Time-Dependent View of Sequential Transport through Molecules with Rapidly Fluctuating Bridges

Bogdan Popescu,[1] P. Benjamin Woiczikowski,[2] Marcus Elstner,[2] and Ulrich Kleinekathöfer[1,*]
[1]*School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany*
[2]*Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*

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Molecules in junctions often fluctuate considerably, especially when subject to the influence of solvent molecules. These fluctuations in site energies and couplings can be sampled, for example, by using molecular dynamics simulations, and can lead to incoherent effects in charge transport. To this end, a popular snapshot-averaged Landauer approach is compared to a time-dependent Green's function scheme. Since sequential transport dominates in systems with rapidly varying bridges, schemes not taking the time order of conformations into account, such as the Landauer approach, are inappropriate.

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Charge transfer through single molecules and wire molecules have attracted a lot of attention over the last years both experimentally as well as theoretically [1,2]. In many of these studies, the conducting molecule is assumed to be in a static conformation. At the same time, external electrostatic or magnetic fields as well as surrounding fluctuating solvents can lead to rapid time-dependent effects in molecules in solution and/or between the leads [3]. Moreover, experiments on combining molecular junctions and laser pulse excitations have become feasible [4,5]. This requires theoretical models that can compute the transport properties such as current and noise in time-dependent scenarios accurately and efficiently [6–12]. In this Letter, however, we concentrate on the time-dependent effects in molecular wires due to solvent fluctuations.

Recent investigations, especially theoretical ones, indicate a severe effect of conformational changes on currents through molecular junctions [13–24]. These effects are especially important if the fluctuations are large in amplitude and change rapidly, which is usually the case if the molecule in the junction is surrounded by a solvent. Standard approaches that can handle the time-dependent system parameters range from the nonequilibrium Green's function (NEGF) techniques [10–12] over quantum master equation (QME) theories [25,26] or path-integral formalisms to the renormalization group methods [1]. QME approaches allow for an easy incorporation of time-dependent effects but are usually based on a perturbative treatment in molecule-lead coupling. Recently, it was shown that incorporating higher orders is feasible in the hierarchical equations of motion approach [26]. The problem is that many of these approaches either involve some approximations or are rather complex. Nowadays, a regularly underlying tight-binding model is being parametrized by using a combination of molecular dynamics (MD) and quantum chemistry approaches. Fluctuations are included by determining snapshots along the trajectory and subsequently employing snapshot-averaging approaches ranging from the simple Landauer scheme [13–20] to more involved theories developed for time-independent scenarios [21–24]. The purpose of this Letter is to show that although the use of a snapshot-averaged Landauer approach is tempting owing to its simplicity, it can lead to currents that are orders of magnitude too low. The importance of sequential transport also highlights the fact that time-dependent approaches need to be made use of, and it is not enough to depend only on snapshot-averaged time-independent theories. The latter schemes cannot reproduce the correct currents, since the charging and discharging effects due to the time-dependent site energies are not properly taken into account.

For the present calculations we utilize a formalism using a decomposition of the spectral density describing a frequency-dependent coupling between the molecule and the leads [25]. When we further use the expansion of the Fermi function, this decomposition leads to exponentially decaying bath correlation functions, which can be further treated analytically. This approach was first used by Tanimura and Kubo in the context of dissipative quantum dynamics [27,28]. In a similar fashion, the approach can be employed in a second-order QME formalism [25] applied successfully to strong-field scenarios [6,29] or in the hierarchical scheme [26]. More recently, a time-dependent nonequilibrium Green's function (TD-NEGF) method was reported using these decompositions [11]. Similar to the QME and the hierarchical schemes, in the TD-NEGF formalism, the time-dependent effects within the system can be treated without further approximations. This renders it an ideal tool for the problems tackled in the present Letter, since the TD-NEGF approach uses a perturbative treatment neither in the molecule-lead coupling nor for time-dependent effects. Part of the results listed below have also been tested with the second-order QME, and no significant differences have been found for the parameters employed here. In the aforementioned TD-NEGF approach, starting from the Keldysh formalism, differential equations are derived for the density operator $\boldsymbol{\rho}(t)$

$$i\hbar \frac{\partial \boldsymbol{\rho}(t)}{\partial t} = [\boldsymbol{H}(t), \boldsymbol{\rho}(t)] + \frac{i}{\hbar} \sum_{\alpha \in \{L,R\}} \{\boldsymbol{\Pi}_\alpha(t) + \boldsymbol{\Pi}_\alpha^\dagger(t)\}. \qquad (1)$$

The current matrices $\boldsymbol{\Pi}_\alpha(t)$ can be determined in closed form, as described in Ref. [11], using the decomposition of spectral densities and Fermi functions, and the time-dependent current $I_\alpha(t)$ from or to the left ($\alpha = L$) or right lead ($\alpha = R$) is given by $I_\alpha(t) = 2e\mathrm{Re}\,\mathrm{Tr}\{\boldsymbol{\Pi}_\alpha(t)\}$. Below, we report the mean current through the system $I(t) = [I_L(t) - I_R(t)]/2$. To obtain a current-voltage characteristic, this current needs to be averaged over a longer time period, leveling out the thermal fluctuations. It should be noted that the above equation can describe the explicit population on the sites of the wire, i.e., also sequential transfer, and that the dephasing processes on the wire are included by the time dependence of the site energies, as described below.

The Hamiltonian of the molecular junction is split into a relevant system part $H_S(t)$, mimicking the wire, two fermionic reservoirs H_R, modeling the leads, and the wire-lead coupling H_{SR}. Thus, the total Hamiltonian is given by $H(t) = H_S(t) + H_R + H_{SR}$. The molecular wire is modeled as a linear chain of N sites. Denoting the creation (annihilation) operator at site i by $c_i^\dagger(c_i)$, the wire Hamiltonian reads as $H_S(t) = \sum_i \epsilon_i(t) c_i^\dagger c_i - \Delta \sum_i (c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i)$. Here $\epsilon_i(t)$ denotes the site energies and Δ the nearest-neighbour couplings. Moreover, the reservoirs are described by noninteracting fermions $H_R = \sum_{\alpha k} \epsilon_{\alpha k} b_{\alpha k}^\dagger b_{\alpha k}$, where $b_{\alpha k}^\dagger(b_{\alpha k})$ creates (annihilates) a particle in state k in reservoir α. For the wire-lead coupling, we assume the standard term $H_{SR} = \sum_{\alpha k i} T_{ki}^\alpha b_{\alpha k}^\dagger c_i + T_{ki}^{\alpha *} b_{\alpha k} c_i^\dagger$, with the restriction that only the left-most (site 1) and the right-most (site N) site of the wire couple to the left and right electrode, respectively. In addition, T_{ki}^α denotes the coupling between reservoir state k and device state i.

As mentioned above, the results obtained by the TD-NEGF scheme are compared to coherent transport calculations based on the Landauer framework, which are often used in related studies [13–20]. In the latter approach, for each time step the energy-dependent transmission function $T(E)$ is computed and, subsequently, the current through the device is obtained using the Landauer relation $I(V) = \frac{e}{h} \int_{-\infty}^{\infty} dE T(E)[f(E - \mu_L) - f(E - \mu_R)]$, with $f(E)$ being the Fermi-Dirac distribution and μ_L, μ_R the chemical potentials of the leads. Since the Landauer theory is derived for a fully coherent transport, it is assumed to be valid for short molecular wires, in which incoherent transport pathways and, therefore, sequential transport are not yet dominating. Nevertheless, we find that even for a two-site model with realistic site fluctuations for molecules in water, incoherent transport is very important, and the Landauer theory can fail, depending on the size and frequency of the fluctuations.

As an example, we study a double-stranded DNA heptamer with base sequence poly(dG)-poly(dC) in water (see Ref. [15] for simulation details and comments on the experiments). The trajectories for the site energies and couplings are determined using the classical MD simulations with an explicit solvent, followed by quantum chemistry calculations using the SCC-DFTB fragment orbital approach, which also accounts for QM/MM interactions of the DNA bases (QM part) with the system's remainder (solvent, DNA backbone). For this purpose, the time-dependent site energies for the seven sites of the DNA wire were obtained from the corresponding ionization potentials of the guanine bases. However, in this study these are approximated as the corresponding HOMO energies of the guanine bases [15]. Note that in the present case, the charge carriers in the DNA are holes, and the cytosine bases do not contribute to the hole conduction since their ionization potential is much higher in energy. The MD simulations of the DNA heptamer surrounded by water molecules and sodium counterions were performed using GROMACS, employing the AMBER parm99/BSC0 force field and using a time step of 1 fs at $T = 300$ K. Leads are not explicitly included in the atomistic modeling, but it is assumed that the molecular orbitals of the first and last base pairs of the heptamer couple to the leads with an energy-independent wire-lead coupling $\Gamma_L = \Gamma_R = 1$ meV. In addition to the molecular parameters, we choose the chemical potentials of the leads as $\mu_L = 6$ eV and $\mu_R = 4$ eV. For the TD-NEGF approach, the sites are initially half populated. As a result of the large bias voltage, the energies of the wire in the site as well as eigenstate representation lie within the transport window at all times. Consequently, all effects discussed here do not stem from the states exiting the transport window, but rather from changes in the energetic configuration of the wire.

Figure 1(a) shows the adverse results of the TD-NEGF and Landauer approaches for a 20 ps-long trajectory of DNA. The first scheme delivers a rapidly fluctuating current, which may even change its direction for short periods. This can be attributed to the time-dependent charging and discharging of the wire. On average, however, the TD-NEGF calculations yield an up to 3 orders of magnitude larger result than the Landauer outcomes. By definition, the Landauer current is unidirectional and has significant values only for certain configurations of the site energies. In contrast to the TD-NEGF approach, the Landauer current at each moment of time is independent of the populations on the sites and the previous configurations. Since the Landauer current has significant values only for a few snapshots, the average value over the trajectory is much smaller than the one obtained by the TD-NEGF approach.

In previous analyses of similar trajectories [14], the site energies and couplings have been averaged to coarse-grained time points. In order to examine the effect of such an averaging procedure on the results from both schemes, we lump together 500 MD snapshots in one new coarse-grained time point. Figure 1(b) depicts the

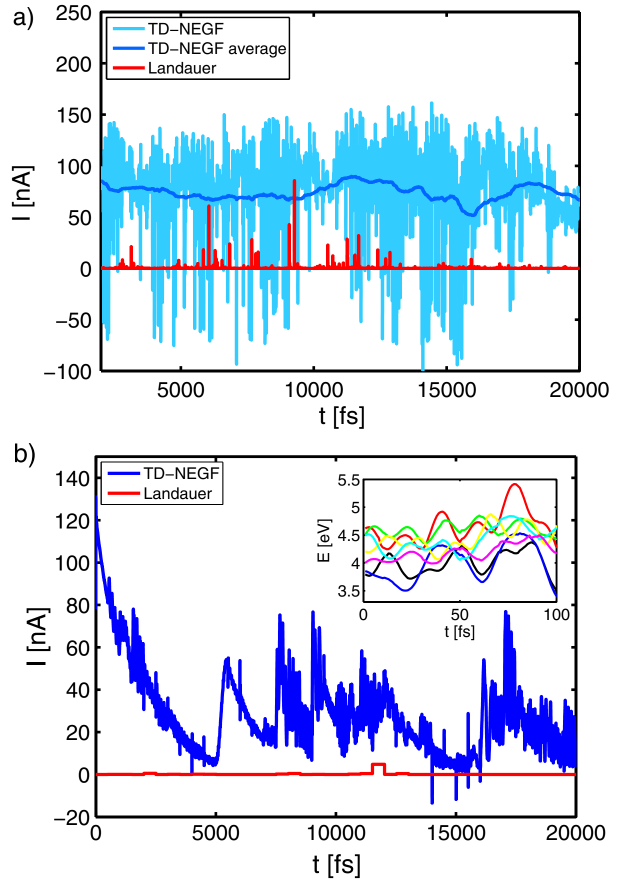

FIG. 1 (color online). TD-NEGF current $I(t)$ through a seven-site DNA molecule compared to the Landauer current. (a) Currents based on a 20-ps MD trajectory using a 1-fs time step. The heavily fluctuating time-resolved TD-NEGF current is displayed in light blue, whereas the dark-blue curve shows its running average over 2000 frames. The lower curve (red) denotes the Landauer results. The average values over the complete trajectory are $I_{\text{TD-NEGF}} = 73.52$ nA and $I_{\text{Landauer}} = 0.0739$ nA. (b) Currents computed using a coarse-grained version of the MD trajectory. The corresponding energies and couplings of 500 snapshots have been averaged to coarse-grained time points. The inset shows the first 100 fs of the seven site energies.

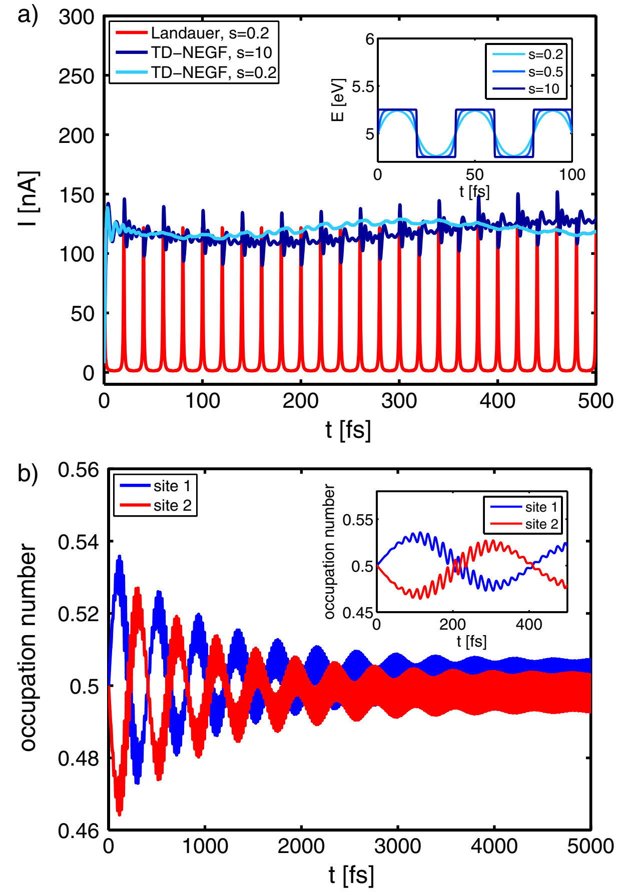

FIG. 2 (color online). A two-site system with a site energies switching time of 40 fs. (a) The TD-NEGF current through the device is shown in blue, compared to the Landauer current, shown in red (lower curve). The inset shows the site energy of the first site as a function of time for different values of the switching parameter s. (b) The occupation number of both sites as a function of time.

currents for the same system using these coarse-grained time points. As can be seen, this coarse graining leads to quite different results. The Landauer approach shows significant current values for even less points, while in the TD-NEGF scheme also the average current reduces considerably. Its early values are actually rather high because of the initially half-occupied sites.

In order to understand the large discrepancies in the current values computed using the two methods, we consider a two-site model system having the same couplings to the leads and chemical potentials as the DNA system above. The site energies E_1 and E_2 oscillate between two values $E_d = 4.75$ eV and $E_u = 5.25$ eV. The switching between these values is obtained by means of a sequence of $\tanh(st)$ functions [see the inset of Fig. 2(a)]. This functional form has the advantage that by varying the parameter s one can obtain oscillations in a form close to sinusoidal ($s = 0.2$) to almost step-like transitions ($s = 10$). As the oscillation period, we choose 40 fs, close to the ones obtained for the DNA system discussed above [see the inset of Fig. 1(b)]. Figure 2(a) shows the TD-NEGF currents computed using two different values for the switching parameter, i.e., $s = 0.2$ and $s = 10$. Although the oscillations do show some differences, the average current is very similar and independent of the parameter s, and has a value of around 120 nA. In contrast, the average currents obtained using the Landauer approach vary slightly between 11 nA for $s = 0.2$ and 2 nA for $s = 10$. So the values obtained for the TD-NEGF current are between a factor of 10 to more than 50 larger than the average Landauer values, with some variations regarding the form of the oscillating function. To explore the differences between the TD-NEGF and Landauer schemes in more detail, the occupation probabilities of the two molecular sites are shown in Fig. 2(b). For the employed parameters and rather independently of the form of the switching function, the occupation probabilities of both the sites are 0.5, with some larger transient oscillations in the initial phase of the simulations. As it is known from, for example, the transient currents due to the switch on or off of electric fields [30], the corresponding currents are usually due to the charging or discharging effects of the molecular sites. If the population on one of the sites has vanished, no sequential transfer at this moment in time would be possible. The corresponding site would first have to be charged, and then discharged, again leading to a current through the site. A direct coherent transfer as determined by the Landauer approach is still possible, but it leads to only small current values, as also seen in this example.

In the following, we investigate the agreement between the results when using the TD-NEGF and the Landauer schemes in some limiting case in a two-level scenario. To this end, we enlarge the oscillation period from 40 fs to 500 fs. The corresponding findings relating to the current and population are shown in Fig. 3. In contrast to the previous case, the results strongly depend on the switching parameter s. As long as the switching is not too abrupt, the population of the two sites oscillate around a finite value and the corresponding current as well. For abrupt changes between the two values, i.e., for $s = 100$, the population of site 1 next to the lead with larger chemical potential goes to unity, while the population of site 2 next to the lead with lower chemical potential vanishes at large times, as shown in Fig. 3(b). In this case, only direct coherent tunneling is possible, and the TD-NEGF theory coincides with the coherent Landauer approach, yielding small but nonvanishing currents. In contrast, for a smoother switching between the two energy values, the resulting currents strongly depend on the form of the switching function, as the lighter blue curves in Fig. 3(a) show. The dependence on the steepness of the switching function might be used to switch currents in molecular junctions. The effect of a smoother transition on the Landauer current merely consists in broader peaks corresponding to the configurations in which the sites have rather close energy values.

Coming back to the DNA example, it is clear that because of the fast site energy oscillations of around 40 fs [31], there are nonvanishing populations on the sites in the TD-NEGF approach. These populations, together with the fast oscillations, lead to sequential currents in the TD-NEGF scheme, which are considerably larger than the currents in the Landauer theory. The DNA example consists of seven sites, and it is very unlikely that these sites form a configuration leading to a large transmission and Landauer current. In contrast, the TD-NEGF scheme can explain the population dynamics and the sequential transport that are entirely neglected in the Landauer theory.

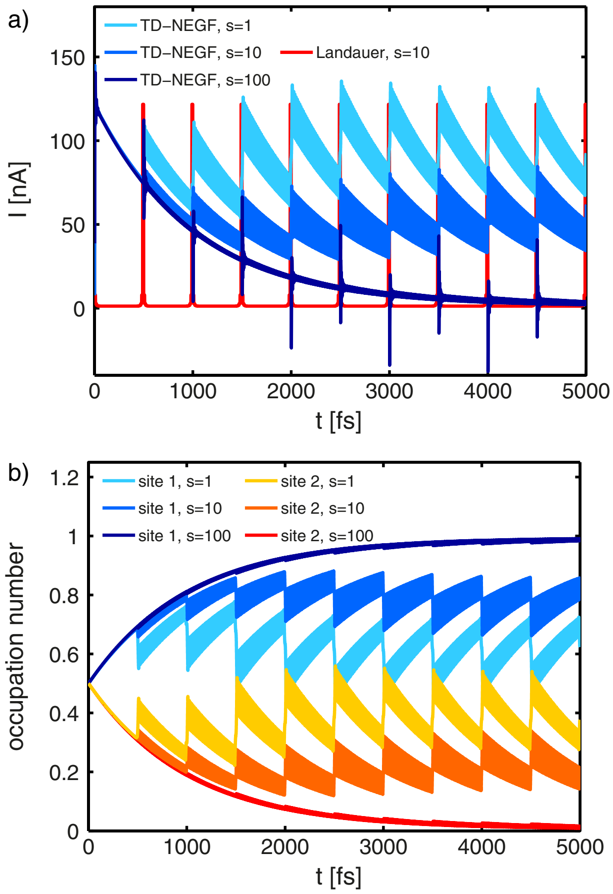

FIG. 3 (color online). A two-site system with a site energies switching time of 500 fs. (a) The TD-NEGF currents for three values of the switching parameter s compared to the Landauer currents. (b) Population dynamics for both sites. The filled regions indicate the fast oscillations not resolved on the present scale.

Because of the indirect modeling of the leads, a quantitative agreement with experimentally measured currents cannot be expected. However, we would like to point out that the obtained TD-NEGF currents are in accordance with the measurements of DNA in a solution of more than 100 nA at large bias voltages [32,33]. The Landauer theory, in contrast, yields currents 3 orders of magnitude lower. Introducing the averaging procedures into the Landauer scheme [14], we can obtain somewhat larger currents, but averaging turns out to be quite arbitrary at the same time. This indicates that the TD-NEGF approach is much more appropriate to capture the physics behind the DNA transport phenomena, leading to a semiquantitative agreement with the experimental results.

In conclusion, although several features of charge transfer in molecular wires can be explained using the Landauer formalism, we point out that this method shows itself incapable of a proper description of the systems with rapidly fluctuating bridges. In realistic systems, these fast fluctuations of the site energies are mainly driven by solvent molecules. Furthermore, it was shown that, as in the case of slower fluctuations, sequential transport is much more important than coherent transport. This sequential transport also cannot be captured using snapshot-averaged higher-level time-independent transport theories. The above results are by no means restricted to the present example of transport through solvated DNA, but are certainly valid for many such scenarios. As the combinations of quantum chemistry calculations along classical MD simulations become more and more feasible [13–24], it needs to be pointed out that employing the Landauer approach for the individual snapshots combined with some averaging procedures (before or after the current determination) will not lead to reliable current values. Since sequential transport is an important factor, a time-dependent approach such as the TD-NEGF scheme, which takes into account the time ordering as well as abundance of the site energies, needs to be used.

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*u.kleinekathoefer@jacobs-university.de

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