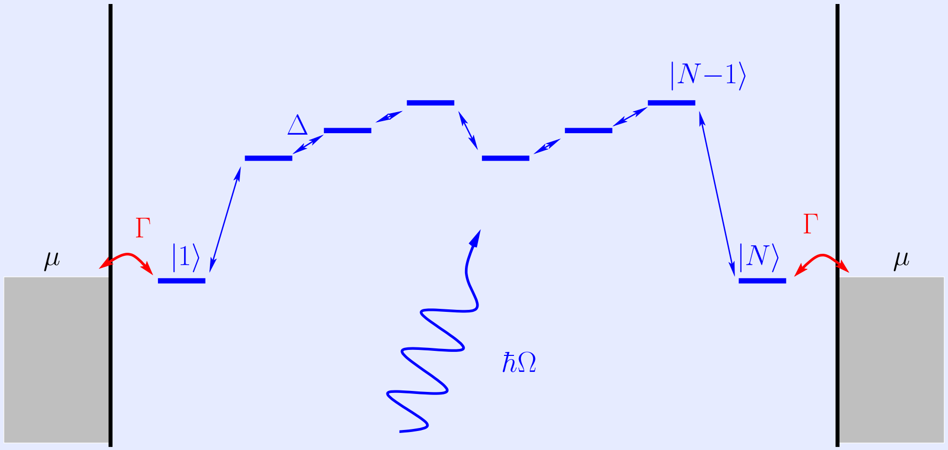
thermal equilibrium

$\Rightarrow$ no directed transport from noise: $\boxed{\bar{I} = 0}$

no perpetuum mobile of the second kind

- here: coherent quantum dynamics, non-adiabatic driving

coherent quantum ratchet



- no transport voltage

$$\mu_\mathrm{L} = \mu_\mathrm{R}$$

- finite periodic system consisting of N_g asymmetric groups

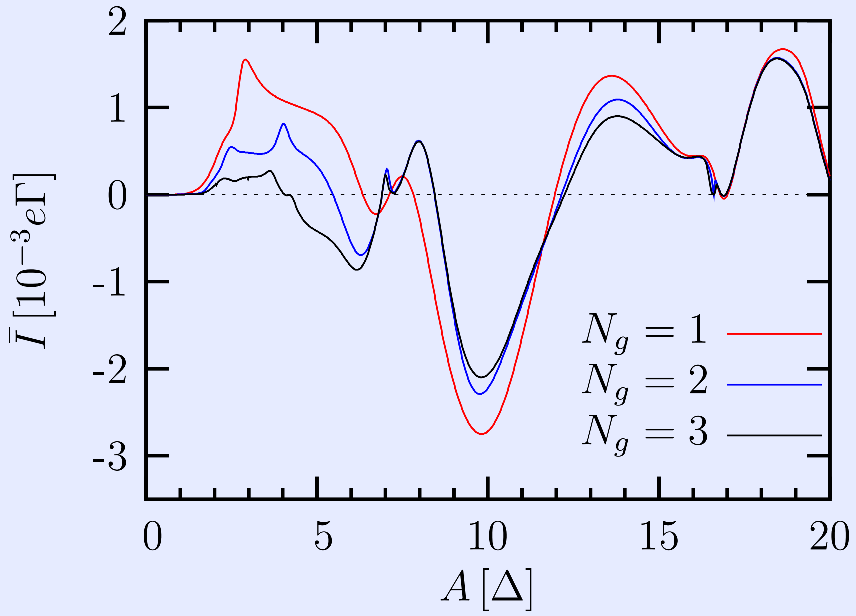
$$H_{nn'}(t) = -\Delta(\delta_{n,n'+1} + \delta_{n+1,n'}) + \Big(E_n + A\,x_n\cos(\Omega t)\Big)\delta_{nn'}$$

- ratchet effect due to effective dissipation from leads?
- length dependence?

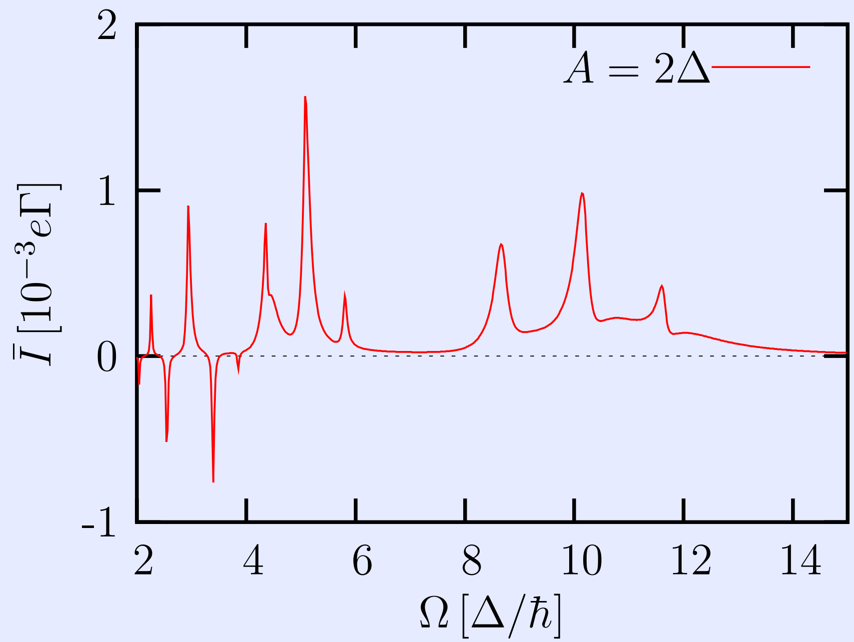
[J. Lehmann, S. Kohler, P. Hänggi, and A. Nitzan, Phys. Rev. Lett. **88**, 228305 (2002)]

coherent quantum ratchet: length dependence

dc current *vs.* driving amplitude



dc current *vs.* driving frequency

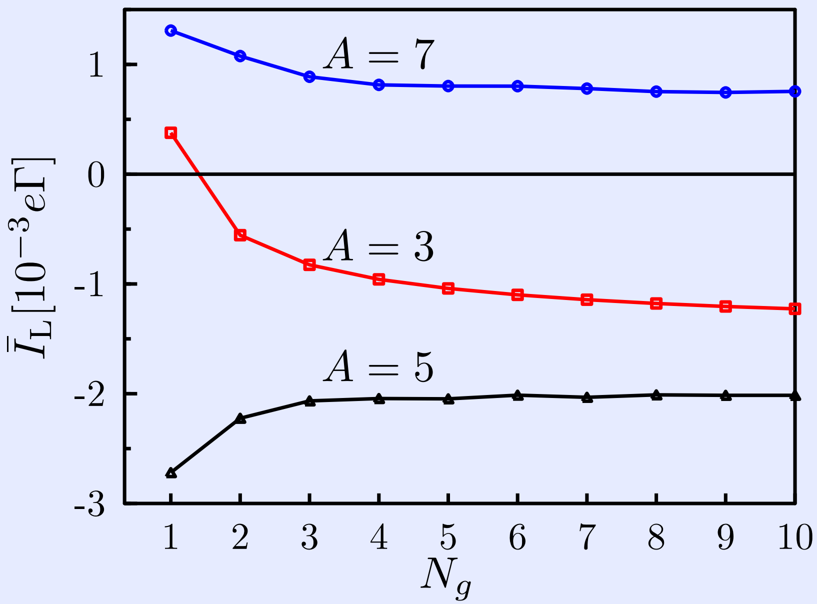


$\Delta = 1,\ \mu_L = \mu_R = 0,\ \Gamma = 0.1,\ kT = 0.25,\ E_D = E_A = 0, E_B = 10,\ E_S = 1$

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

coherent quantum ratchet

dc current *vs.* length



$\Delta = 1$, $\hbar\Omega = 3$, $\Gamma = 0.1$,
$kT = 0.25$, $\mu = 0$, $E_{\mathrm{B}} = 10$,
$E_{\mathrm{S}} = 1$

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

coherent quantum ratchet: symmetries

no ratchet current for parity $x \to -x$

- parity of a time-dependent Hamiltonian

$$\mathcal{H} = H_0(x) - xa(t)$$

  [$H_0(x) = H_0(-x)$ symmetric]

- symmetry of Hamiltonian
  $\longrightarrow$ two different scattering events have equal probability

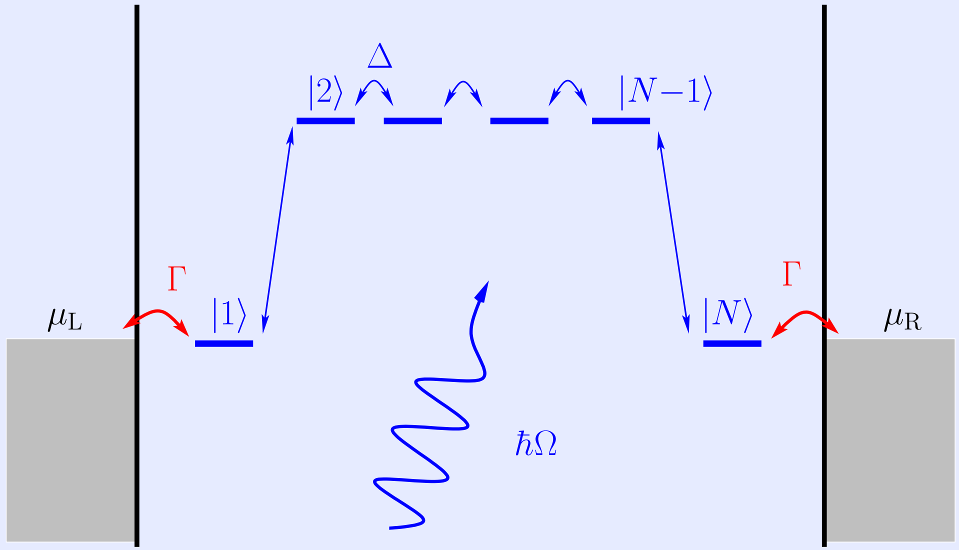
- harmonic driving [$a(t) = \sin(\Omega t)$]: three symmetries
  - time reversal $t \to \mathcal{T}/2 - t$ not relevant for $\bar{I}$
  - generalized parity $(x, t) \to (-x, t + T/2) \Longrightarrow \boxed{\bar{I} = 0}$
  - time-reversal parity $(x, t) \to (-x, -t) \Longrightarrow \boxed{\bar{I} = \mathcal{O}(\Gamma^2)}$

harmonic mixing

symmetry breaking due to driving

- mixing with higher harmonics

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

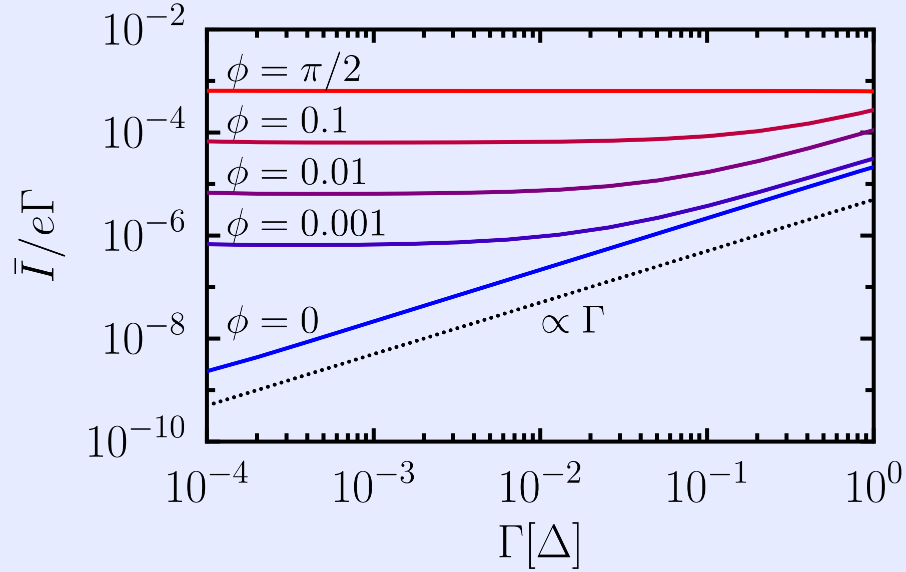


- $\mu_L = \mu_R$
- time-reversal parity for $\phi = 0$

[J. Lehmann, S. Kohler, P. Hänggi, and A. Nitzan, J. Chem. Phys. **118**, 3283 (2003)]

harmonic mixing: dc current

dc current *vs.* coupling strength



- influence of the phase ϕ:

  $\bar{I} \propto \Gamma$ 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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- Sébastien Camalet (Lyon)
- Abraham Nitzan (Tel Aviv)

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