WDS'10 Proceedings of Contributed Papers, Part III, 175–180, 2010. ISBN 978-80-7378-141-5 © MATFYZPRESS

Charge Transport Through Single Molecules: Different Theoretical Approaches

I. A. Pshenichnyuk and M. Čížek

Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic.

Abstract. Two different methods which allow to calculate electric current through molecular junctions are compared. The first method is based on the scattering theory and Landauer formula, and the second on the master equation technique. Two models of the junction with different molecular bridges (with and without an internal vibrational degree of freedom) were used to compare and discuss features of both methods. The way to improve the scattering approach in the inelastic transport regime using realistic vibrational states populations instead of Boltzmann factors in the Landauer formula is proposed.

Introduction

Charge transport through individual molecules is promising subject of research nowadays. Work in this field is stimulated by the idea to create a new type of electronics (which is called "molecular electronics" or "moletronics") in the future, where individual molecules will be used as building blocks for electronic circuits [Ratner and Ratner, 2002]. A whole class of experimental methods was established where a molecule (or a chain of molecules which is called a molecular bridge) can be connected between two solid electrodes [Selzer and Allara, 2006]. Such molecular junctions allow to measure electric current through the bridging molecule. Molecular bridges are complicated quantum systems with many internal degrees of freedom which may actively participate in the energy exchange during the charge transport process. There are few theoretical approaches available to treat such junctions [Galperin et al., 2007]. In this paper, we compare two of them. In the approach based on the Landauer formula [Datta, 1997] the current can be expressed through the transmission function of the bridge. Calculation scheme includes consecutive computation of self-energies of the leads and Green's function of the bridge. Scattering theory formulas should be used afterwards to transform the Green's function to the T-matrix and, finally, to the tunneling probability [Troisi et al., 2003]. Another possible way to calculate the current is to use the master equation (ME) theory. By solving the Wangsness-Bloch-Redfield ME [Timm, 2008] the reduced density matrix (RDM) of the molecular bridge can be determined. RDM contains detailed information about the bridge while the leads are treated "half rigorously" as large particle reservoirs in equilibrium in this method. The RDM can be used to calculate any observable of interest, including the current [Hartle et al., 2009]. Both methods will be discussed in the next two sections.

Theory

To compare methods we formulate two models of molecular junctions. In model 1 molecular bridge has only one vacant electronic level with energy ε_0 available for tunneling. Interactions with internal degrees of freedom are neglected in this model and the tunneling process is elastic. In model 2 we add one active vibrational degree of freedom on the bridge which can exchange energy with electrons (Fig. 1). Such a situation is theoretically described in terms of the so-called independent boson model (see Mahan [1993] for details), where harmonic oscillator is coupled to the electronic state. This model reflects the fact that the bridge, when occupied by an electron, has a potential energy which is different from the energy of the unoccupied bridge (see Fig. 1). This is schematically depicted in Fig. 1 as two different harmonic potentials with different sets of vibrational states. In this paper we denote the energy spectra of unoccupied

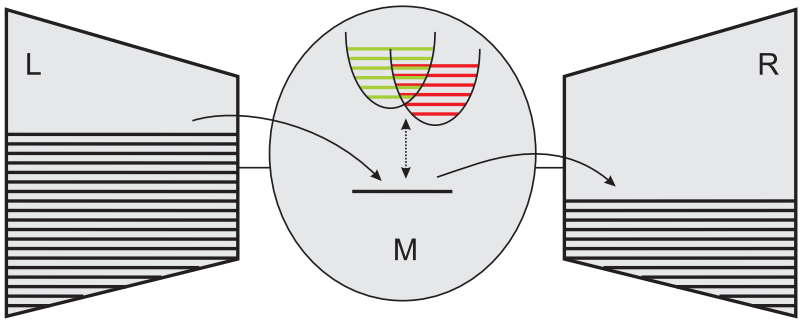

Figure 1. Schematic representation of the molecular junction in model 2. Electrons travel from the left lead to the right through the molecular bridge with one electronic state available for tunneling. Passing through the bridge they exchange energy with the internal vibrational mode of the bridge. Vibrational potentials are different for occupied and unoccupied bridge configurations.

and occupied bridges by E_m and E_v, respectively. Vibrational states which correspond to these energies are denoted as $|m\rangle$ and $|v\rangle$. Leads for both elastic and inelastic junctions are simulated using one dimensional half infinite nearest neighbor tight binding chain [Ashcroft and Mermin, 1976]. This is an easy way to simulate the metallic lead with one conduction band. Each lead is characterized by two parameters: width of the conduction band and chemical potential. Difference between chemical potentials of left and right leads provides the voltage applied to the bridge. Electronic states available in each lead are populated according to the Fermi-Dirac distribution. More information about the models and their parametrization can be found in Cizek et al. [2004].

The model 1 is useful for comparison of the two approaches because formulas for the current through the elastic bridge in both theories can be derived analytically (atomic units are assumed here)

$$I_1^{\mathrm{scat}} = \frac{1}{2\pi}\int dE\, \frac{\Gamma_L(E)\Gamma_R(E)}{[E-\varepsilon_0-\Delta_L(E)-\Delta_R(E)]^2+\frac{1}{4}[\Gamma_L(E)+\Gamma_R(E)]^2}[f_L(E)-f_R(E)], \qquad (1)$$

$$I_1^{\mathrm{me}} = \frac{\Gamma_L(\varepsilon_0)\Gamma_R(\varepsilon_0)[f_L(\varepsilon_0)-f_R(\varepsilon_0)]}{\Gamma_L(\varepsilon_0)+\Gamma_R(\varepsilon_0)}. \qquad (2)$$

Real and imaginary parts of the self-energy function $\Sigma = \Delta - \frac{i}{2}\Gamma$ are used in the formulas throughout the paper. This function of energy possesses information about the leads and the leads-bridge coupling and may be calculated analytically. Both leads have their own self-energy and indices L/R are used to distinguish them. Additional information about the self-energy function can be found, for example, in Cizek et al. [2004]. Functions f_L and f_R in Eqs. (1) and (2) are Fermi-Dirac distributions in the left and right lead respectively.

Expressions for the current for the model 2 are more complicated. In the case of innelastic bridge both methods require certain quantities to be calculated numerically. Scattering theory approach gives the formula

$$I_2^{\mathrm{scat}} = \sum_m P_m \sum_{m'} W_{mm'}^{R\leftarrow L} - \sum_m P_m \sum_{m'} W_{mm'}^{L\leftarrow R}, \qquad (3)$$

where transition rates for electron scattering from left to the right lead and vice versa read

$$\begin{aligned} W_{mm'}^{R\leftarrow L} &= \tfrac{1}{2\pi}\textstyle\int dE[1-f_R(E-E_{m'})]\Gamma_R(E-E_{m'})|\langle m'|G_M|m\rangle|^2\Gamma_L(E-E_m)f_L(E-E_m), \\ W_{mm'}^{L\leftarrow R} &= \tfrac{1}{2\pi}\textstyle\int dE[1-f_L(E-E_{m'})]\Gamma_L(E-E_{m'})|\langle m'|G_M|m\rangle|^2\Gamma_R(E-E_m)f_R(E-E_m). \end{aligned} \qquad (4)$$

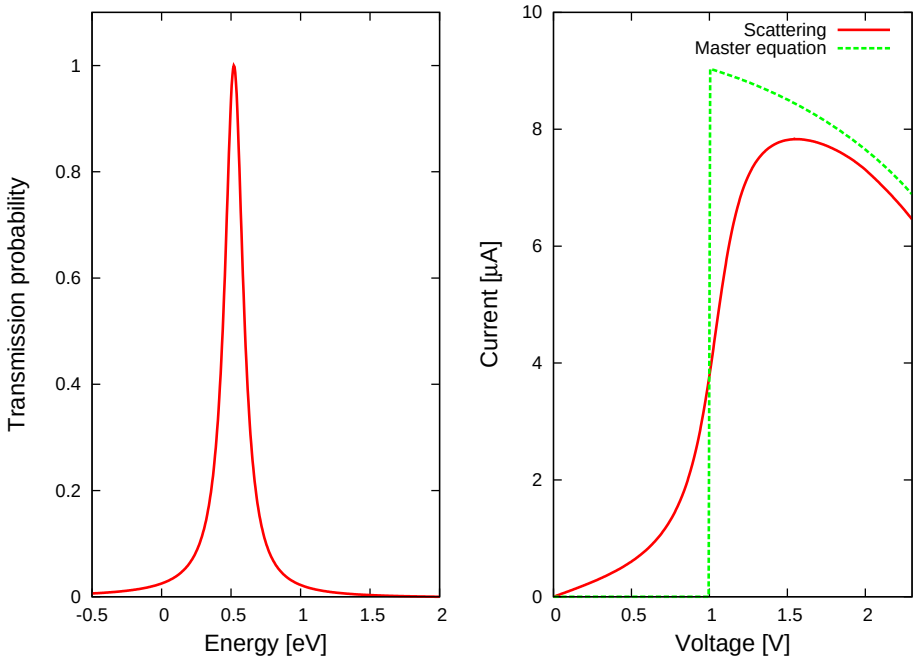

Figure 2. Results for model 1. On the left graph the transmission function of the bridge, obtained from scattering approach, is shown. Right graph shows the current voltage characteristics of the bridge calculated using both methods.

Green's function of the bridge G_M in the Eq. (4) should be calculated numerically. P_m factors give populations of the vibrational states $|m\rangle$ on the bridge. In the Landauer formula which is used to derive Eq. (3), states are populated according to the Boltzmann distribution $P(E_m)$.

The formula for the current obtained in the ME approach was simplified to make the comparison more visual. In addition to standard approximations which were made in the ME theory itself, we got rid of the real parts of the self-energies. They introduce small energy shifts in the equations and have negligible influence upon the final results. In the final formula we also excluded coherences (non diagonal elements) of RDM which, according to our observations, doesn't influence the current. Formula which was obtained in the end reads

$$I_2^{\mathrm{me}} = \sum_m \rho_m \sum_v W_{mv}^{M\leftarrow L} - \sum_v \rho_v \sum_m W_{vm}^{L\leftarrow M}, \tag{5}$$

where

$$\begin{aligned} W_{mv}^{M\leftarrow L} &= f_L(E_v - E_m)\Gamma_L(E_v - E_m)|\langle m|v\rangle|^2, \\ W_{vm}^{L\leftarrow M} &= [1 - f_L(E_v - E_m)]\Gamma_L(E_v - E_m)|\langle m|v\rangle|^2. \end{aligned} \tag{6}$$

To get populations $\rho_m \equiv \langle m|\rho|m\rangle$ and $\rho_v \equiv \langle v|\rho|v\rangle$ one should solve the ME numerically. Frank-Condon factors $\langle m|v\rangle$ in Eq. (6) give overlaps between vibrational states of unoccupied and occupied bridge.

Results and Discussion

Current-voltage dependence and transmission function for the model 1 are shown in Fig. 2 (right). At the first glance curves obtained using different approaches may look different but they have many similarities. Both curves go down after reaching the maximum. It is connected with the fact that left and right leads have finite conduction band widths. While we increase the voltage left lead band goes higher in energy and right lead goes lower, decreasing the overlap between bands. As a result the current goes lower and, at certain voltage (which is not on the

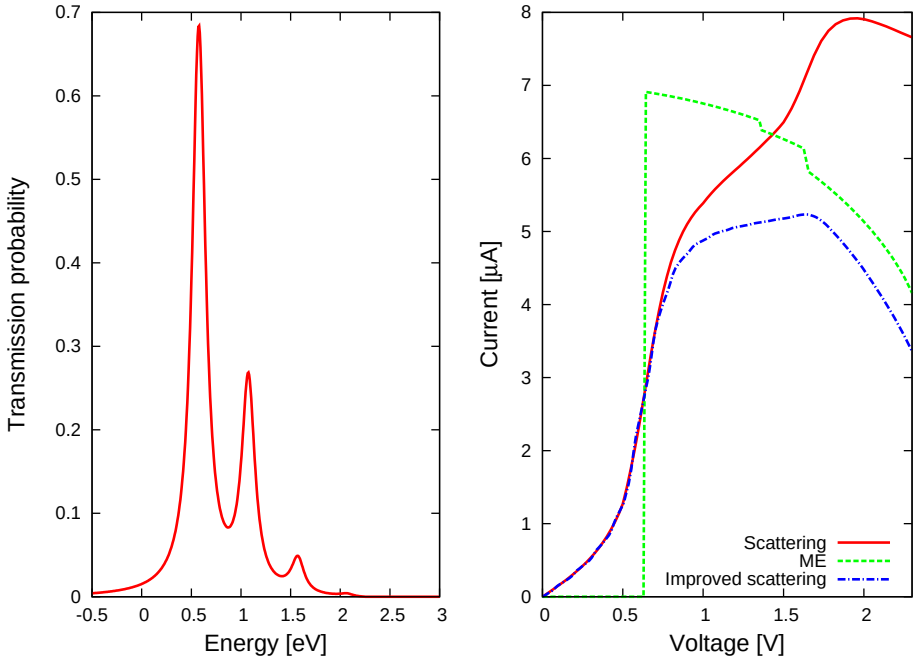

Figure 3. Transmission function and current-voltage characteristics of the bridge in model 2. Dash-dotted line on the right graph shows the result of using of the realistic vibrational populations distribution instead of Boltzmann factors in the Landauer formula.

graph) disappears at all. Both current-voltage dependences in Fig. 2 have the step at the same voltage which correspond to the situation when the Fermi sea level in the lead reaches the energy of the bridge state ε_0. The obvious difference between the two curves is that the step in the scattering approach result is much wider. It happens because the information about the width of the bridge's transmission function (which gives the probability for electron to pass through the bridge at certain energy) peak is lost in the ME approach as a result of approximations which are made in the theory. In ME approach the width of the step is defined by the width of the Fermi-Dirac distribution which is approximately $4kT$ (in the linear approximation). Complete information about the transmission function which is plotted in Fig. 2 (left), can be obtained from the scattering approach. Thus, additional information about the transmission peaks width may be listed among the advantages of this approach. One of the conditions which make the ME applicable requires that the coupling between the molecular bridge and leads should be small. It may be proved that in the case of small coupling the width of the transmission function peak also becomes small and the results, obtained using different methods, become closer to each other. Eqs. (1) and (2) coincide when coupling goes to zero.

Current and transmission function for the model 2 are shown in Fig. 3. Since the bridge in this model has internal degrees of freedom and the tunneling probability depends on the state of the bridge the concept of the transmission function should be clarified. Left graph in Fig. 3 illustrate the probability that the electron at a certain energy will pass through the bridge and change its vibrational state from the ground to any other state. As we can see from the picture, existence of vibrational degrees of freedom on the bridge leads to the situation when the transmission function has multiple peaks which correspond to different vibrational transitions. It leads also to additional step-like structures in the current-voltage characteristics. In the case of model 2 scattering approach and ME approach results which are plotted with solid and dashed lines in Fig. 3, have significant differences. While the first step at both graphs can be understood in the framework of what we already know from the previous example (the same peak with different widths), there are obviously no similarities at higher voltages.

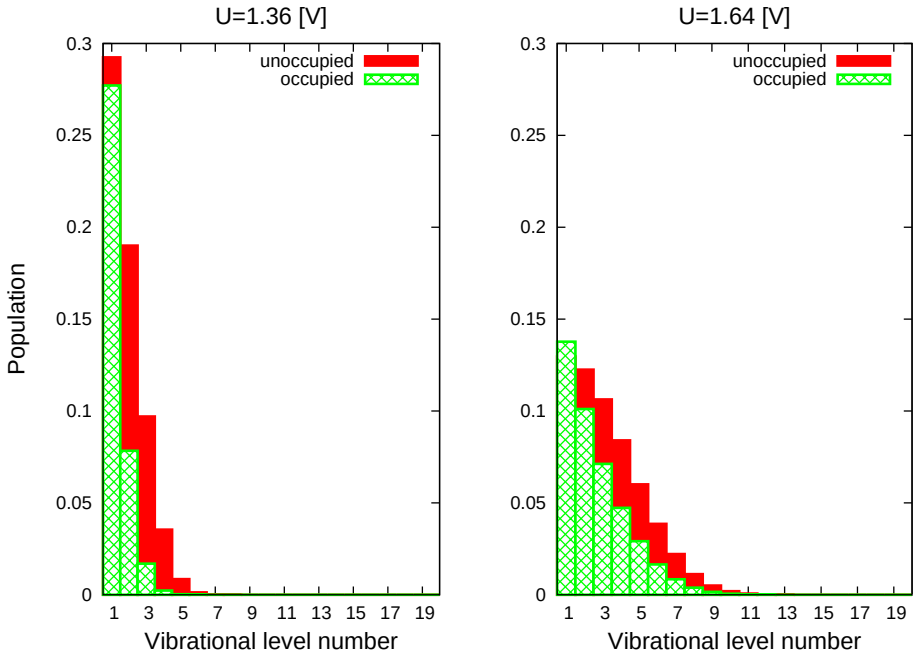

Figure 4. Stationary vibrational states populations distributions of the bridge (model 2) calculated using the ME technique for two different voltages. Pictures show populations for both unoccupied and occupied bridge configurations.

Analyzing the structure of Eqs. (3) and (5) we may notice that the Boltzmann factors P_m and populations ρ_m of vibrational states of unoccupied bridge play similar role and, in principle, should be the same. In practice they are very different at nonzero voltages. Stationary population distributions, obtained from the ME calculations, are shown in Fig. 4 for two different voltages. When we use the scattering approach to calculate the current at the same voltages, Boltzmann factors provide the distribution where the ground state is almost completely populated and all other states populations are negligibly small. This means that the Boltzmann distribution P_m is a very poor approximation of the real vibrational states populations, especially at high voltages.

To get the realistic populations picture inside the framework of the scattering theory approach we formulate dynamical equation for the time evolution of P_m. To do it, we start by using the Eq. (4) to introduce the quantity

$$W_{mm'} = W_{mm'}^{R\leftarrow L} + W_{mm'}^{L\leftarrow R} + W_{mm'}^{L\leftarrow L} + W_{mm'}^{R\leftarrow R}, \tag{7}$$

which gives the rate to change the bridge's vibrational state from m to m' as a result of all possible tunneling events and reflections. We use it to write the dynamical equation in the form

$$\frac{dP_m}{dt} = \sum_{m'} W_{m'm} P_{m'} - \sum_{m''} W_{mm''} P_m. \tag{8}$$

Physically, it means that the population P_m change itself as a result of two probability fluxes: one goes from the state m to all other states m'' and another one comes from all states m' to m. To get the stationary population distribution we have to solve the "balance equation," when the right hand side of Eq. (8) is equal to zero. This procedure allows to get distributions which are very similar to those in Fig. 4, staying at the same time inside the framework of the scattering theory approach. Using this populations in the Landauer formula (Eq. (3)) we obtain the curve which is plotted by the dash-dotted line in Fig. 3. This result is based on the realistic

population distribution and poses also the information about the transmission peaks width. In this sense it unites the advantages of both methods.

Conclusion

As it follows from the origins of the scattering theory, it describes the transport process, where electrons tunnel through the bridge one by one. This method can't take into account correlations between electrons. After each tunneling event the bridge automatically returns to the thermal equilibrium with vibrational populations given by the Boltzmann factors. It was shown that such approximate treatment may distort the results significantly. Computational accuracy, however, may be improved if we use the "balance equation" to calculate the stationary vibrational population distribution for each voltage. In the second order WBR ME the information about transmission function width is lost, while the scattering approach formulas keep this information. As a result steps in the current voltage characteristics in ME method are much sharper than they are in reality. They are broadened only by the Fermi-Dirac distribution in leads. Some numerical challenges may be expected in attempts to solve the ME. But as soon as it is solved and the RDM of the bridge is calculated, we got very detailed information about the state of the bridge. It may be used to calculate not only the current but all the observables we need. Of curse there are other approaches which allow to calculate the current. There is, for example, a powerful method which is based on the non-equilibrium Green functions technique. Incorporation of this method to the common comparison scheme may become the topic of future works in this direction.

Acknowledgments. The present work was supported by the Charles University Grant Agency under Contract 116-10/143107.

References

Ashcroft, N. W. and Mermin, N. D., *Solid State Physics*, Brooks Cole, 1976.

Cizek, M., Thoss, M., and Domcke, W., Theory of vibrationally inelastic electron transport through molecular bridges, *Phys. Rev. B*, *70*, 125 406, 2004.

Datta, S., *Electronic transport in mesoscopic systems*, Cambridge Univ Pr, 1997.

Galperin, M., Ratner, M., and Nitzan, A., Molecular transport junctions: vibrational effects, *Journal of Physics: Condensed Matter*, *19*, 103 201, 2007.

Hartle, R., Benesch, C., and Thoss, M., Vibrational nonequilibrium effects in the conductance of single molecules with multiple electronic states, *Phys.Rev.Lett.*, *102*, 146 801, 2009.

Mahan, G. D., *Many-Particle Physics*, Plenum Press, 1993.

Ratner, M. and Ratner, D., *Nanotechnology: A gentle introduction to the next big idea*, Prentice Hall Press Upper Saddle River, NJ, USA, 2002.

Selzer, Y. and Allara, D., Single-molecule electrical junctions, *Annual Review of Physical Chemistry*, *57*, 593–623, 2006.

Timm, C., Tunneling through molecules and quantum dots: Master-equation approaches, *Phys.Rev.B*, *77*, 195 416, 2008.

Troisi, A., Ratner, M., and Nitzan, A., Vibronic effects in off-resonant molecular wire conduction, *The Journal of Chemical Physics*, *118*, 6072, 2003.