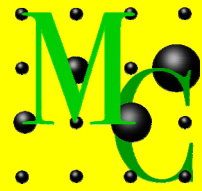


Rectification effects in quantum transport through single aromatic molecules

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The signatures of truly molecular mediated quantum transport in single molecule experiments have to be selectively identified and often their theoretical mechanisms still need to be understood. We investigated the behavior of a donor-acceptor molecular junction in the coherent regime using a model Hamiltonian [1] as well as density functional based nonequilibrium transport calculations [2]. Additionally, we studied the system in the situation of weak coupling to the leads where charging effects do play an important role and we could show that the intrinsic energetic asymmetry of a donor-acceptor molecule remains responsible for the rectification effects even in the Coulomb blockade regime [3]. Contact to the experiments by Elbing *et al.* [4] is also provided.

Introduction

Transport measurements of systems composed of single molecules attached to metallic electrodes state the ultimate limit of nanoelectronics. However, important questions remain:

- Is really a single molecule device measured?
 - What is the relation between measured effects and intrinsic molecular properties?
- ⇒ **Search for signatures of single molecular properties in nanoelectronic experiments, e.g.:**
- vibrations
 - **rectifying behavior** due to conformational and electronic asymmetries

Motivation: Single molecule diodes

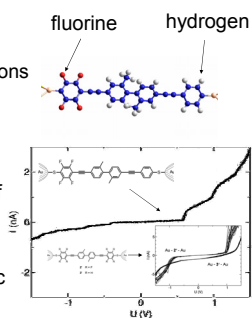
Aviram and Ratner [5]:
theoretical proposal (1974)

- molecule divided into π -conjugated acceptor and donor part
- weakly coupled via a σ -bonded tunneling bridge

diode-like behavior due to different inelastic tunneling thresholds for positive and negative bias

- Elbing *et al.* [2]:**
experimental realization
- contacted via break junctions
 - separation by reduced overlap of π -systems

- different donor/acceptor properties: substitution of hydrogen by fluorine
- control experiments: no rectification for symmetric molecules (H/H) or (F/F)



Recent DFT-based analysis

- phenomenological level analysis of the extended molecule in an external field (Elbing *et al.* [4])
- DFT based transport characteristics and extended molecule level analysis (Stokbro *et al.* [6])

Objectives

- simulation of **coherent quantum transport** through single-molecule diodes
- insight of coherent **rectification mechanisms**
- exploring **charging regime** using a **novel Ansatz**

References

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- [4] M. Elbing *et al.*, *Proc. Natl. Acad. Sci. USA* **102**, 8815 (2005).
- [5] A. Aviram and M.A. Ratner, *Chem. Phys. Lett* **29**, 277 (1974).
- [6] K. Stokbro *et al.*, *J. Am. Chem. Soc.* **125**, 3675 (2003).
- [7] *Introducing Molecular Electronics*, edited by G. Cuniberti, G. Fagas, and K. Richter, *Lecture Notes in Physics Vol. 680*, Springer, Berlin (2005).
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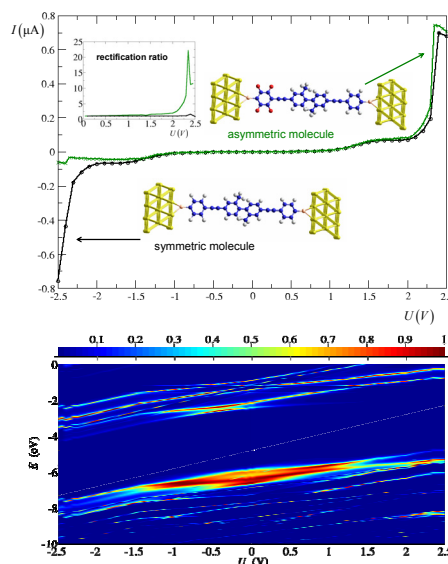
DFT-Keldysh Approach

Non equilibrium (Keldysh) Green functions technique: finite voltage current relation from DFT based calculations of the "extended" molecular region [7]

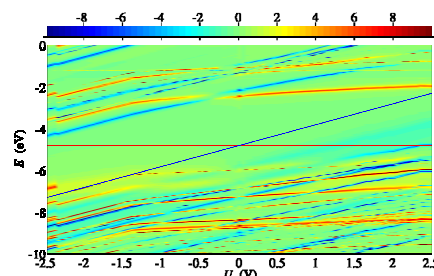
- DFTB: DFT-based two-center charge self consistent tight-binding method [8]
- Extensions to quantum transport: SCC loop over non-equilibrium Green function, Density Matrix and Poisson equation
- "extended molecule" (thiolated molecule bonded to ideal Au clusters) attached to Au surface
- coherent non equilibrium current:

$$I(U) = \frac{2e}{h} \int T(E, U) (f(E - \mu_R) - f(E - \mu_L)) dE$$

Results: IV-characteristics and Transmission function of molecules studied by Elbing *et al.* [2]:



difference of LDOS projected on F and H part:



localization of molecular levels: change in slope

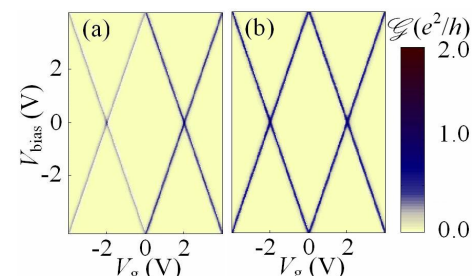
Model Approach: EOM + NEGF Song *et al.* [3]

We perform an *Ansatz* consisting in substituting the *Dyson-first-order* $G_{\sigma,1}^{(1)asc}$ with the *EOM one* $G_{\sigma}^{(1)asc}$ to consider more many-particle correlations

$$\begin{array}{ccc} \tilde{G}_{\sigma} & \tilde{G}_{\sigma}^{(1)} & \text{EOM} \\ \downarrow & \downarrow & \\ \tilde{G}_{\sigma} = \tilde{G}_{\sigma,0} + \tilde{G}_{\sigma,0} \tilde{\Sigma}_{\sigma,1} \tilde{G}_{\sigma,1} & & \text{Dyson} \end{array}$$

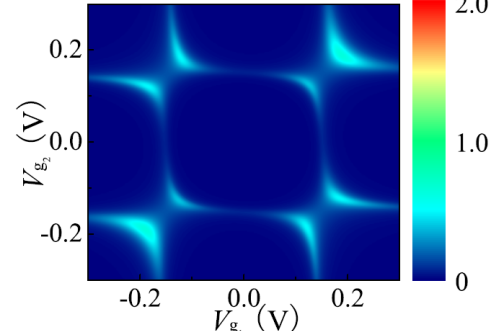
Then applying the Langreth theorem, one can obtain the lesser GF working well for *Coulomb blockade*.

Stability diagram of single site junction

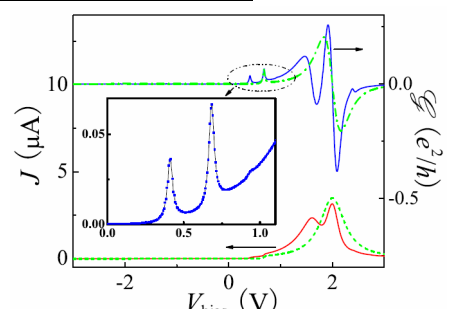


- (a) The incorrect result obtained by means of the widely used formula of NEGF [3, 7].
(b) Results obtained by means of our *Ansatz* shows correctly symmetric, which is *basically no different* from Master equation's results [3].

Stability diagram of double site junction



Simulation of molecular diode



The dash and dot-dash curves are for current and conductance with $U = 0$, respectively.

Conclusions

- DFT based transport calculations: Rectifying behavior
- Coulomb Blockade effects using NEGF
- Evidence for the voltage induced level shift
- Charging effects: Rectification is conserved