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One of the symptoms of an approaching nervous breakdown is the belief that one's work is terribly important.

BERTRAND RUSSELL (1872-1970) in "Conquest of Happiness"

We are like dwarfs on the shoulders of giants, so that we can see more than they, and things at a great distance, not by virtue of any sight on our part, or any physical distinction, but because we are carried high and raised up by their giant size.

BERNARD OF CHARTRES (12th Century)

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Citations to Previously Published Work

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Full counting statistics of strongly non-Ohmic transport through single molecules, J. Koch, M. E. Raikh, and F. von Oppen, Phys. Rev. Lett. **95**, 056801 (2005), [cond-mat/0501065](#).

Chapters 5 and 6 are based upon

Effects of charge-dependent vibrational frequencies and anharmonicities in transport through molecules, J. Koch and F. von Oppen, Phys. Rev. B **72**, 113308 (2005), [cond-mat/0508011](#);

Current-induced nonequilibrium vibrations in single-molecule devices, J. Koch, M. Semmelhack, F. von Oppen, and A. Nitzan, Phys. Rev. B **73**, 155306 (2006), [cond-mat/0504095](#).

Chapter 7 appears in its entirety as

Thermopower of Single-Molecule Devices, J. Koch, F. von Oppen, Y. Oreg, and E. Sela, Phys. Rev. B **70**, 195107 (2004), [cond-mat/0405453](#).

Central parts of Chapter 8 have been published as

Pair tunneling through single molecules, J. Koch, M. E. Raikh, and F. von Oppen, Phys. Rev. Lett. **96**, 056803 (2006), [cond-mat/0510249](#);

Fractional Shot Noise in the Kondo Regime, E. Sela, Y. Oreg, F. von Oppen, and J. Koch, [cond-mat/0603442](#) (submitted to Phys. Rev. Lett.)

A compact review of the topics discussed in Chapters 3 and 8 has also been published as

Novel quantum transport effects in single-molecule transistors, F. von Oppen and J. Koch, Advances in Solid State Physics **46** (Springer-Verlag Berlin, 2006).

Finally, publications on the material presented in Chapter 4 (together with F. von Oppen and A. V. Andreev) and Chapter 8 (together with E. Sela, Y. Oreg, and F. von Oppen) are currently in preparation.

Electronic preprints (shown in typewriter font) are available on the Internet at the following URL:

<http://arXiv.org>

Notation

In order to avoid unnecessarily complicated notation, we have refrained from marking operators with “hats.” The c -number vs. operator nature of quantities should be clear from the context. Vectors are denoted in bold face, e.g. \mathbf{v} , matrices are indicated by sans-serif font, e.g. W . For the convenience of the reader, we provide a list of the symbols and abbreviations most frequently used throughout the text.

Symbol Description

$\lfloor x \rfloor$	floor function, gives the largest integer less than or equal to x
a	index for the left and right lead ($a = L, R$)
b, b^\dagger	annihilation and creation operator for a vibrational excitation of the molecule
β_m	parameter for the inverse width of the Morse potential
$c_{\mathbf{a}\mathbf{p}\sigma}, c_{\mathbf{a}\mathbf{p}\sigma}^\dagger$	annihilation and creation operator for an electron in lead a with momentum \mathbf{p} and spin projection σ
D	parameter for the depth of the Morse potential
$d_\sigma, d_\sigma^\dagger$	annihilation and creation operator for a spin- σ electron in the molecular orbital
ε_d	one-particle energy of the molecular orbital which dominates the transport
E_q^n	eigenenergy of the molecular state $ n, q\rangle$
F, F_{ex}	(zero-frequency) Fano factor, excess noise Fano factor
$f(\epsilon)$	Dirac-Fermi distribution, $f(\epsilon) = (e^{\beta\epsilon} + 1)^{-1}$
$f_a(\epsilon)$	Dirac-Fermi distribution for lead a , $f_a(\epsilon) = f(\epsilon - \mu_a)$
G	linear conductance
G_T	thermal linear-response coefficient
Γ	total tunneling-induced level width, $\Gamma = \sum_a \Gamma_a$
Γ_a	partial level width induced by tunneling in junction a , $\Gamma_a = 2\pi\rho t_a ^2$
$H_n(x)$	Hermite polynomial
$I_\nu(x)$	modified Bessel function
λ	dimensionless parameter characterizing the electron-phonon coupling strength
ℓ_{osc}	harmonic oscillator length (measure of the spatial extent of the vibrational ground state)
$L_n^m(x)$	generalized Laguerre polynomial
μ_a	chemical potential of lead a
$M_{qq'}$	Franck-Condon matrix element for a phonon transition $q \rightarrow q'$
n	electronic occupation number of the molecule
$n_B(\epsilon)$	Bose function, $n_B(\epsilon) = (e^{\beta\epsilon} - 1)^{-1}$
$n_{d\sigma}, n_d$	spin-resolved and total occupation-number operator for the molecular orbital
ω	(angular) frequency in the noise-power spectrum
ω_0	(angular) frequency for the vibrational mode of the molecule
P_q^{eq}	thermal equilibrium distribution for vibrational excitations
P_q^n	stationary occupation probability for the molecular state $ n, q\rangle$
$\psi(x)$	digamma function (logarithmic derivative of the Γ function)
q	vibrational excitation number for the molecule
ρ	density of states of the leads (constant in the wide-band limit)
σ	S_z component of the electronic spin ($\sigma = \uparrow, \downarrow$)
$s(n, n')$	spin factor
S	thermopower
$S(\omega)$	noise power spectrum for the current shot noise
T, β	temperature, $\beta = 1/k_B T$
τ	vibrational relaxation rate
t_a	tunneling matrix element for junction a
U	charging energy of the relevant molecular orbital
V	bias voltage
$W_{qq'}^{nm'}$	rate for the tunneling-induced transition $ n, q\rangle \rightarrow n', q'\rangle$

Abbreviation	Description
FC	Franck-Condon
HOMO	highest occupied molecular orbital
<i>IV</i>	current-voltage
LUMO	lowest unoccupied molecular orbital
MC	Monte-Carlo
NDC, NDR	negative differential conductance, negative differential resistance
PHLR	particle-hole/left-right
STM	scanning tunneling microscope
WHM	width at half maximum