A minimalistic diode

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received 26 May 2014; accepted in final form 6 August 2014
published online 22 August 2014

PACS 85.65.+h - Molecular electronic devices
PACS 72.10.-d - Theory of electronic transport; scattering mechanisms
PACS 73.63.-b - Electronic transport in nanoscale materials and structures

Abstract – In this work we present a minimalistic model sufficient for current asymmetries in molecules. In particular, we search for an interaction on the molecule which causes current asymmetries independent of additional assumptions or the precise form of its environment. To this end we first discuss earlier proposals and clarify the importance of additional assumptions. We then present a minimal model of a strongly polarizable molecule which shows a strongly asymmetric $I/V$ calculated within time-dependent DMRG.

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Introduction. – Diodes are a base ingredient to electronics, so the development of new molecule-based diodes could improve molecular electronics. The first theoretical proposal of a molecule-based diode was given in [1] by Aviram and Ratner (AR). Since then, there have been many experimental realizations and numerical studies of molecular diodes [2–10], which have mainly used strongly polarizable molecules. However, the mechanisms causing rectification are still being discussed [11–17]. For example, ref. [8] lists two more mechanisms in addition to the AR proposal. They both assume an asymmetric coupling of the molecule to the leads. In one case, this coupling causes the energy level of the molecule to slightly adjust to the energy level of one of the leads. This was called “asymmetric field” [8]. In the other case, which was called “asymmetric charging” [8], the tunneling shows an asymmetry. Testing single mechanisms experimentally proves to be hard as typically all mechanisms named above can be present in an asymmetric coupling. It is difficult to disentangle the importance of these. Therefore, we investigate simple models which distil the proposed mechanisms and study their properties.

In [14], a simple model containing the essence of the “asymmetric charging” was examined. There, the author had to assume restrictions on the form of the band structure of the leads appended to the molecule in order to find current asymmetries.

In this paper, after an introduction to our methods and a review of the mentioned mechanisms, we present a simple model of a molecular diode based on a correlated hopping interaction leading to a strong polarizability of the molecule. Finally we show that within our model the observed current asymmetry is independent of the exact specifications of the leads. This means that the rectification is a device property and independent of the type of leads applied.

Methods. – We define the quantity

$$A(V) = \frac{I(V) + I(-V)}{I(V) - I(-V)},$$

with $I$ being a current, as the current asymmetry.

We measure a current in the observed systems, we apply two physically different quenching protocols used, for example, in [18]: In both cases we quench the potentials to be equal for times larger than zero, the voltage term

$$H_V = V/2 \left( \sum_x \hat{n}_x - \sum_x \hat{n}_x \right)$$

with $V$ being the applied bias voltage and $\hat{n}_x$ the particle density at site $x$ (see footnote 1). If we start with leads at different chemical potentials and quench the potential to be equal for times larger than zero, the voltage

Since we do not investigate spin interactions, we freeze out the spin of the fermions in our calculations, effectively looking at spinless fermions.
influences the initial density distribution. This situation corresponds to scattering theory calculations where particles are injected in one lead and will either be reflected in the same lead or transmitted to the other lead. In those calculations, the effect of the energy dispersion gets cancelled by the density of states. In contrast, if $\mathcal{H}_V$ is turned on at $t = 0$, the resulting current will be influenced by the finite band width. E.g., the current vanishes for voltages larger than the band width, for details see [18].

Our goal will be to find current asymmetries using the former method, since those asymmetries will not depend on the band structure of the leads. Within this paper we use the different quenching schemes to judge sensitivity to details of the lead structure.

The initial state of the system is obtained as the ground state of the system before the quench via finite lattice DMRG [19]. The time evolution of this state after the quench is calculated using the time-dependent DMRG (td-DMRG) and the Krylov space approximation for the matrix exponential as described in [18,20,21].

The resulting current expectation value reaches a plateau with some small oscillations after some transient regime (initial adjusting), and later drops due to reflection of the charge density wavefront. The value of the plateau gives us the current in the large lead limit, for details see [18]. In the case of the non-interacting model in the next section, we use a free-fermion picture for scattering theory calculations as well as exact diagonalization instead of the DMRG procedure. Since we can only compute finite systems in numerical calculations, we will set our system size to $M$ instead of $\infty$. This means that, e.g., for systems with probes restricted to one site, the summation boundaries of the leads are $-\infty$ instead of $-\infty$ and $\frac{M}{2} - 1$ instead of $\infty$. In cases where the probe consists of an odd number of sites, the sizes of the leads differ in our calculations by one site since we have to use an even number of sites to obtain an integer particle number for half or quarter filling. An odd number of those sites models our probe, so we are left with an odd number of sites for two leads. For finite-size estimates we compare the current obtained in a system with swapped leads to the original current.

The Aviram-Ratner proposal. – In their paper, AR looked at a class of molecules effectively consisting of two two-level systems separated by a bridge part.

One of the two-level systems is an acceptor, with the upper level having slightly higher energy than the Fermi surface. The other one is a donor, with the lower level being closely below the Fermi surface. The authors implicitly assumed a screening interaction which causes the chemical potential to increase or decrease linearly between the two leads, which can be identified as the “asymmetric field” mechanism. They also assumed that electrons would relax after hopping onto a two-level system. Now they argued that for shifted chemical potentials, significant current would start to flow from acceptor to donor once the donor lower level was higher\(^2\) than the Fermi surface in the nearest lead, while a significant current flow in the other direction would require the donor lower level to be at least of the same height as the acceptor upper level\(^3\). As argued, e.g., in Chapt. 5 of [22], the influence of screening and therefore the “asymmetric field” mechanism depends on the form of the leads. Since we want to find asymmetries independent of external factors, we neglect screening interactions. The same goes for relaxation effects. Also, ref. [11] suggests that the assumption of a linear change in chemical potential between the leads might be wrong. In the remaining part of the section, we show that in scattering theory without the assumption of additional screening and relaxation, the AR system does not rectify currents.

The Hamiltonian we assume for the system with constant chemical potential is sketched in fig. 1 and reads

$$\mathcal{H} = -J \sum_{x=-\infty}^{-1}(c_{x}^{\dagger}c_{x-1}^{\dagger}) - J \sum_{x=5}(c_{x}^{\dagger}c_{x-1}^{\dagger})$$
$$- J_{1} (c_{0}^{\dagger}c_{-1}^{\dagger} + c_{1}^{\dagger}c_{-1}^{\dagger} + c_{4}^{\dagger}c_{3}^{\dagger} + c_{1}^{\dagger}c_{2}^{\dagger})$$
$$- J_{2} (c_{2}^{\dagger}c_{0}^{\dagger} + c_{3}^{\dagger}c_{0}^{\dagger} + c_{2}^{\dagger}c_{1}^{\dagger} + c_{3}^{\dagger}c_{1}^{\dagger}) + h.c.$$
$$+ \sum_{i=0}^{3} w_{i} \hat{n}_{i}. \quad (3)$$

Here, $c_{x}^{\dagger}$ and $c_{x}$ are creation and annihilation operators at site $x$, $J$ is the lead hopping, $J_{1}$ denotes hopping from leads to the two level systems, $J_{2}$ hopping between the two level systems and the $w_{i}$ are the energies of the different energy levels. Making a plane wave ansatz for the eigenfunctions

$$c_{x}^{\dagger} = \sum_{i=-\infty}^{-1}(e^{ikx} + re^{-ikx}) c_{x}^{\dagger}$$
$$+ \sum_{x=4}^{\infty}te^{ikx} c_{x}^{\dagger}$$
$$+ \sum_{i=0}^{3} a_{i} c_{i}^{\dagger} \quad (4)$$

\[^2\text{Energy measured relative to the chemical potential.}\]

\[^3\text{The requirement could also be that the upper level of the donor is lower than the Fermi surface in the lead, depending on parameters.}\]
r being the reflection and t the transmission amplitude, and \( a_i \) are the amplitudes on the two level systems, we solve for the transmission amplitude with the requirement of the ansatz being an eigenstate with eigenenergy \( E_k \):

\[
[\mathcal{H}, c_k^\dagger] = E_k c_k^\dagger.
\]

From there we calculate the current via [23–25]

\[
I = \frac{e}{\hbar} \int \frac{dE}{\mathcal{V}} |t(E)|^2.
\]

The results obtained from this scattering theory ansatz and exact diagonalization are shown for one set of parameters in fig. 2. We use exact diagonalization for a finite system size \( M \) to calculate the current for the quench to different chemical potentials. The result for the according simulation with \( \mathcal{H}_V \) in the time evolution operator is shown in fig. 3. For chemical potentials outside the range of \( V \in [-2J, 2J] \), we could not obtain reliable results due to a very slowly decaying transient current. While one sees a slight asymmetry in the latter case for large voltages, there is no asymmetry in the scattering theory calculation or in the latter case for small voltage. These results demonstrate that that the system described by the Hamiltonian of eq. (3) is not sufficient to describe a diode, the additional assumptions made by AR are essential.

**The Roy model.** – The Hamiltonian of the model of Roy [14] corresponds to an interacting resonant level model (IRLM) with asymmetric couplings, which is also sketched in fig. 4, and reads

\[
\mathcal{H} = -J \sum_{x=-\infty}^{\infty} \left( \hat{c}_x^\dagger \hat{c}_{x+1} + \hat{c}_{x+1}^\dagger \hat{c}_x \right) - J_c \sum_{x=1}^{\infty} \left( \hat{c}_x^\dagger \hat{c}_{x+1} + \hat{c}_{x+1}^\dagger \hat{c}_x \right) - J_{n_1} \left( \hat{n}_{-1} \hat{n}_0 + \hat{n}_0 \hat{n}_{-1} \right) - J_{n_2} \left( \hat{n}_0 \hat{n}_1 + \hat{n}_1 \hat{n}_0 \right)
\]

with \( \hat{n}_x \) being the particle number operator at position \( x \) and the different \( J \)'s being various hopping and coupling parameters. The prediction is that asymmetric junctions, which means \( J_{c_1} \neq J_{c_2} \) and is equivalent to asymmetric charging, and a nonlinear dispersion relation would lead to an asymmetric \( I-V \) curve. We increased the importance of nonlinear terms in the cosine dispersion relation of the tight binding leads by filling the leads only up to crystal momentum \( k = \frac{\pi}{4} \) instead of \( \frac{\pi}{2} \).

The results of our calculations are displayed in figs. 5–7. In fig. 4 we compare the \( I(V) \) and \( I(-V) \) characteristic obtained by time-dependent simulations, where the charge imbalance is put into the time evolution operator. As predicted by Roy, we do not find an asymmetry in the \( I/V \) characteristic.
characteristic. This also holds true for the case of voltage influencing the initial density distribution. In fig. 5 we show that, consistent with Roy’s prediction, there is an asymmetry in the case of symmetric interactions and asymmetric junctions, provided the charge imbalance term is put into the time evolution operator. If the charge imbalance determines the initial density distribution and therefore the band structure does not influence the result, this asymmetry reduces to the order of the finite-size effects. This is shown in fig. 6. As a consequence, we infer that the asymmetry stemming from “asymmetric charging” depends heavily on external factors.

Proposed model and results. – In order to find a model which causes an asymmetric \( I/V \) under scattering theory, independently of specific lead properties, it is instructive to look at the way how scattering theory works. In scattering theory [26] one searches for eigenstates of the Hamiltonian which are asymptotically given by incoming and outgoing (typically plane) waves. For transport calculations this corresponds to occupied eigenstates of one lead, and empty eigenstates of the other lead before being connected to the structure under investigation. The voltage enters via the different electrochemical potentials of the two leads. Within the Landauer description [23–25] the current is given by

\[
I = \int_{\mu_L}^{\mu_R} T(E) dE,
\]

where \( T(E) \) is the transmission at energy \( E \) and the voltage is given by \( \mu_L - \mu_R \). As long as the transmission does not depend on the voltage, the current only depends on it via the integration borders, so scattering theory gives an antisymmetric \( I/V \), at least for systems with time-reversal symmetry. In order to obtain a symmetric contribution to the \( I/V \) characteristic we introduce a strong polarizability via a correlated hopping interaction. We embed it into a noninteracting resonant level model, obtaining the
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Fig. 8: (Colour on-line) Sketch of our proposed model. Red lines below the dots denote hopping, the green lines above the dots denote the correlated hopping term.

Fig. 9: (Colour on-line) Result for the value of the current plateau (measured at \(x=0\)) for \(J_1 = 0.11J\), \(J_2 = 0.5J\), \(J_n = 0.5J\), system size \(M = 110\) and time step size \(\Delta t = 0.25\hbar/J\).

Hamiltonian of the system sketched in fig. 8:

\[
\mathcal{H} = -J \sum_{x=-M}^{M-2} \left( \hat{c}_x^\dagger \hat{c}_{x+1} + \hat{c}_{x+1}^\dagger \hat{c}_x \right) + \frac{1}{2} \sum_{x=1}^{M-1} \left( \hat{c}_x^\dagger \hat{c}_{x+1}^\dagger \hat{c}_{x+1} + \hat{c}_{x+1} \hat{c}_x \right) - J_2 \left( \hat{c}_0^\dagger \hat{c}_1 + \hat{c}_1^\dagger \hat{c}_0 \right) - (J_n \hat{n}_1 - J_1) \left( \hat{c}_0^\dagger \hat{c}_0 + \hat{c}_1^\dagger \hat{c}_1 \right).
\]  

(9)

Numerical computation of the current for different voltages gives the result shown in fig. 9. The steps in the \(I-V\) curve are finite-size effects\(^4\) and get smoother for bigger systems. The parameters in this curve are tuned in a way to maximize similarity to a diode. In general we find a mix of the standard resonant level model result — approximately an arcus tangens curve — and an asymmetric function\(^5\) with minimum at around \(V_{SD} = -J\), with weights depending on the choice of \(J_1\) and \(J_n\).

We want to point out that the asymmetry in fig. 8 is visible for both kinds of quenches applied. Figure 11 shows the current over time in the transient regime. For large reverse bias, by which we mean bias in the weak conduction regime, shown here for \(eV_{SD} = -2J\), the current peaks at very short times, before it drops and transient ringing decays unusually fast. This behaviour fits nicely to the underlying mechanism. When the flow of electrons is switched on, the particles first see a resonant level. It is only after building up the polarization cloud that the structure starts blocking the current.

**Conclusion.** — Our goal in this paper was to find hints at interactions or other mechanisms which reliably cause a diode-like behaviour independent of external factors. Revisiting the proposals in [1] and [14], the asymmetries we found in the \(I/V\) were crucially dependent on the band structure of the leads. However, for universally applicable devices, one desires systems where the properties are given by the system itself and are not being crucially dependent

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\(^4\)These effects are due to the finite size of the leads, resulting in a finite number of discrete energy levels.

\(^5\)See fig. 10.
on the structure of the leads. Here we presented a mim-
imalistic structure that resembles a diode independent on
the quenching schemes. From this we conclude that its
$I/V$ characteristic is given by the structure itself and that
it is robust against band structure properties of the leads.
We achieved this property by introducing a correlated
hopping interaction leading to strong polarizability of the
system.

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We would like to thank Ferdinand Evers for insight-
ful discussions. TC thanks Guy Cohen for discussions
about rectifying models. Parts of this work was performed
on the computational resource bwUniCluster funded by
the Ministry of Science, Research and Arts and the Uni-
versities of the State of Baden-Württemberg, Germany,
within the framework program bwHPC.

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