Bond-bending Model for Negative Differential Resistance in Transport Through Single Molecules

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We develop a theory for strong negative differential resistance (NDR) in the transport through single, organic molecules, such as the Au-(2' – amino – 4 – ethynylphenyl - 4' – ethynylphenyl - 5' – nitro – 1 – benzenethiolate)-Au device studied recently by Chen *et al*. [1]. The theory employs a phenomenological model for bond-bending of the attached NO_2 side-group and treats the transport between localized states within the molecule via incoherent, photon-assisted tunneling. We derive and solve, in the stationary limit, a non-linear master equation for the transport through the molecule. We show that the source of the NDR is the non-linear capture of molecules by the NO_2 side-group which leads to a deformation of the molecule.

The model is illustrated in figure 1. While the method is general, we specify to the triple benzene ring plus NO_2 group for definiteness. We assume that the electron affinity of a single benzene molecule is stabilized by the nearby gold contacts (otherwise it is negative). Further, we assume that individual localized states exist for each benzene as well as for the attached side-group. The bare energies of the eigenstates localized on the benzenes and the NO_2, which enter the model as parameters, are augmented by the energy they acquire from the electric field between the gold contacts, eEz, where z is the average position (along the current direction) of the center of the wave function of the state. They are, in addition, supplemented by energy from their interaction with image charges in the gold contacts. Furthermore, it is assumed that the bond between the NO_2 and the benzene ring to which it is attached can bend, requiring a stereoscopic energy of $K\theta^2/2$. The transition rates between molecular states are determined from the dipole limit of photon assisted tunneling and are, for the case of emission, proportional to $\Delta E^3(1+n_B(\Delta E))$, where ΔE is the energy difference between the states and n_B is the Bose-Einstein distribution. A similar expression results for absorption which is, however, negligible in this case. The energy of the NO_2 state in particular depends on the degree of bending in its bond through the bond bending energy and the electric field term, which further depends on the occupancy of that state. Thus, when an electron transits to the NO_2, it can, for sufficiently strong fields, bend the bond and lower its energy relative to the benzene from which it tunneled. This can lead to a trapping of the charge and a resulting collapse of the current through the molecule as a whole, due to the interaction between this localized charge and other charges entering the molecule from the leads.

We discuss the dynamics of the trapping process by numerically solving the time dependent, non-linear master equation of motion. We further discuss the estimate of the energy parameters, which lead to the values for onset of current and its subsequent collapse, in terms of a density functional model for electron affinity of benzene in the vicinity of a half-space of metal.
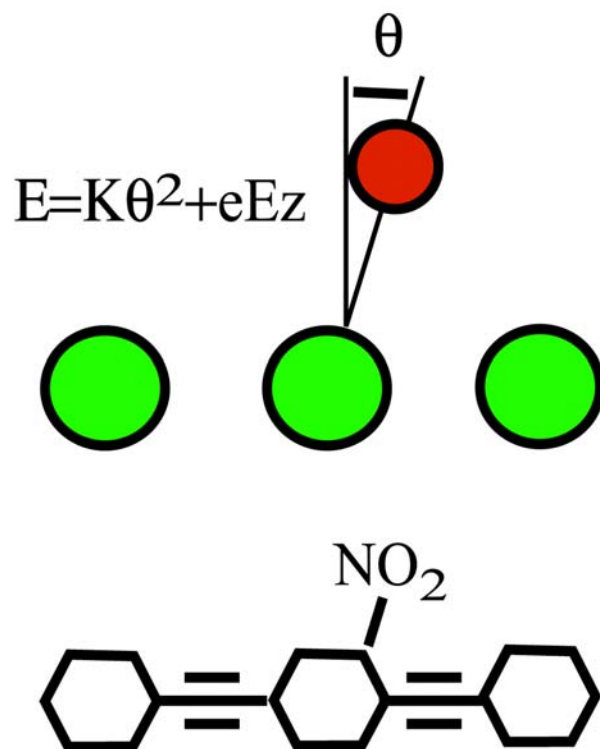
[1] Chen et al., Science **286**, 1550 (1998).

Fig. 1 Schematic model for NDR in transport through a triple benzene ring with an attached side-group with a positive electron affinity (in this case NO_2). The energy to bend the bond between the NO_2 and the benzene is included as is the energy due to the electric field between the contacts. The result is that the bond bending can lead to a self-consistent trapping of the electron in the NO_2 which thereupon suppresses further current through the molecule and gives the NDR.