Negative differential conductance in a benzene-molecular device

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Abstract

We predict a *negative differential conductance effect* in the nonlinear transport through a molecular device containing a weakly coupled benzene ring. An effective *interacting* Hamiltonian for the π electrons (derived from an electronic structure calculation) serves as input for the transport calculation.

Key words: molecular; electronics; blockade; device;

Introduction Single molecule electronic devices offer exciting perspectives for further minituarization of electronic circuits with a potentially large impact in applications. Several experiments have demonstrated the possibility to attach individual molecules to leads and to measure the electrical transport. [1–4] In contrast to single electron transistors (SETs) based on quantum dots [5] the electronic structure of molecular devices can be chemically 'designed' for specific applications. When the molecule is coupled *weakly* to the electrodes, i.e. via electron tunneling, charging effects, semi-classically determined by the small capacitance of the molecule, become important. The interplay of charging effects with the specific structure of the molecular orbitals leads to nontrivial current voltage (I-V) characteristics [6,7]. Using benzene as a prototypical example we investigate novel effects that arise when transport through several competing electronic configurations becomes possible. We derive a semi-quantitative model for the conducting many-body states of the system from electronic structure calculations. For weak coupling to the electrode we compute the transport within the golden rule approximation (sequential tunneling) and include screening of the applied electric field as well as radiative transitions between the electronic states of the molecule. We predict a current collapse in the I-V and strong negative differential conductance (NDC) when the molecule is coupled to the electrode at the para-position. The mechanism for this effect is the occupation of a so-called "blocking state" of the molecule, which cannot decay for symmetry reasons. For coupling at the meta-position, the I-V displays a series of steps, but no NDC.

Model We first perform a Hartree-Fock calculation in a suitable basis and then transform the Hamiltonian to the molecular orbital basis. Next we integrate out the σ electrons arriving at an effective *interacting* model Hamiltonian for the π electrons of the system in the presence of the atomic cores and the "frozen" density of the σ electrons:

$$H_\pi = \sum_{ijs} \epsilon_{ij} c^\dagger_{s,i} c_{s,j} + \sum_{ijklss'} U_{ijkl} c^\dagger_{s,i} c^\dagger_{s',j} c_{s',k} c_{s,l} \qquad (1)$$

The operators $c^\dagger_{s,i}, c_{s,i}$ create/destroy electrons of spin s in orthogonalized Wannier-like orbitals centered at the carbon atoms. This model neglects σ-π mixing for certain excited states of the molecule [8,9]. When applying a symmetric bias over the molecule we thus neglect the higher order effect of field screening by σ electrons. We diagonalize the Hamiltonian eq. (1) in the appropriate charge/spin/symmetry sectors and obtain the many-body eigenstates $|s\rangle$ with the corresponding

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energies E_s and their total spin S_s. The low-energy spectrum obtained for the neutral states compares favorably with the spectrum directly obtained from accurate multi-reference configuration interaction calculations [9,10]. The restriction to a pure π-electron system is more severe for the states of the charged molecule (anion). We can account for the effect of an external bias potential V^{ext} on the electrons by adding an extra term to the Hamiltonian H_π. Here we consider a bias voltage $V_{bias} = V_L - V_R$ aligned with the transport direction. We use a Master equation approach [7] to calculate the occupation probabilities P_s of $|s\rangle$ in a non-equilibrium stationary state. The transition rate $\Sigma_{ss'} = \sum_{\alpha,p=\pm} \Sigma^{\alpha p}_{ss'} + \Sigma^{d}_{s,s'}$ from state s' to s is computed in perturbation theory using the golden rule. For simplicity, we assume that tunneling is only possible through two "contact" carbon atoms at the 1 and 4 (para) positions. $\Sigma^{\alpha p}_{ss'}$ is the rate for tunneling to/from electrode $\alpha = L, R$ on $(p = +)$ and off $(p = -)$ the molecule. As we do not consider the leads microscopically, the coupling of molecule is determined by the overall coupling strength Γ and the relative wave function amplitude of the state $|s\rangle$ at the coupling carbon atom. We must have $\Gamma \ll k_b T \approx 40 meV$ for perturbation theory to apply at room temperature T. When including relaxation by radiative transitions, we use the dipole approximation for the transition rate $\Sigma^{d}_{s,s'}$ with transition moments obtained from the electronic structure calculations. The current in the left and right electrode is calculated via $I_\alpha = e \sum_{s,s'} (\Sigma^{\alpha +}_{ss'} P_{s'} - \Sigma^{\alpha -}_{s's} P_s)$.

Results Without radiative relaxation (solid line in Fig. 1) the *I-V* consists of a series of steps of which only a few are well resolved on this scale. The inclusion of radiative transitions has a dramatic effect on the *I-V* (dashed line). We observe a collapse of the current over a substantial range of the applied bias (2.1-3.4 eV). The reason for this collapse is the population of a "blocking" state in the cascade of transitions that becomes possible when exited states of the neutral molecule and anion become accessible. Above approximately 2.1 eV bias an excited state of the anion at about 5.6 eV (see Fig. 2), becomes partially populated in the transport cascade. This state can decay by photon emission to either a symmetric or an antisymmetric (with respect to the plane through the transport axis and perpendicular to the molecular plane) many body state of the anion. In the bias range where the current collapses this state cannot decay by coupling to the leads, because the lowest neutral states are symmetric (see Fig. 2) and the tunneling preserves the symmetry. Since there are no further radiative transitions possible on the molecule, in the stationary state the probability of occupying the "blocking" state is unity and the current ceases to flow. At a larger bias (3.4 eV), the first escape channel opens, and the system can decay to the first antisymmetric excited state of the neutral molecule, which can then decay further. If we couple the right electrode to the meta position of benzene (left panel, dash-dotted curve) we find no current collapse with or without radiative relaxation or bias effect.

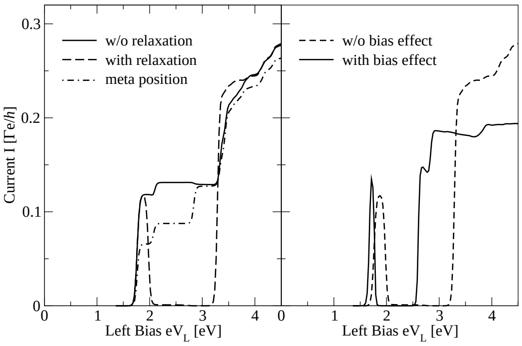

Fig. 1. *I-V* characteristics for symmetric bias. *Left Panel*: *I-V* without (solid line) and with radiative relaxation (dashed line), bias effect not included. For coupling of the right electrode at the meta position (dash-dotted line) no current collapse is observed. *Right Panel*: With the bias effect included (solid line) the onset of current is generally shifted to lower bias, but the current collapse remains.

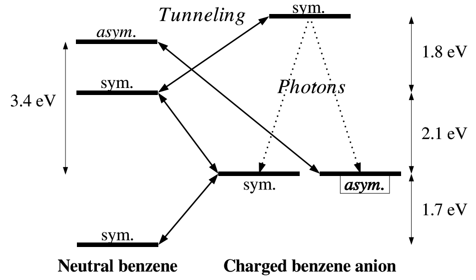

Fig. 2. Energy and symmetry of the relevant states.

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