Non–Linear Transport through a Molecular Nanojunction

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Abstract. – We present a simple model of electrical transport through a metal–molecule–metal nanojunction that includes charging effects as well as aspects of the electronic structure of the molecule. The interplay of a large charging energy and an asymmetry of the metal–molecule coupling can lead to various effects in non–linear electrical transport. In particular, strong negative differential conductance is observed under certain conditions.

Introduction. Single molecule electron transistors offer exciting perspectives for further miniaturisation of electronic devices with a potentially large impact in applications. To date several experiments have shown the possibility to attach individual molecules to leads and to measure the electrical transport. Two terminal transport through a single molecule \textsuperscript{1,2} or other nanoscale objects \textsuperscript{3,4} has been achieved by deposition of the object between two fixed electrodes or a conducting-tip STM above an object attached to a conducting substrate \textsuperscript{5,6}. Interesting and novel effects, such as negative differential conductance (NDC), were observed in one experiment \textsuperscript{7}, which still needs satisfactory theoretical explanation.

Several factors are important for single-molecule transport: For nanoscale objects the capacitance \(C\) is very small. Consequently, the energy to charge (or uncharge) the molecule \(E_C = e^2/2C\) can be very large, of the order of electron volts. This leads to the phenomenon of Coulomb blockade and makes room temperature single-electron transistors (SET) based on such molecules a distinct possibility. In contrast to SETs based on metallic islands \textsuperscript{8,9}, molecular devices have a more complicated electronic structure that, in principle, can be chemically 'designed'. Gaps in the I–V curve are not only determined by \(E_C\) but predominantly by the structure of the molecular bands \textsuperscript{10,11}. Therefore, it is important to consider the interplay of charging effects with the specific structure of the molecular orbitals. For electronic transport we will see that, in particular, the specific spatial structure of the molecular orbitals is crucial.

In this letter we study the impact of such a low-energy electronic structure on electronic transport and demonstrate that it can result in non–trivial conductance under reasonable generic assumptions. A full quantitative treatment of a molecule in contact with metal electrodes including many–body interactions on the molecule and strong molecule-electrode coupling is still out of reach. In this paper, we therefore study a simple model for a 'generic'
molecule that can be derived in principle from full electronic structure calculations and that includes capacitive interactions within the Coulomb blockade model as well as absorption and emission of photons. In contrast to most other theoretical work [15–19], we assume weak coupling between electrodes and the functional part of the molecule, a scenario that can be realized by proper design of molecule and contacts. We predict that the interplay of charging effects, the spatially non–trivial electronic structure and resulting asymmetric coupling to the electrodes leads to interesting phenomena in non–linear transport. We find that the I–V curve can show strong NDC behaviour and thus may provide a possible mechanism to explain recent experiments [12] showing similar NDC behaviour. Finally, we give a specific example that displays the required electronic structure in a simple aromatic molecule.

The Model. In the low-voltage regime only a few of the molecular levels will contribute to transport. For the purpose of this paper, we assume without loss of generality that there are only two participating molecular levels that are both unoccupied at zero voltage, which we designate as LUMO and LUMO+1. In particular in π electron systems of aromatic molecules it is relatively easy to realize a situation, where two closely spaced MOs are separated far from both the HOMO and the other LUMOs. The other MOs are assumed inert (always occupied or always empty), as we ignore co-tunnelling effects.

The MO Hamiltonian of the ‘reduced’ system can be written as:

\[ H = \sum_{i\sigma} \epsilon_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} + \sum_{ijkl\sigma\sigma'} V_{ijkl} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma}, \]

where the operators \( c_{i\sigma}, c_{i\sigma}^\dagger \) destroy/create electrons with spin \( \sigma \) in MO \( i \). This Hamiltonian contains a large number of parameters even for the two level system. In order to make contact with the quantum dot physics and to elucidate similarities and crucial differences that occur in single molecule transport it is useful to introduce an effective model for the molecular Hamiltonian:

\[ H_{mol} = \epsilon_1 N_1 + \epsilon_2 N_2 + E_C (N_1 + N_2)^2 + \frac{U}{2} \sum_l N_l (N_l - 1) + \frac{\Delta_{ex}}{2} \sum_{\sigma,\sigma'} c_{1\sigma}^\dagger c_{2\sigma'}^\dagger c_{1\sigma'} c_{2\sigma}, \]

where \( N_l \) is the occupation of the MO \( l \). As unit of energy we take \( \Delta\epsilon = \epsilon_2 - \epsilon_1 \), the “bare” MO splitting. The diagonal electronic repulsion terms of Eq. (1) for the two MOs together with capacitive interactions with the leads can be rewritten as \( E_C (N_1 + N_2)^2 + U \sum_l N_l (N_l - 1) \). (for simplicity, we assumed an orbital independent Hubbard-like repulsion \( U \) for double occupancy of a MO). \( \Delta_{ex} \) is a Hund’s rule triplet-singlet splitting for the two electronic levels. In comparison to Eq. (1) we have neglected single electron hopping mediated by two-electron screening effects (which are small for most π systems in the chosen basis).

The bias is dropped symmetrically over the molecule, so no capacitive shifts of energies appear (this can be easily included). A likely energetic ‘term scheme’ for the single- and two-particle states described by model Hamiltonian Eq. (2) is depicted in the left panel of Fig. 1. The electrodes are considered as non–interacting electron reservoirs. The reservoirs are assumed to be occupied according to an equilibrium Fermi distribution function \( f_\alpha(\omega) = f(\omega - \mu_\alpha) \), where \( \mu_\alpha \) denotes the electrochemical potential of electrode \( \alpha = L, R \). The MOs couple to the electrodes via tunnelling contacts with (possibly) very different coupling strength \( t_{i\sigma}^\alpha \).

\[ H_{mol-leads} = (\frac{\Gamma}{2\pi \rho_e})^{1/2} \sum_{k\sigma\alpha} \left( t_{i\sigma}^\alpha a_{k\sigma\alpha}^\dagger + h.c. \right), \]

(3)
Fig. 1 – Equilibrium molecule energies for model Hamiltonian $H$ and resulting current–voltage characteristics. We choose energies such that the triplet states ($T$) lies below the singlets ($S_{12}$, $S_1$, $S_2$) and between the two possible doublets. $\epsilon_1 = -12$, $\epsilon_2 = -11$, ($\Delta \epsilon = 1$), $U = 2$, $\Delta_{ex} = 0.5$, $E_C = 4$, $\Gamma = 0.004$, $\Delta = 0.25$.

where $\rho_\alpha$ is the density of states (assumed constant) of the non–interacting electrons in the leads, described by operators $a_\alpha^\dagger a_\alpha$. $\Gamma$ denotes the scale of the broadening of the MOs due to the coupling to the leads. The dimensionless tunnelling parameters $t_{i\sigma}^\alpha$ can depend on $\alpha, l$.

In order to investigate whether the predicted effects are robust, we include a coupling of the molecule to a (broad band) boson field which simulates the relaxation of excited states in a real molecule by coupling of the electrons to an electromagnetic field (photons) and vibrations (phonons) in the molecule.

**Theoretical Approach.** We use a Master equation approach for the occupation probabilities $P_s$ of the molecular many–body states. The transition rate $\Sigma_{ss'}$ from state $s'$ to $s$ is computed up to linear order in $\Gamma$ using golden rule (second order perturbation theory) in both the electrode–molecule and the bosonic coupling. For the transition rates we have $\Sigma_{ss'} = \sum_{\alpha} \sigma_{\alpha}^\pm \Sigma_{ss'}^\alpha$, where $\Sigma_{ss'}^\alpha$ is the tunnelling rate to/from electrode $\alpha$ for creation ($p=+\alpha$) or destruction ($p=\alpha$) of an electron on the molecule. We have

$$\Sigma_{ss'}^\alpha = \Gamma f_{\alpha} (E_s - E_{s'}) \sum_{\sigma} \sum_{l} | t_{l\sigma}^\alpha |^2 \delta \left( | s \rangle | s' \rangle - | s' \rangle | s \rangle \right),$$

and a corresponding equation for $\Sigma_{ss'}^{-\alpha}$ by replacing $f_{\alpha} \to 1 - f_{\alpha}$. The boson-mediated rates $\Sigma_{ss'}^b$ describe absorption and emission of bosons. For photons we have

$$\Sigma_{ss'}^b = g_{ph} \frac{4e^2}{3h^2c^3} (E_s - E_{s'}) N_b (E_s - E_{s'}) | \langle s | d | s' \rangle |^2,$$

where $d$ is the dipole operator and $N_b (E)$ denotes the equilibrium Bose function. $g_{ph}$ is a parameter that allows us to modify the strength of the coupling to simulate increased dipole moment or other sources of relaxation. $g_{ph} = 1$, unless noted. This value corresponds to a dipole of charge $e$ and length $1\text{Å}$.

We determine the $P_s$ by solution of the stationarity condition:

$$\dot{P}_s = 0 = \sum_{s'} (\Sigma_{ss'} P_{s'} - \Sigma_{s's} P_s).$$
Fig. 2 – Left Panel: I–V–characteristics for various coupling $t_2^R$. A pronounced NDC effect is observed for reduced $t_2^R$. Right Panel: Occupation probability $P_s$ of the relevant molecule states for $t_2^R = 0.03$. The fat solid line indicating $P_{S_2}$ reaches nearly unity in the blocking regime at bias $V_{\text{bias}} > 6$. We multiply the probabilities with the corresponding degeneracy, so the sum of the $P_s$ adds up to unity.

The current in the left and right electrode can then be calculated via

$$I_\alpha = e \sum_{s,s'} (\Sigma^\alpha_{s,s'} P_{s'} - \Sigma^\alpha_{s,s} P_s).$$

(7)

The bosonic transition rates do not contribute directly to the current, since they do not change the particle number on the molecule.

Results. The effective Hamiltonian Eq. (2) affords several generic scenarios for NDC. The NDC is generic in the sense that NDC will occur at some bias for an initially charged molecule (case (1)) as well as an initially empty molecule (case (2)).

Case (1): The right panel of Fig. 1 shows the I–V–characteristics for equal tunnelling couplings $t_1^R = 1$ with a symmetric bias, $\mu_L = -\mu_R$. There are four characteristic steps which are related to the onset of the triplet and the three singlet states. From the plateau widths all characteristic energy scales can be deduced.

Strong NDC behaviour is observed if one MO couples much more weakly to the right side than the other MO, e.g. $t_2^R = 0.03; t_1^R = t_1^L = t_2^L = 1$, see Fig. 2. For a certain bias region the current is suppressed by a factor $(t_2^R)^2$. The reason for this current decrease is the occupation of a molecule state ($S_2$ in this case) from which the molecule can not escape anymore due to a combination of blocking Fermi sea, Coulomb blockade and the small coupling of an MO to the electrode.

Initially, the molecule is singly occupied in state $D_1$. The current starts at a bias when the first two–electron state (triplet) becomes occupied (the “empty” state has higher energy for the given parameters). The current can flow via sequential hops through MO1. The electron on MO2 is essentially stuck since its tunnelling time to the right reservoir is suppressed by a factor $(t_2^R)^2$, and tunnelling to the left is suppressed because of the blocking Fermi sea.

But at larger bias the electrons tunnelling onto the molecule from the left can also form the state $S_2$, with both electrons in MO2 as depicted in Fig. 2. No other electron can enter the molecule at this bias because of the charging energy. Since the relaxation due to the boson coupling is very slow, the only relevant decay of this state is via the small coupling to the right electrode. Consequently, the molecule is stuck for a long time in state $S_2$. As the right panel of Fig. 2 shows the average probability $P_{S_2}$ is nearly unity. A relative suppression of $t_2^R$ by 0.3 is sufficient to achieve a pronounced NDC effect. Increasing the temperature will
broaden the plateau steps and shift the current maximum slightly to larger bias (not shown). At much larger bias (not shown), states with an additional electron become occupied, and the current rises again.

The left panel of Fig. 3 shows that for the same set of energy parameters NDC is observed also if $t_1^R$ is suppressed instead of $t_2^R$. In this case the blocking state is $S_1$ as indicated by the occupation probabilities in the right panel of Fig. 3.

Case (2): NDC is also observed if we start from an initially uncharged molecule, see the left panel of Fig. 4. Note that NDC is observed for $t_2^R = 0.03$ for positive bias only, whereas for negative bias there is a simple step (dashed curve). This is because if the bias is negative MO2 and consequently $D_2$ will not become occupied at all, so the current through $D_1$ continues to flow. We also want to point out that if both the left and right coupling of an MO is reduced, NDC is observed for both signs of bias, however, it is limited to a Peak to Valley Ratio (PVR) of 2 [21], whereas the PVR for the one sided suppression is limited by $1/(t_2^R)^2 \gg 1$.

In the right panel of Fig. 4 we show the influence of internal molecule relaxation by increasing the boson coupling $g_{ph}$ for case (2) (case (1) shows similar behaviour). An increase in the bosonic relaxation rate by six orders of magnitude over the one obtained in dipole approximation is necessary to completely eliminate NDC behaviour. It is debatable whether coupling to vibrations of the molecule can provide such a rate. However, even in a situation where the coupling $g_{ph}$ is nominally large there can be selection rules that prevent decay of certain states. An example would be the inhibition of (direct) transitions between states of different total spin, i.e. singlet–triplet transitions. Then, NDC will take place if the triplet states ($T$) are lower in energy than the singlets ($S_1, S_{12}, S_2$) and $S_1$ is the singlet of lowest energy, different from the situation shown in Fig. 1. The blocking state is $S_1$, the singlet of lowest energy. Because of the energy balance “decay” (emission of a boson) of this state could only involve the triplets. But this is “forbidden” by the different total spin of the triplets. Therefore, as long as there is no absorption of bosons to speak of, this scenario of NDC is stable even in the presence of a boson coupling. The rate of absorption processes will strongly depend on the number of bosons present. The number of bosons increases with temperature, therefore the NDC effect will in general decrease as the temperature is increased due to fact that the molecule can escape the blocking state by absorption of bosons.

The proposed scenarios for NDC are possible explanations for a recent experiment [22]
Fig. 4 – I–V–characteristics of the initially neutral molecule. $\epsilon_1 = -0.5$, $\epsilon_2 = 0.5$, $U = 1.5$, $\Delta_{e_1} = 0.5$ and $E_C = 1.5$. Left Panel: NDC is observed for $t_{2}^{R} = 0.03$ involving $D_2$ as the blocking state. If both $t_{2}^{R}$ and $t_{2}^{L}$ are suppressed the size of the NDC is limited (see text). Right Panel: Relaxation by photon emission $g_{ph}$ destroys NDC, but only if the coupling $g_{ph}$ is increased by several orders of magnitude over the dipole approximation.

showing a PVR of more than 1000 at $T \sim 100K$. But in that experiment one is probing transport through a whole array of molecules and the nature of one contact side is unknown. The temperature dependence is strong ($PVR \sim 1.5$ at room temperature) and shows a peak shift to smaller bias with increasing temperature. Whereas the decrease of the PVR could be understood by the increased absorption of bosons (see discussion above) the shift is without the reach of the considered model.

Physical Realization. The energetic arrangement of two closely spaced molecular orbitals that couple very differently to the left and right electrodes can be realized in principle with very simple aromatic molecules that are suitably substituted to break their full symmetry. As an example, Fig. 5 shows the LUMO and LUMO+1 for a 1,3-dimethyl benzene (meta-xylene) that are closely spaced energetically and that couple very differently on various possible unsubstituted contact sites. There will be MOs which are antisymmetric with respect to the 2,5-axis mirror symmetry with vanishing wave function amplitude at the 2 and the 5 position. In contrast, the symmetric MOs will in general have non-vanishing wave function at these po-

Fig. 5 – The LUMO and LUMO+1 for a double methyl substituted benzene. By (anti)-symmetry, one of the MOs will have no coupling at the 2 position.
sitions. If one couples the molecule at the 2 and 6 positions to electrodes, the LUMO couples to both electrodes whereas the LUMO+1 would have no coupling to the electrode ‘connected’ to the 2 position \[22\]. Thus, the situation of a strongly MO and electrode dependent coupling seems to be generic for small aromatic molecules with ligand groups.

**Conclusions.** We have developed a model of non–linear charge transport through a metal–molecule–metal nanojunction. We have shown that the interplay of charging effects and the spatially non–trivial electronic structure of the molecule can lead to current peaks and strong negative differential conductance. NDC will be observed no matter whether the tunnel coupling of the lower or the higher MO is suppressed. For a coupling to photons in dipole approximation the relaxation rate induced by the photons is several orders of magnitude too small in comparison to typical tunnelling rates to have an effect. We believe that the model is sufficiently generic to be realized in certain classes of aromatic molecules with tunnel contacts to electrodes.

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