Non-equilibrium transport response from equilibrium transport theory

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Outline

1) Introduction: non-equilibrium Green’s functions (NEGF)

2) Non-equilibrium transport effects

3) $I$-$V$ characteristics from equilibrium electronic structure
1) Non-equilibrium Green’s functions (NEGF)

- Transport simulation

\[ \sum_n f_n c_n^* c_n f_n = \rho_{\mu\nu} \]

Equilibrium

\[ \rho_{\mu\nu} = \sum_n c_n^* c_n f_n (\varepsilon_n - \mu) \]

Non-equilibrium

\[ \rho_{\mu\nu} = \frac{1}{2\pi i} \int G_{\mu\nu}^\leq (E) dE \]
- Non-equilibrium

\[ \hat{\rho} = \hat{\rho}_\text{eq} + \hat{\rho}_V \]

\[ \hat{\rho}_\text{eq} = -\frac{1}{\pi} \int \text{Im} \hat{G}^R (E) f (E - \mu_L) dE \]

\[ \hat{\rho}_V = \frac{1}{2\pi} \int \text{Im} [\hat{G}^R \hat{\Gamma}_R \hat{G}^{R+}] (E) [f (E - \mu_R) - f (E - \mu_L)] dE \]

\[ I = \frac{e}{h} \int \text{Tr} [\hat{\Gamma}_L \hat{G}^{R+} \hat{\Gamma}_R \hat{G}^R] (E) [f (E - \mu_L) - f (E - \mu_R)] dE \]
2) Non-equilibrium transport effects

- Charge transfer

The HOMO or LUMO gets pinned to the Fermi level due to charge transfer to or from the molecule.

The molecule wins charge and the levels move up in energy.
- Bias-induced movement of levels

Asymmetric levels or levels localized on certain regions follow differently the bias potential

Destruction of transmission resonances → Negative differential resistance (NDR), rectification.
3) *I*-*V* characteristics from equilibrium electronic structure

- “Molecular break junctions”

Atomic chains with different atoms at the edges and separated by a gap

![Diagram of atomic chains with different atoms at the edges and separated by a gap.](attachment:diagram.png)

Different *I*-*V* characteristics depending on the localization of the edge states and the separation between them
Effect of increasing the distance between the edge atoms and the rest of the chain \((a)\). From ohmic \(I-V\) to NDR

Small coupling: localized states
- From equilibrium to non-equilibrium in molecular break junctions

Bonding and antibonding symmetric states in equilibrium. Individual non-symmetric states out of equilibrium

• This non-equilibrium effect can be reproduced by moving the states associated to the atoms and the rest of states in the leads by $\pm eV/2$
- Modified Hamiltonian obtained by rigidly shifting certain molecular states and all states in the electrodes

\[
\hat{H}' = \begin{pmatrix}
H_1 + \frac{eV}{2} S_1 & H_{10} + \frac{eV}{2} S_{10} & 0 \\
H_{01} + \frac{eV}{2} S_{01} & H_0 [\rho_{eq}] & H_{02} - \frac{eV}{2} S_{02} \\
0 & H_{20} - \frac{eV}{2} S_{20} & H_2 - \frac{eV}{2} S_2
\end{pmatrix}
\]

This is not the same as including a potential voltage ramp in the scattering region and self-consistently calculating the electronic structure.

The common Fermi level of the equilibrium simulation screens the potential.

NEGF assumes that the electrodes are infinite electron reservoirs.
Comparison with NEGF

The approach is able to match perfectly the non-equilibrium curves in this case.

The current calculated from the unchanged equilibrium electronic structure always grows.
- Special configuration in many molecular junctions: frontier orbital localized at or close to the contacts

HOMO near the Fermi level localized at the sulfur atoms

The central part of the molecule is not affected by the bias due to screening

The potential falls at the contacts
- More involved simulations

Porphyrin wires chemisorbed between graphene electrodes

Localized states at the contact atoms. Expected \( I-V \) characteristic with strong NDR behavior
Conclusions

- Many molecular junctions have electronic configurations where the frontier orbitals are located near the electrodes

- By exploiting the position of the frontier molecular orbitals it is possible to reproduce $I$-$V$ curves from the equilibrium electronic structure

Thank you