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**Quantum transport
through single-molecule devices**

Abstract

In the emerging field of molecular electronics, the coupling of electronic degrees of freedom to molecular vibrations has been identified as a prime difference between electronic transport through single molecules and transport through conventional nanostructures such as quantum dots. In the present work, the consequences of this electron-phonon coupling are investigated, and we show that, beyond the well-known appearance of vibrational sidebands in current-voltage characteristics, it gives rise to novel collective transport effects.

The electron-phonon coupling originates from the fact that the spatial structure of the molecule depends on its charge state. Its two main effects are: (i) The tunneling of electrons through the molecular junction will result in excitation or deexcitation of molecular vibrations, described by Franck-Condon physics. (ii) Due to the interaction, the system gains energy and, as a result, the charging energy of the molecule is reduced (polaron shift). By calculating current-voltage characteristics, noise spectra, thermoelectric linear-response functions, and simulating the time evolution of tunneling events with Monte-Carlo methods, we show that both effects produce a variety of fascinating transport regimes.

The most striking result of the Franck-Condon physics (i) is found for strong electron-phonon coupling, characterized by large displacements of the molecular potential surfaces for different charge states. In this case, the lack of overlap between vibrational states causes a significant low-bias current suppression, the Franck-Condon blockade. In the blockade regime, relaxation of vibrations towards the thermal equilibrium plays a crucial role in determining the underlying transport mechanism: While strong relaxation leads to the conventional transfer of electrons one by one, weak relaxation and the resulting nonequilibrium situation feature transport of electrons in a hierarchy of self-similar avalanches. We show that this surprising transport mechanism has characteristic consequences for the current shot noise and the full counting statistics, which may serve as valuable fingerprints for an experimental verification of this regime.

Intriguingly, in resemblance to the formation of Cooper pairs induced by electron-phonon interaction in solids, the polaron shift (ii) opens up the possibility of single-molecule devices with an effectively attractive on-site interaction. This negative-U scenario leads to profoundly different transport characteristics as compared to Coulomb-blockade physics. In particular, we show that transport is dominated by tunneling of electron pairs resulting in a rather unconventional conductance peak, and in current rectification and gate-controlled switching at finite bias. By an exact canonical transformation, we establish a one-to-one mapping between the negative-U model and the conventional Anderson model. This allows for an analytical study of the charge-Kondo effect originating from the degeneracy of two even-number charge states.