Charge transport through bio-molecular wires in a solvent: Bridging molecular dynamics and model Hamiltonian approaches

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We present a hybrid method based on a combination of quantum/classical molecular dynamics (MD) simulations and a model Hamiltonian approach to describe charge transport through bio-molecular wires with variable lengths in presence of a solvent. The core of our approach consists in a mapping of the bio-molecular electronic structure, as obtained from density-functional based tight-binding calculations of molecular structures along MD trajectories, onto a low dimensional model Hamiltonian including the coupling to a dissipative bosonic environment. The latter encodes fluctuation effects arising from the solvent and from the molecular conformational dynamics. We apply this approach to the case of pG-pC and pA-pT DNA oligomers as paradigmatic cases and show that the DNA conformational fluctuations are essential in determining and supporting charge transport.

PACS numbers:

Can a DNA molecular wire support an electrical current? The variety of partially contradictory experimental results obtained in the past years [1, 2, 3, 4, 5, 6, 7] has hinted not only at the difficulties encountered to carry out well-controlled transport measurements, but also at the strong sensitivity of charge migration to intrinsic (base-pair sequence, internal vibrations) and extrinsic (solvent fluctuations, molecule-electrode contact) factors. Recently [6, 7], two experimental groups have measured similar high electrical currents on the order of 50-100 nA despite the fact that the electrically probed base sequences and lengths were rather different. In spite of considerable theoretical research, the dominant mechanisms for charge transport through DNA wires have not been, however, fully elucidated, see e.g., Ref. [8] for a recent review. Electron transfer experiments [9, 10] as well as related theoretical studies [11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24] have clearly pointed out the crucial role of dynamical fluctuations in favouring or hindering hole transfer. We may thus expect that this may also be the case for charge transport. Studies based on model Hamiltonian formulations describing disordered sequences [25, 26], or the coupling to dynamical degrees of freedom [18, 19, 20, 21, 22] involve many free parameters which are in general difficult to determine for realistic situations. First-principle calculations [27, 28, 29, 30, 31, 32], performed on static structures, provide, on the other hand, orders of magnitude for the electronic coupling parameters but can hardly deal with the coupling to dynamical degrees of freedom. The inclusion of dynamical effects in quantum transport calculations has only been addressed in few special cases [14, 15, 33, 34] in a systematic way. Thus, a general approach able to combine dynamical information drawn from a realistic description of bio-molecular conformational dynamics with a treatment of quantum transport is highly desirable.

In this Letter, we present a study of charge transport through bio-molecular wires with different lengths by using a hybrid approach based on a mapping of the time-fluctuating electronic structure along a molecular dynamics (MD) trajectory onto a low-dimensional model Hamiltonian.
tonian. Charge transport will be studied for an effective model describing the coupling of the electronic system to a bosonic bath which comprises internal vibrations and solvent effects. The bath thus encodes dynamical information drawn from the MD simulations. Our treatment allows (i) the determination of electronic coupling parameters under realistic conditions, and (ii) the calculation of the bath spectral density from time series generated during the MD simulation. In this way, it does not contain any free parameters describing the molecular electronic structure or the coupling to the structural fluctuations. We show, by considering as paradigmatic cases pG-pC and pA-pT oligomers, that the electrical transport properties in such bio-molecular systems are strongly dominated by the conformational dynamics. Despite some limitations of the model Hamiltonian approach related to the used approximations (see later), we nevertheless stress that the range of applicability of our method is not limited to DNA molecular wires; indeed, it provides a solid basis for the parameter-free inclusion of dynamical effects in a model-based treatment of quantum transport as well as for a multi-scale approach to the description of the electronic properties of bio-molecules and their response to external fields. Our approach exploits a fragment orbital description of the bio-molecules, which allows for an efficient and well controlled coarse graining of the electronic structure problem. A combination of quantum mechanics/molecular mechanics methods (to describe solvent effects), MD simulations, and a parametrized density-functional tight-binding methodology has been used to extract the relevant electronic information in the form of time series. This leads to a time-dependent Hamiltonian: $H = \sum_j \epsilon_j(t) d_j^\dagger d_j + \sum_{j,j+1} V_{j,j+1}(t) (d_j^\dagger d_{j+1} + \text{h.c.})$, where both $\epsilon_j(t)$ and $V_{j,j+1}(t)$ are random variables as a function of the simulation time. These parameters describe, respectively, the effective ionization energy of a single base-pair—which defines a fragment in our calculations—and the coupling between nearest-neighbor fragments. We have approached the transport problem from two complementary perspectives.

**Time averaging and dynamical fluctuations** — In Fig. 1 we show the time-averaged transmission function $(T(E))_t$ for pG-pC and pA-pT wires containing seven base pairs. These calculations have been carried out for a $T_{MD} = 30$ ns long MD simulation with a time step of 1 fs. The first point to note is the apparently higher transmission of pA-pT compared to that of pG-pC. This is just the opposite of what a purely static calculation would yield. This fact represents a first hint at the importance of dynamical effects in determining charge propagation. The fragmented structure of the spectrum is simply mirroring the broad distribution of onsite energies induced by the dynamical disorder. We have further defined a coherence parameter (CP) for a given chain length $N$ as $C_N(E) = \frac{1 + \sigma_T(E)}{\langle T(E) \rangle^2}$, which can provide a quantitative measure for the role of structural fluctuations. $C_N(E) \ll 1$ can indicate the dominance of the conformational dynamics. Hereby, $\sigma_T(E) = \langle [T(E) - \langle T(E) \rangle]^2 \rangle$ is the mean-square deviation of the transmission and the brackets always indicate time averaging. Obviously, the CP has only a clear meaning in the spectral region where the transmission function itself is non-negligible (spectral support). The
CP is shown in Fig 2 for seven base pairs of pA-pT and pG-pC, from where it is seen that (i) transport is dominated by the bio-molecular dynamics, $C_N(E) \ll 1$, and (ii) the CP for pG-pC is roughly one order of magnitude smaller (within the spectral support domain) than for pA-pT, reflecting the fact that the latter system seems to be less affected by dynamical disorder. The inset of the same figure displays the energy-averaged CP for four different numbers of base pairs. Longer chains are clearly more affected by dynamical disorder than shorter chains, independent of the base sequence. In a second step, we have investigated the dependence of the time-average current $\langle I(V) \rangle_t$ on the averaging procedure, i.e., calculating a set of partial currents $I(V, \tau_W)$ obtained upon averaging of the electronic parameters over time windows of length $\tau_W = n_d \delta t$ along the time series, where $\delta t = 1$ ps is the time step at which molecular conformations were extracted along the MD trajectory. The index $\ell = 1, \cdots, \int [T_{MD}/\tau_W] = L$ labels the number of time frames once $n_d$ has been fixed. The total current is thus given by $\langle I(V) \rangle_t = (1/L) \sum_{\ell} I_c(V, \tau_W)$. The different sizes of the time windows (different values of $\tau_W$) are mirroring in a phenomenological way differences in electronic time scales (an information not provided by the MD simulations); a charge will explore different fluctuating environments in dependence of $\tau_W$ and thus the total current must be affected by this fact. Hence e.g., $\tau_W \ll \omega^{-1}$, with $\omega^{-1}$ being some typical time scale for dynamic fluctuations, would correspond to the non-adiabatic limit where a time-averaged electronic frame is felt by the charge, while the opposite limit $\tau_W \gg \omega^{-1}$ defines the adiabatic regime, where instantaneous atomic configurations are “seen”. Of course, this provides only a qualitative picture, since the DNA structural fluctuations involve many different time scales making the effective interaction of a charge with different degrees of freedom very complex. In Fig. 3, we show the time-averaged current for a fixed number of base pairs and three different values of the time frame: $\tau_W = 5, 20$, and 50 ps. We see a slow increase of the current with increasing $\tau_W$, since a moving charge will effectively sample an increasingly larger number of realizations of $\epsilon_j(t)$ and $V_{j,j+1}(t)$. We remark that the current calculation using a Landauer-like expression is only meaningful near the adiabatic limit; in the strongly non-adiabatic regime golden-rule like expressions should be used.

Effective charge-bath model — As a complementary way to deal with charge transport — allowing for a flexible treatment of different transport mechanisms while still relying on a realistic description of the bio-molecular dynamics— an effective model has been formulated describing the electronic system coupled to a fluctuating environment (bosonic bath):

$$\begin{align*}
H &= \sum_j \langle \epsilon_j \rangle_t d_j^\dagger d_j + \sum_{j} \langle V_{j,j+1} \rangle_t (d_j^\dagger d_{j+1} + \text{h.c.}) \\
&+ \sum_{s,j} \lambda_{sj} d_j^\dagger d_j (B_s + B_s^\dagger) + \sum_s \Omega_s B_s^\dagger B_s.
\end{align*}$$

Here, the time averages of the electronic parameters $\langle \epsilon_j \rangle_t$, $\langle V_{j,j+1} \rangle_t$ have been split off, e.g., $\epsilon_j(t) = \langle \epsilon_j \rangle_t + \delta \epsilon_j(t)$. Some approximations are involved by the formulation of this model: (i) only local energy fluctuations are considered and included in the bath (last term of Eq. (1)). (ii) $\lambda_{sj}$ (s numbers the bath modes) depends in general on the site $j$. This will be partially taken into account and is reflected in a renormalization of the average hopping $\langle V_{j,j+1} \rangle_t$; (iii) no fluctuations in the coupling parameters $V_{j,j+1}(t)$ are considered. The bath will be characterized by a site-averaged spectral density $J(\omega) = \langle \delta \epsilon^2(0) \rangle (2/\pi \hbar) \tanh (\hbar \omega/k_B T) \int_0^\infty dt \cos(\omega t) C(t)$, with $C(t) = (1/N) \sum_j \langle \delta \epsilon_j(t) \delta \epsilon_j(0) \rangle$ being the (site-averaged) autocorrelation function of the onsite energy fluctuations. Using the model of Eq. (1), the electrical current through pG-pC and pA-pT oligomers containing $N=7$, 11, and 15 base pairs was computed. The Fermi level was fixed in each case outside the spectral support of $T(E)$ to obtain a zero-current gap, which is thus arbitrary in these calculations. In Fig. 4, where the $I$-$V$ characteristics of the different sequences and lengths are shown, we observe that apart from the shortest ($N=7$) oligomer, the current for pG-pC is somewhat larger than for pA-pT. These features are possibly associated to two factors. Firstly,
the neglect of non-local onsite energy fluctuations: fluctuations between neighboring sites decay faster on sub-ps time scales, see the inset of Fig. 4, but can nevertheless induce non-vanishing correlations over few base pairs thus modifying the electrical response of the system. Secondly, the use of an averaged spectral density effectively makes the coupling of all electronic sites to the bath very similar. Since fluctuations become more important with increasing length, this approximation may become problematic. In spite of these limitations, Eq. (1) provides a reasonable starting point to bridge MD simulations with charge transport models and, more important, offers the possibility of systematically improving the model Hamiltonian approach.

In conclusion, we have presented a combined molecular dynamics/model Hamiltonian approach which allows for a very flexible treatment of charge transport through biomolecular systems taking into account dynamical disorder. The method can allow, as illustrated in the special case of DNA wires, the straightforward study of the base-sequence and length dependence of the electrical response of such systems. The results presented here strongly support the view that charge transport through DNA wires is dominated by conformational fluctuations. In this sense, transport approaches based on band-like coherent transport or on purely static structures can not yield a realistic description of charge motion in such highly dynamical systems. Finally, we would like to stress that our approach can be applied as well to investigate the interplay of charge transport/transfer and conformational dynamics in other complex bio-molecular systems. This flexibility relies on the fact that the degree of coarse-graining —leading to the formulation of effective tight-binding models— can be “tuned” by an appropriate re-definition of the fragment orbitals while still retaining the relevant dynamical information.

The authors thank Stanislaw Avdosenko and Jewgeni Starikov for useful discussions. This work has been partially supported by the Deutsche Forschungsgemeinschaft (DFG) under contracts CU 44/5-2 and CU 44/3-2 and by the South Korea Ministry of Education, Science and Technology Program "World Class University" under contract R31-2008-000-10100-0.

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The current is calculated at this stage using the expression \( \langle I(V) \rangle_t = \frac{2e}{h} R \int dE (f_L(E) - f_R(E)) (T(E))_t \), where \( T(E) = \Gamma_L \Gamma_R |G_{1N}(E)|^2 \) is the transmission probability for a linear chain of length \( N \). The coupling to the \( \alpha \)-electrode \( \Gamma_\alpha \) is treated as a free, energy-independent parameter (wide-band approximation). For the sake of simplicity we further assume \( \Gamma_L = \Gamma_R = \Gamma \). Though our approach allows to determine the influence of the dynamics onto the molecule-electrode coupling, this increases the complexity of our analysis and will be left for future investigations.

Quantum dissipative systems; Weiss, U., Ed.; World Scientific: Singapore, New Jersey, London, Hong Kong, 2008.

In short, we perform a polaron unitary transformation in Eq. (1) to eliminate the linear coupling to the bosonic bath [40]. An important point related dependence of the linear charge-bath coupling \( \lambda_{sj} \) on the site \( j \) along the linear chain is that the average nearest-neighbor electronic coupling \( \langle V_{j,j+1} \rangle_t \) will be exponentially renormalized by an expression containing the bath operators, only. For the sake of simplicity, this effect is taken into account through a mean-field-like approximation, by substituting terms containing boson operators by their thermal averages. A very rough estimation yields a factor of the order of \( \exp[-\langle \delta \epsilon^2 \rangle / 2(\hbar \omega_c)^2] \), where \( \langle \delta \epsilon^2 \rangle \) is a typical mean-square fluctuation of the onsite energies (which is larger for pG-pC than for pA-pT) and can be obtained from the MD simulations. \( \omega_c \) is a typical bath high-frequency cut-off, which we set around 150 meV. Finally, for a bath in thermal equilibrium, an expression for the current from lead \( \alpha \) can be found: 

\[
I_\alpha(V) = \frac{2e}{h} R \int dE dE' \text{Tr} \left\{ \Gamma_E \left[ f_E^\alpha G_{E'-E}^E \Psi_{E'} + (1 - f_E^\alpha) G_{E'-E}^E \Psi_{-E'} \right] \right\},
\]

\( f_E^\alpha \) is the Fermi function for lead \( \alpha \). The function \( \Psi_E \) is the Fourier transform of 

\[
- \int_0^\infty d\omega \frac{2i\omega}{\cosh(\frac{\omega}{2k_B T})} (1 - \cos \omega t) + i \sin \omega t \]

In the current expression, additional terms scaling as \( O(\langle V_{j,j+1} \rangle_t^2 \Gamma^2) \) have been neglected, which is consistent with the mean-field approximation in the bath operators and with the exponential reduction of the electronic coupling.