Out of equilibrium charge transport in molecular electronic devices

Andrea Nava, Domenico Giuliano, Luca Lepori and Marco Rossi
Dipartimento di Fisica, Università della Calabria, Arcavacata di Rende I-87036, Cosenza, Italy
INFN - Gruppo collegato di Cosenza, Arcavacata di Rende I-87036, Cosenza, Italy
E-mail: andrea.nava@fis.unical.it

Abstract. Using the Lindblad equation approach, we study the nonequilibrium stationary state of a benzene ring connected to two reservoirs in the large bias regime, a prototype of a generic molecular electronic device. We show the emergence of an optimal working point (corresponding to a change in the monotonicity of the stationary current, as a function of the applied bias) and its robustness against chemical potential and bond disorder.

1. Introduction
Molecular electronics is a promising theoretical and experimental research field focusing on the possibility to implement single molecules in quantum circuit in order to realize molecular switches, logic gate, and junctions. It is, therefore, of the utmost importance to provide models describing molecules attached to two, or more, macroscopic contacts gates and the currents across as a function of the voltage bias or of the temperature gradient between the contacts.

In this manuscript, we model the charge transport mechanisms in such systems using the master equation formalism, already implemented for one-dimensional chains [1, 2, 3]. To be specific, we resort to the Lindblad equation (LE) approach to open quantum systems. This approach allows to derive the effective dynamics of the system by integrating over the reservoir degrees of freedom under the Markovian approximation, consisting in neglecting memory effects of the reservoirs. In the following, we first describe the general method and then apply it to a simple paradigmatic example, the benzene ring.

2. The model
The starting point is the Hückel Hamiltonian for the π-electrons of a generic N-atom molecule,

\[ H = - \sum_{j \neq k=1}^{N} t_{j,k} c_j^{\dagger} c_k + \sum_{j=0}^{N} \epsilon_j c_j^{\dagger} c_j. \]  \hspace{1cm} (1)

In Eq. (1), \( c_j^{\dagger}, c_j \) are single-electron creation and annihilation operators at molecular site \( j \), satisfying the canonical anticommutation relations \( \{ c_j, c_k^{\dagger} \} = \delta_{j,k} \), \( t_{j,k} \) is the single-electron hopping strength between the \( j \)-th and the \( k \)-th atoms and \( \epsilon_j \) is the on-site energy. For the sake of simplicity, we neglect the interaction between electrons, which can be easily implemented following Ref. [3].
We are interested in studying the behavior of the molecule when it is connected to two or more external reservoirs through some of its atoms. The LE consists of a first order differential equation for the time evolution of the system density matrix $\rho(t)$, given by

$$
\dot{\rho}(t) = -i[H,\rho(t)] + \sum_k (L_k \rho(t) L_k^\dagger - \frac{1}{2} \{L_k^\dagger L_k, \rho(t)\}) .
$$

(2)

The first term at the right-hand side of Eq.[2] is the Liouvillian that describes the unitary evolution determined by the Hamiltonian, $H$. The second term, the Lindbladian, includes dissipation and decoherence on the system dynamics introduced by the reservoirs. It depends on the so-called “jump” operators $L_k$.

In the following, we consider reservoirs that locally inject fermions to, or extract fermions from, a generic site $j$ of the molecule, at given and fixed rates. We describe the injecting and extracting reservoirs at site $j$ in terms of the Lindblad operators $L_{in,j}$ and $L_{out,j}$, given by $L_{in,j} = \sqrt{\gamma_j} c_j$, $L_{out,j} = \sqrt{\gamma_j} c_j^\dagger$, with $\gamma_j$ and $\gamma_j$ being the coupling strengths respectively determining the creation and the annihilation of a fermion at site $j$. Once we determine $\rho(t)$ by solving Eq.[2], we compute the (time dependent) expectation value of any observable $O$ using $\langle O(t) \rangle = Tr[O \rho(t)]$. For the sake of our analysis, we compute the currents flowing from the reservoirs into the site $j$, $I_{in,j}(t)$, or from site $j$ to the reservoir, $I_{out,j}(t)$. These are given by $I_{in,j}(t) = \gamma_j (1 - \langle n_j(t) \rangle)$ and $I_{out,j}(t) = \gamma_j \langle n_j(t) \rangle$, with $n_j(t) = c_j^\dagger c_j$ the number operator. The net current exchanged at time $t$ between the reservoirs and the site $j$ is given by $I_j(t) = I_{in,j}(t) - I_{out,j}(t)$.

Using Eq.[2], we compute the current across a small Benzene ring connected to two reservoirs. The system asymptotically evolves to a non-equilibrium steady state (NESS), which we determine from the condition $\dot{\rho} = 0$. In such a state we compute the stationary current in order to find the optimal working point (OWP), i.e. the change in the monotonicity of the stationary current as a function of the applied bias, for a molecular electronic device.

3. Benzene ring

The Hückel Hamiltonian for the Benzene ring is given by

$$
H_B = 
\begin{pmatrix}
\epsilon_1 & -t_{12} & 0 & 0 & 0 & -t_{16} \\
-t_{21} & \epsilon_2 & -t_{23} & 0 & 0 & 0 \\
0 & -t_{32} & \epsilon_3 & -t_{34} & 0 & 0 \\
0 & 0 & -t_{43} & \epsilon_4 & -t_{45} & 0 \\
0 & 0 & 0 & -t_{54} & \epsilon_5 & -t_{56} \\
-t_{61} & 0 & 0 & 0 & -t_{65} & \epsilon_6
\end{pmatrix},
$$

(3)

which has real hopping amplitude, $t_{ij} = t_{ji}^*$, between consecutive atoms of the ring. In the following we set $t_{ij} = t = 2eV$ and $\epsilon_j = 0$ except for $j = 5$, where a local gate potential, $\epsilon_5$, is applied (values are taken from Ref.[4]). We connect the Benzene molecule to two reservoirs, one located on the site 1 and another located on the site $L$ with $L = 2$ for the ortho-configuration, $L = 3$ for the meta-configuration and $L = 4$ for the para-configuration (see Fig.[4] for a pictorial representation of the setup).

As a paradigmatic regime, we consider the large bias limit, in which one of the reservoirs, the one coupled to the site 1, acts as an electron “source”, by only injecting electrons in the system ($\gamma_1 = 0$), and the other, the one coupled to the site $L$, acts as an electron “drain”, by only absorbing electrons from the system ($\Gamma_L = 0$). As a result, electrons entering at the site 1 must travel all the way down to the site $L$, before leaving the system. Accordingly, the boundary dynamics is determined only by the coupling strengths, $\Gamma_1 = \gamma_L \equiv \Gamma$, while the bulk...
dynamics only depends on the hopping strengths $t$ and the gate voltage $\epsilon_g$. In Fig.[2a] we plot the stationary current across the benzene ring, $I = I_{in,1} = -I_{out,L}$, against the coupling strength to the two reservoirs for the para, ortho and meta configurations, comparing it with the case of the one-dimensional chain discussed in Ref.[3]. Two interesting features emerge: first, the OWP, already observed for a linear chain [3], is present also in the benzene ring; second, the para and ortho configurations exhibit higher values of the current compared to the one-dimensional chain. This suggests that the introduction of molecular electronic devices within a quantum network can, in principle, improve its performance. In Fig.[2b] we compute the current across the ring as a function of the gate voltage $\epsilon_g$, at fixed applied bias. Interestingly, the stationary current of the three possible configurations show opposite behaviors as a function of $\epsilon_g$, decreasing in the para configuration, increasing in the meta configuration and keeping almost constant in the ortho configuration.

An interesting test concerns the robustness of the OWP against disorder. To introduce disorder in the benzene ring we can, e.g., randomize the on-site energy $\epsilon$ and/or the bond electron hopping strength $t$. Disorder is, in general, expected to substantially affect the transport properties of the system, especially in lower dimensions. In the following, we compare the current across the benzene ring, in the para, meta and ortho configurations, with the current across a one
Figure 3. Current across a disordered benzene molecule in terms of the coupling strength $\Gamma = \Gamma_1 = \gamma L$ in the large bias regime for the three configurations. Dashed black curve corresponds to the current across a clean chain of 6 sites (like in Fig. [2]), dashed blue curve to the current across a disordered chain of 6 sites. We set $t = 2eV$, $\epsilon_g = 0$ and a) strong "chemical potential disorder", $\sigma_\epsilon = 1.2$, $\sigma_t = 0$, b) strong "bond disorder", $\sigma_\epsilon = 0$, $\sigma_t = 1.2$.

dimensional chain [3]. Technically, we realize this by setting $\epsilon_{\text{eff}} \rightarrow \epsilon_j = \epsilon + \delta \epsilon_j$ and $t_{\text{eff}} \rightarrow t_{i,j} = t + \delta t_{i,j}$ with $i < j = 1, \ldots, L$. The $\{\delta \epsilon_j\}$ are independent random variables described by a probability distribution $P(\{\delta \epsilon_j\}) = \prod_{j=1}^{L} p_\epsilon(\delta \epsilon_j)$. Specifically, we choose $p_\epsilon(\delta \epsilon)$ to be the probability distribution for the $\{\delta \epsilon\}$, with average $\overline{\delta \epsilon} = \int dx x P(\delta \epsilon) = 0$, and with variance $\sigma_\epsilon^2 = \int dx x^2 P(\delta \epsilon)$. We use the uniform probability distributions given by

$$p_\epsilon(\delta \epsilon) = \begin{cases} \frac{1}{2\sqrt{3}\sigma_\epsilon}, & \text{for } -\sqrt{3}\sigma_\epsilon \leq \delta \epsilon \leq \sqrt{3}\sigma_\epsilon \\ 0, & \text{otherwise} \end{cases},$$

with equivalent formulas holding for the hopping strength fluctuations $\delta t_{i,j}$. Having assumed the probability distribution in Eq. [4], we can estimate the disorder-averaged current distribution at given values of $\sigma_\epsilon$ and $\sigma_t$. In Fig. [3], we show the behavior of the stationary current, as a function of applied bias, in the presence of a strong chemical potential disorder (panel a) or a strong bond disorder (panel b). Interestingly, while the one-dimensional chain is strongly affected by disorder with a remarkable reduction of the current, the benzene ring is much more robust. Indeed, comparing panel a) and b), we observe that the para configuration is robust against chemical potential disorder but is affected by the bond one, the meta configuration current is enhanced by chemical disorder and the ortho configuration is quite unaffected by the disorder. These effects are expected to be a consequence of the interferences between the two branches of the ring.

4. Conclusions
Using the LE framework, we have discussed the main features of the NESS arising in a small disordered molecular electronic device connected to two reservoirs in the large bias limit. The preliminary results shown in the manuscript suggest that the LE framework can be successfully extended to non-linear systems, like molecular electronic devices, small DNA chains or junctions of quantum wires in the presence of two or more reservoirs in order to investigate their transport properties under the effect of a large voltage bias [6, 7, 8, 9, 10]. Furthermore, the role of disorder and/or interaction can be discussed and, if a multi-site Lindblad bath is considered [11], it is also possible to introduce a temperature bias to investigate the thermal transport across such devices and, for example, the breakdown of the Wiedemann-Franz law [12, 13].
Acknowledgments
A. N. was financially supported by POR Calabria FESR-FSE 2014/2020 - Linea B) Azione 10.5.12, grant no. A.5.1. D. G., L. L. and M. R. acknowledge financial support from Italy’s MIUR PRIN projects TOP-SPIN (Grant No. PRIN 20177SL7HC).

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