Chapter 9

Conclusions and outlook

In this thesis, we have investigated the effects of molecular vibrations on electronic transport through single-molecule devices, whose study is at the heart of the field called molecular electronics. A prominent effect of the coupling between electronic and vibrational degrees of freedom, which previously has enjoyed much attention from experiments and theory, is the appearance of vibrational sidebands in the current-voltage characteristics. Here, we have shown that the consequences of the electron-phonon coupling go far beyond these well-known IV sidebands. The interaction between electrons and vibrations can fundamentally change the mode in which electrons are transferred across the molecule, and we have identified and characterized several fascinating transport regimes. An essential ingredient in gaining insight into these novel regimes consisted of extending the conventional transport calculations of linear conductance and nonlinear current-voltage characteristics to the consideration of current shot noise, thermoelectric response functions, and simulations of the time-dependent tunneling dynamics.

Motivated by the experimental finding that both Coulomb blockade and the Kondo effect are relevant for molecular junctions, we have based our investigation on the Anderson-Holstein Hamiltonian (Chapter 1). This description serves as the simplest model which yet incorporates Coulomb blockade, the Kondo effect, and vibrational sidebands, and allows for a systematic perturbative treatment with respect to the tunneling, appropriate for devices with weak coupling between molecule and leads (Chapter 2). The physical origin of the electron-phonon coupling encoded in this model is given by the fact that the spatial structure of the molecule generally depends on the molecular charge state. Consequently, the tunneling of electrons can alter the vibrational state of the molecule. The induced phonon dynamics has been shown to differ qualitatively depending on the electron-phonon coupling strength, and may itself act back on the tunneling dynamics, thus resulting in interesting collective effects.

We have established that vibrational nonequilibrium is most pronounced for weak electron-phonon coupling (Chapter 5). In this regime, the tunneling-induced phonon dynamics is appropriately described by a generalized diffusion process. Analytical expressions for the phonon distribution may be obtained from the corresponding Fokker-Planck distribution and agree nicely with our numerical results from the rate equations. For real single-molecule devices the large deviations from thermal equilibrium may have the drastic consequence of molecular dissociation and thus destruction of the device. In the extreme

case of negligible vibrational relaxation through interaction with the environment, we have analyzed the resulting dissociation rate by means of Monte-Carlo simulations for a Morse-potential model.

For the opposite limit of strong electron-phonon coupling (i.e. large displacements between potential surfaces of different charge states, Chapters 3 and 4), we have demonstrated that the low-bias transport is dominated by the Franck-Condon blockade, a current suppression caused by the lack of overlap between low-lying vibrational states. Our analysis of phonon distributions shows that vibrational nonequilibrium is less pronounced in total. Nevertheless, small deviations from thermal equilibrium have dramatic effects on the transport mode. In particular, depending on the typical relaxation time, transport either proceeds by transfer of single electrons (strong relaxation) or by large avalanches of electrons (weak relaxation). These avalanches occur whenever molecular vibrations are excited, and consist themselves of subavalanches, thus featuring a hierarchy of self-similar avalanches. This vibration-mediated bunching of electrons is particularly interesting in view of the conventional anti-bunching of fermions due to the Pauli principle, usually leading to sub-Poissonian shot noise. We have discussed the characteristic fingerprints of this peculiar transport mode – largely increased Fano factors, power-law behavior of the noise power spectrum, and strongly non-Ohmic full counting statistics –, which may serve as a future tool for an unambiguous identification of this regime through experiments. This challenge crucially depends on specifically choosing a molecule exhibiting strong electron-phonon coupling. An interesting class of candidates is given by molecules exhibiting the Jahn-Teller effect, which naturally leads to strong coupling. A theoretical investigation of this promising direction is currently under way.[1]

A second interesting consequence of the exponential suppression of sequential rates at strong electron-phonon coupling is the extraordinary sensitivity of transport to higher-order contributions such as cotunneling. We have presented a complete analysis taking account of cotunneling, which shows that the linear conductance and the low-bias IV are dominated by cotunneling processes. Intriguingly, cotunneling also gives rise to new effects missed by the sequential approximation. For weak vibrational relaxation, the presence of inelastic cotunneling may cause absorption-induced vibrational sidebands inside the usual Coulomb-blockade regime. Such additional sidebands have indeed been observed in experiments with suspended carbon nanotubes. Independently of vibrational relaxation, we find that the unusual dominance of cotunneling over sequential tunneling at strong electron-phonon coupling can generate telegraph noise in the low-bias current, which is reflected in a significant Fano factor enhancement.

Sensitivity to cotunneling processes has also been proven for the thermopower (Chapter 7). We have shown that this thermoelectric linear-response function has several appealing properties that go beyond the information that can be extracted from the current-voltage characteristics. In particular, a nonvanishing thermopower reflects the breaking of particle-hole symmetry with respect to the Fermi energy, and its sign reveals whether transport is accommodated by a flow of electrons or holes. As a consequence, the thermopower allows one to determine whether the molecular HOMO or LUMO mediate the transport. In contrast to the linear conductance, the thermopower also permits to probe vibrational excitations in a linear-response measurement. This may provide information complementary

[1] M. Schultz, T. Nunner, and F. von Oppen, in preparation.

to finite-bias IV measurements.

Acknowledging the rather complex nature of real molecules, we have performed a study of an extended model, taking into account the anharmonicity of potential surfaces and the fact that vibrational frequencies may depend on the molecular charge state (Chapter 5). In this case, the vibrational mode cannot be captured by a single energy scale, which is directly reflected in the spacings of vibrational sidebands in the current-voltage characteristics. Moreover, for weak vibrational relaxation which allows accumulation of phonon excitations, the incommensurability of excitation energies leads to a splitting of these sidebands into a multitude of subbands. At finite temperatures, this provides an additional effective broadening mechanism for vibrational sidebands beyond the mechanisms previously established in the literature.

Apart from tunneling-induced vibrational excitations associated with Franck-Condon matrix elements, the electron-phonon coupling has a second important consequence: the polaron shift of the molecular charging energy (Chapter 8). This downward renormalization opens the possibility of an overcompensation of the charging energy by the polaron shift, leading to an effectively attractive on-site interaction between electrons. This negative-U scenario bears some resemblance to the phonon-induced Cooper-pair formation in solids, and is in fact observed for a variety of molecules in electrochemical voltammogram measurements. For negative charging energy, the system favors even occupation numbers, and we have shown that the low-bias transport is dominated by tunneling of electron pairs. This peculiar transport mode has striking consequences for the linear conductance and the nonlinear current-voltage characteristics, which can directly be probed in experiments. Specifically, the investigation of the pair-tunneling conductance peak for different temperatures reveals that the width of the peak scales with temperature, while its height is fixed to a constant. This result is in stark contrast to conventional Coulomb-blockade peaks, which show a correlation between width and height so that their integral strength remains temperature independent. Further differences appear in the nonlinear current-voltage characteristics, which exhibit current rectification and gate-controlled switching for asymmetrically coupled devices. We have identified the phase-space behavior of pair-tunneling rates as the crucial origin of these distinctive features. Our analysis of current shot noise in this regime has also indicated that the transfer of electron pairs across the molecule leads to super-Poissonian noise.

Intriguingly, the degeneracy between two charge states in the negative-U model causes Kondo correlations at low temperatures. This charge-Kondo effect, which had been studied primarily numerically so far, may be analyzed by exploiting the relation between the negative-U model and the conventional Anderson model with an additional local Zeeman field. We have devised an exact canonical mapping suitable for the transport situation, the particle-hole/left-right transformation, which provides a one-to-one mapping between these two models. This has allowed us to derive analytical results for the logarithmic Kondo corrections above the Kondo temperature, as well as for the low-temperature Kondo regime itself. Our findings substantiate the fragility of the charge-Kondo effect as compared to the conventional spin-Kondo effect, which manifests itself in a departure from the unitary limit as soon as the system is detuned from the charge-degeneracy point.

In closing, we comment on interesting future directions of research, which follow from this thesis. (i) An important open question is the fate of the Franck-Condon blockade in the

low-temperature regime where the tunneling-induced level broadening becomes larger than temperature. In this case, perturbation theory in the tunneling is not a good starting point, and alternative approaches must be developed. (ii) The consideration of molecules with two distinct conformational configurations (so-called conformational stereoisomers) leads to the interesting possibility of current-induced switching between states. Experimentally, such behavior has been observed already in STM-type experiments. In a simplified model, the potential surface may be described by a double-well potential, and it is evident that Franck-Condon physics will play a crucial role in determining the transport dynamics. (iii) Several interesting projects could follow up on our investigation of pair tunneling. Specifically, we have focused on low energies allowing for the restriction to occupancy of the vibrational ground state only. For energies comparable to the phonon energy, *inelastic* pair-tunneling processes become relevant and lead to phonon dynamics. This interplay between both consequences of the electron-phonon coupling (the FC matrix elements and the renormalization of the charging energy) has not been considered so far. In addition, at even higher energies of the order of $|U|$, a crossover towards sequential tunneling takes place, which has not been addressed in the literature. (iv) Finally, a very promising future direction consists of the concerted consideration of vibrational and magnetic degrees of freedom. So far, vibrational and magnetic effects have been analyzed separately, and an investigation of the interplay between the two is lacking to date. In view of the interesting effects established for each, we expect that the interaction between them may lead to further fascinating collective effects in transport through molecular junctions.