Charge Transport through Biomolecular 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 classical molecular dynamics simulations, quantum-chemical calculations, and a model Hamiltonian approach to describe charge transport through biomolecular wires with variable lengths in presence of a solvent. The core of our approach consists in a mapping of the biomolecular electronic structure, as obtained from density-functional based tight-binding calculations of molecular structures along molecular dynamics 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.

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Can a DNA molecular wire support an electrical current? The variety of partially contradictory experimental results obtained in the past years [1–7] 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 groups have measured similar high electrical currents on the order of 50–150 nA despite the fact that the electrically probed base sequences and lengths were rather different. Despite considerable theoretical research, the dominant mechanisms for DNA charge transport have not been, however, fully elucidated (see, e.g., Ref. [8] for a recent review). Electron transfer experiments [9,10] and related theoretical studies [11–21] have clearly pointed out the crucial role of dynamical fluctuations in favoring or hindering hole transfer. We may thus expect that this may also be the case for charge transport. Studies based on model Hamiltonian formulations [18,19,22,23] involve many free parameters which are in general difficult to determine for realistic situations. First-principle calculations [24–28] performed on static structures provide, on the other hand, orders of magnitude for the electronic coupling 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 cases [14,16,29] in a systematic way. Thus, a general approach able to combine dynamical information drawn from a realistic description of biomolecular conformational dynamics with a treatment of quantum transport is highly desirable.

In this Letter, we present a study of charge transport through biomolecular 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. Charge transport will be studied for a 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 MD generated time series. Hence, it does not contain any free parameters describing the molecular electronic structure or the coupling to structural fluctuations. We show, by considering as paradigmatic cases pG-pC and pA-pT oligomers, that the electrical transport properties in such biomolecular systems are strongly dominated by the conformational dynamics. Despite some limitations of the model Hamiltonian approach (see later), we nevertheless stress that the range of applicability of our method is not limited to DNA 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 multiscale approach to the description of the electronic properties of biomolecules. Our approach exploits a fragment orbital description [30] of the biomolecules, which allows for an efficient and well-controlled coarse graining of the electronic structure problem [31]. A hybrid quantum mechanics–molecular mechanics (QM/MM) approach (to describe the solvent

effects) implemented within a density-functional based tight-binding methodology [32] has been used to extract relevant electronic information in the form of time series. This leads to a time-dependent Hamiltonian: $H = \sum_j \epsilon_j(t) d_j^\dagger d_j + \sum_j V_{j,j+1}(t)(d_j^\dagger d_{j+1} + \text{H.c.})$, 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 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 $\langle T(E)\rangle_t$ for pG-pC and pA-pT wires containing seven base pairs. These calculations have been carried out for a $T_{\text{MD}} =$ 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 on-site energies induced by the dynamical disorder. We have further defined a coherence parameter (CP) for a given chain length N as $C_N(E) = [1 + \sigma_T(E)/\langle T(E)\rangle_t^2]^{-1}$, 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, $\sigma_T(E) = \langle [T(E) - \langle T(E)\rangle_t]^2\rangle_t$ is the mean-square deviation of the transmission, and the brackets 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 biomolecular dynamics, $C_N(E) \ll 1$, and (ii) the CP for pG-pC is roughly 1 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 $I_l(V, \tau_W)$ 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 $l = 1, \cdots, \text{int}[T_{\text{MD}}/\tau_W] = L$ labels the number of time frames once n_d has been fixed. The total current is thus given by $\langle I(V)\rangle_t = (1/L)\sum_l I_l(V, \tau_W)$. The different sizes of the time windows (different values of τ_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 τ_W and thus the total current must be affected by this fact. Hence, e.g., $\tau_W \ll \omega^{-1}$, with ω^{-1} being some typical time scale for dynamic fluctuations, would correspond to the nonadiabatic limit where a time-averaged atomic 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

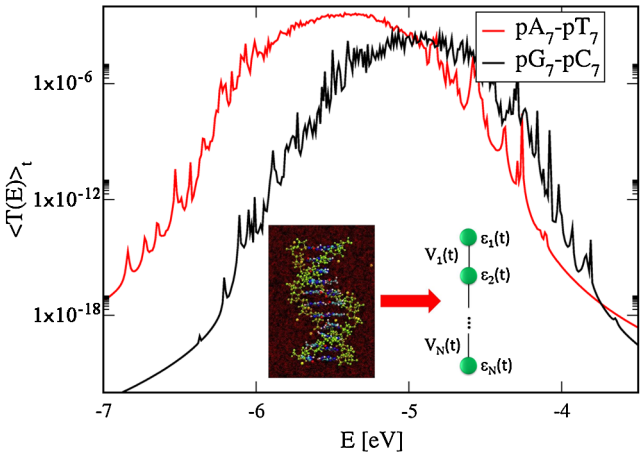

FIG. 1 (color online). Typical time-averaged transmission function $\langle T(E)\rangle_t$ for pG-pC and pA-pT wires with seven base pairs each. The simulation time is 100 ps, and the average was performed every 5 ps. Inset: A snapshot of a pG-pC oligomer in a solvent drawn from the MD simulation. To avoid spurious boundary effects, only the innermost seven base pairs are used. The electronic structure at each snapshot is mapped onto an effective low-dimensional model Hamiltonian.

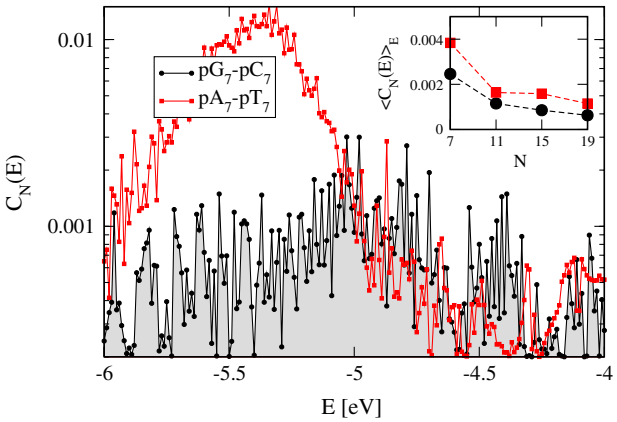

FIG. 2 (color online). Coherence parameter $C_N(E)$ providing a qualitative measure for the importance of dynamical disorder; $C_N(E) \ll 1$ hints at the dominant role of fluctuations in determining the transport properties. The inset shows the energy-averaged $\langle C_N(E)\rangle_E$ as a function of the number of base pairs in the DNA chain.

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 τ_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 emphasize that the change in the current obtained in this way strongly depends on the base sequence.

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 biomolecular dynamics—an effective model has been formulated describing the electronic system coupled to a fluctuating environment (bosonic bath):

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

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 [third term of Eq. (1)]. (ii) λ_{sj} (s denotes the number of bath modes) depends in general on the site j. This 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 [33]. This latter approximation can be justified via an extensive statistical analysis of the simulation data [31] or by looking at the hopping correlation function in the inset of Fig. 3, which decays on much shorter time scales than the on-site correlations. The bath will be characterized by a site-averaged spectral density $J(\omega) = \langle \delta\epsilon^2(0) \rangle (2/\pi\hbar) \times \tanh(\hbar\omega/k_B T) \int_0^\infty dt \cos(\omega t) C(t)$, 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 on-site 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. In Fig. 4, where the I-V characteristics of the different sequences and lengths are shown, we find a decrease of the saturation current with chain length, a fact related to the increased dominance of dynamical disorder (see the inset of Fig. 2). Further, apart from the shortest ($N = 7$) oligomer, the current for pG-pC is somewhat larger than for pA-pT. This last feature is related to two factors. First, the neglect of nonlocal on-site energy fluctuations: fluctuations between neighboring sites decay faster on sub-ps time scales (see the inset of Fig. 3) but can nevertheless induce nonvanishing correlations over few base pairs [31], thus modifying the electrical response of the system. Second, 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.

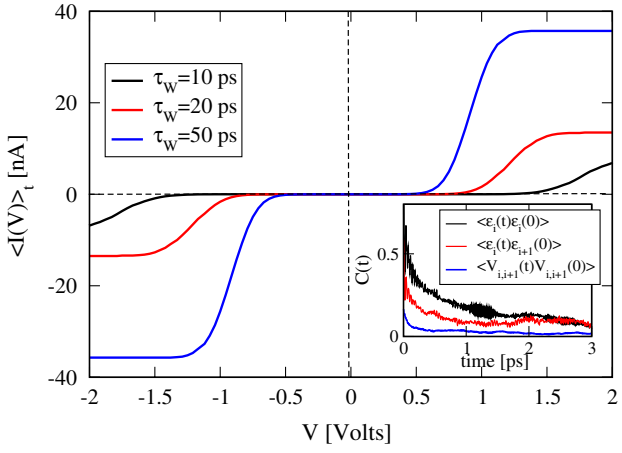

FIG. 3 (color online). Time-averaged current $\langle I(V) \rangle_t$ for a pG_7-pC_7 oligomer. Results are shown for three different choices of the time frame $\tau_W = 5$, 20, and 50 ps (for a definition see the main text). Inset: Autocorrelation function of the energy fluctuations $\langle \epsilon_i(t) \epsilon_i(0) \rangle$, nearest-neighbor correlation $\langle \epsilon_i(t) \epsilon_{i+1}(0) \rangle$, and hopping correlations $\langle V_{i,i+1}(t) V_{i,i+1}(0) \rangle$.

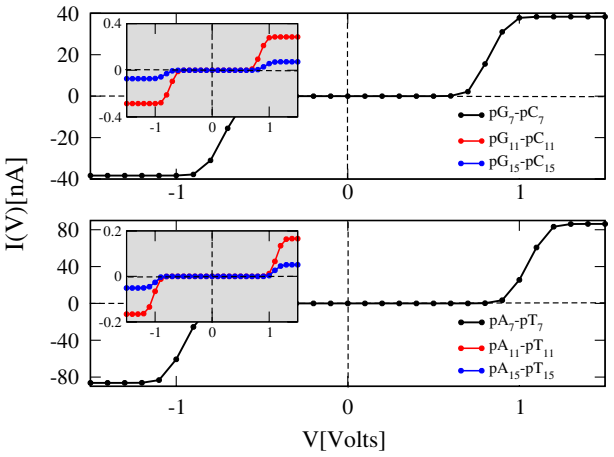

FIG. 4 (color online). I-V characteristics of pG-pC (upper panel) and pA-pT (lower panel) oligomers with three different numbers of base pairs $N = 7$, 11, 15 calculated with the effective charge-bath model Hamiltonian [see Eq. (1)]. In all cases the effective electrode-molecule coupling parameter was chosen as $\Gamma = 5$ meV within a wide-band limit. Though for the shortest oligomer, pA-pT has a larger current than pG-pC, this behavior is weakened with increasing length.

In conclusion, we have presented a combined molecular dynamics and 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 bandlike coherent transport or on purely static structures cannot yield a realistic description of charge motion in such highly dynamical systems. Finally, we stress that our approach can be applied as well to investigate the interplay of charge transport and conformational dynamics in other biomolecular systems. This flexibility relies on the fact that the degree of coarse graining—leading to the formulation of effective models—can be ''tuned'' by an appropriate redefinition of the fragment orbitals while still retaining the relevant dynamical information.

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[33] A unitary transformation in Eq. (1) allows the elimination of the coupling to the bath. As a result, the average coupling $\langle V_{j,j+1}\rangle_t$ is exponentially renormalized by bosonic operators [34]. Within a mean-field-like approach, a rough estimation yields a renormalization $\sim\langle V_{j,j+1}\rangle_t \times \exp[-\langle\delta\epsilon^2\rangle/2(\hbar\omega_c)^2]$; $\langle\delta\epsilon^2\rangle$ is a typical rms fluctuation of the site energies, which is larger for pG-pC ($\sim$0.40 eV) than for pA-pT ($\sim$0.32 eV), and ω_c is some typical bath frequency (set at 150 meV). Both parameters can be estimated from the MD simulations [31]. The averaged site energies lie around -4.8 eV (pG-pC) and -5.2 eV (pA-pT) for all the lengths studied here. The unrenormalized averaged coupling terms have values around 30 meV (pG-pC) and 60 meV (pA-pT).
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