Quantum transport through a DNA wire in a dissipative environment

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Electronic transport through DNA wires in the presence of a strong dissipative environment is investigated. We show that new bath-induced electronic states are formed within the bandgap. These states show up in the linear conductance spectrum as a temperature dependent background and lead to a crossover from tunneling to thermal activated behavior with increasing temperature. Depending on the strength of the electron-bath coupling, the conductance at the Fermi level can show a weak exponential or even an algebraic length dependence. Our results suggest a new environmental-induced transport mechanism. This might be relevant for the understanding of molecular conduction experiments in liquid solution, like those recently performed on poly(GC) oligomers in a water buffer (B. Xu *et al.*, Nano Lett. **4**, 1105 (2004)).

In the emerging field of molecular electronics, DNA oligomers have drawn in the last decade the attention of both experimentalists and theoreticians [1]. This has been mainly motivated by DNA exciting potential applications which include its use as a template in molecular devices or by exploiting its self-assembling and self-recognition properties [2]. Alternatively, DNA strands might act as molecular wires either in periodic conformations as in poly(GC), or by doping with metal cations as is the case of M-DNA [3]. As a consequence, the identification of the relevant charge transport channels in DNA systems becomes a crucial issue. Transport experiments in DNA derivatives are however quite controversial [4, 5]. DNA has been characterized as insulating [6], semiconducting [7] or metallic [8, 9]. It becomes then apparent that sample preparation and experimental conditions are more critical than in transport experiments on other nanoscale systems. Meanwhile, a variety of factors that appreciably control charge propagation along the double helix have been theoretically identified: static [10] and dynamical [11] disorder related to random base pair sequences and structural fluctuations, respectively, as well as environmental effects associated with correlated fluctuations of counterions [12] or with the formation of localised states within the bandgap [4, 13].

Recently, Xu *et al.* [9] have carried out transport experiments on poly(GC) oligomers in aqueous solution. These experiments are remarkable for different reasons: (i) it was shown that transport characteristics of *single* molecules were probed, (ii) the molecules displayed ohmic-like behavior in the low-bias *I*-*V* characteristics and (iii) the linear conductance showed an algebraic dependence $g \sim N^{-1}$ on the number N of base pairs. This latter result suggests the dominance of incoherent charge transport processes. Complex band structure calculations [14] for *dry* poly(GC) oligomers predict, on the contrary, a rather strong exponential dependence of the conductance on the wire length, a typical result for coherent tunneling through band gaps. Hence, Xu *et al.* exper-

iments suggest the potential role of the environment in modifying the DC conductivity of DNA.

In the light of these results, we explore in this Letter the possibility that a strong perturbation of the electronic system by a dissipative environment may lead to a modification of the low-energy electronic structure of the molecular wire. As a result, the linear transport properties may be qualitatively different when comparing with the "dry" wire.

Our description assumes that only the frontier orbitals of the poly(GC) stack are relevant for charge transport,
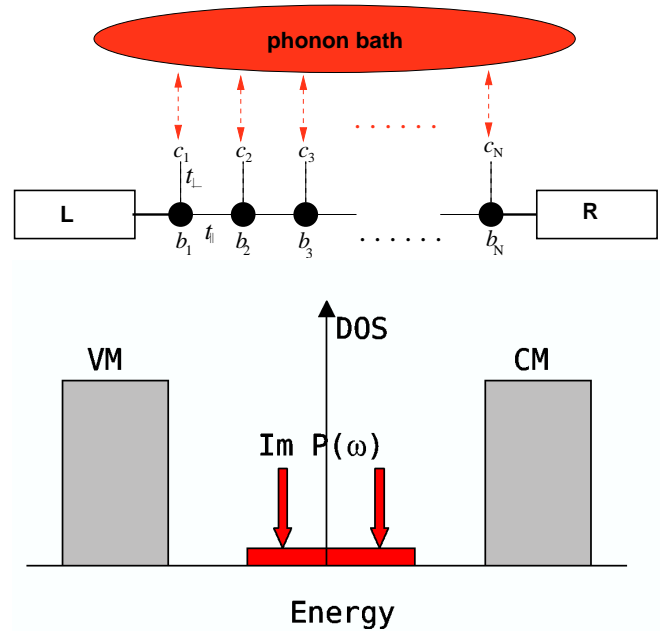

FIG. 1: Schematic representation of the DNA molecular wire in contact with a phonon bath (upper panel) and of the corresponding density of states (lower panel). In the absence of the phonon bath, valence (VM) and conduction (CM) manifolds are separated by a gap. Upon coupling to the environment, a new set of states emerge within the gap. Though strongly damped by the dissipative coupling, they yield a finite density of states and eventually lead to a conductance enhancement with increasing temperature.

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a reasonable approximation at low bias. Frontier orbitals are the highest-occupied (HOMO) and the lowest-unoccupied (LUMO) molecular states. They both have π character and are derived from linear combinations of the p_z orbitals of individual base pairs. The π orbital stack can be thus represented in a localised orbital picture. As shown by first principle calculations [15], the HOMO charge density is mainly concentrated on the guanine bases and the LUMO charge density on the citosyne bases. Hence, within a *minimal model*, we will focus *e.g.* only on the π-stack along the guanine strand (HOMO) for hole transport and consider the opening of the HOMO-LUMO gap as a perturbation of this π-stack, induced by the complementary strand and, eventually by the backbone subsystem. [16] The environment is conventionally described by a harmonic phonon bath.

We address the temperature and length dependence of the conductance in the strong coupling limit to the bath degrees of freedom. Our results can be summarized as follows. First, *bath-induced* states appear in the gap region, see Fig. 1 for illustration. They are however washed out due to the strong effect of the environment, so that they do not manifest as well-defined resonances in the transmission spectrum. Nevertheless, they induce a temperature dependent density of states within the gap. This leads to a transition from a tunneling regime at low temperatures, with a zero current gap, to an activated regime at higher temperatures, with a finite current at low voltages. Second, a weak exponential or even algebraic length dependence together with an Arrhenius-like behavior of the transmission at the Fermi energy are found, reflecting the strong contribution of incoherent processes.

We describe the system consisting of a poly(GC) wire containing N base pairs, contacted to left and right electrodes ($\mathcal{H}_{\text{leads}}$), and in interaction with a phonon bath ($\mathcal{H}_{\text{B}}$) by the following Hamilton operator, see Fig. 1:

$$\mathcal{H} = \mathcal{H}_{\text{C}} + \mathcal{H}_{\text{C-c}} + \mathcal{H}_{\text{leads}} + \mathcal{H}_{\text{B}}, \tag{1}$$

$$\mathcal{H}_{\text{C}} = \epsilon_b \sum_j b_j^\dagger b_j - t_{||} \sum_j \left(b_j^\dagger b_{j+1} + \text{H.c.} \right),$$

$$\mathcal{H}_{\text{C-c}} = \epsilon \sum_j c_j^\dagger c_j - t_\perp \sum_j \left(b_j^\dagger c_j + \text{H.c.} \right),$$

$$\mathcal{H}_{\text{leads}} = \sum_{\mathbf{k} \in \text{L,R},\sigma} \epsilon_{\mathbf{k}\sigma} d_{\mathbf{k}\sigma}^\dagger d_{\mathbf{k}\sigma} + \sum_{\mathbf{k} \in \text{L},\sigma} \left(V_{\mathbf{k},1} d_{\mathbf{k}\sigma}^\dagger b_1 + \text{H.c.} \right),$$

$$+ \sum_{\mathbf{k} \in \text{R},\sigma} \left(V_{\mathbf{k},N} d_{\mathbf{k}\sigma}^\dagger b_N + \text{H.c.} \right),$$

$$\mathcal{H}_{\text{B}} = \sum_\alpha \Omega_\alpha B_\alpha^\dagger B_\alpha + \sum_{\alpha,j} \lambda_\alpha c_j^\dagger c_j \left(B_\alpha + B_\alpha^\dagger \right).$$

In the previous expression, $\mathcal{H}_{\text{C}}$ describes the HOMO π-stack as a one-dimensional tight-binding chain with onsite energies ϵ_b and intra-strand hopping $t_{||}$. The perturbation arising from the complementary strand is described via the side-chain Hamiltonian $\mathcal{H}_{\text{C-c}}$. The inter-chain hopping $t_\perp$ is assumed to be a small parameter, according to recent numerical estimates.[17] As a result,

the probability of inter-chain charge hopping will be very small and we may thus neglect in a first approximation charge propagation on the side chain, *i.e.* charge transport occurs only on pathways along the central chain.

In Eq. (1), the onsite energies ϵ_b and ϵ will be set equal to zero for a homogeneous wire. When simulating the introduction of A$-$T bases on a finite segment of the molecular wire, we set $\epsilon_b \neq 0$. The set of bath frequencies Ω_α and corresponding coupling constants λ_α, $\alpha = 1, \ldots, M$, does not need to be further specified. By performing the thermodynamic limit ($M \to \infty$) later on, the bath can be described by a spectral density $J(\omega) = \sum_\alpha \lambda_\alpha^2 \delta(\omega - \Omega_\alpha) = J_0(\omega/\omega_c)^s e^{-\omega/\omega_c} \Theta(\omega)$, where ω_c is a cut-off frequency and $\Theta(\omega)$ is the Heaviside function. [18] In what follows, we consider only the case $s = 1$ which corresponds to an ohmic bath. The form of the spectral density will of course depend on the specific type of environment. In the case of an aqueous environment, a Debye model for dielectric relaxation might seem more appropriate. [19] However, its low-frequency behavior is similar to that of the ohmic bath; hence, we can safely approximate it by the above spectral density. We do not expect that the exponential cut-off at high frequencies will have a very dramatic effect on our results.

For $\lambda_\alpha = 0 \, \forall \alpha$, the model shows a temperature independent gap in the electronic spectrum, the gap being basically proportional to $t_\perp$. Valence and conduction manifolds, involving N states each, are symmetric w.r.t. the Fermi level which is the zero of energy (particle-hole symmetry). For nonzero coupling to the bath a more involved behavior may be expected depending on the electron-phonon coupling strength. The interaction with the bath degrees of freedom can be eliminated by performing a unitary transformation [18]. As a result the transversal coupling Hamiltonian $\mathcal{H}_{\text{C-c}}$ will be renormalized by the bath operators [20].

Since we are mainly interested in the temperature and length dependence of the linear conductance, we address only the low-bias regime, thus neglecting nonequilibrium effects as well as inelastic tunneling which become more relevant at large applied voltages. As a result, the current can still be written as [21] $I(V) = (2e/h) \int dE \left(f(E - eV/2) - f(E + eV/2) \right) t(E)$. Note that the function $t(E) = 4\text{Tr} \left\{ \text{Im}\Sigma_{\text{L}} \, \mathbf{G} \, \text{Im}\Sigma_{\text{R}} \, \mathbf{G}^\dagger \right\}$ contains contributions from the electron-bath interaction via the wire Green function $\mathbf{G}$. It hence describes processes where the incoming and outgoing electron energies are equal, though virtual phonon emission and absorption is allowed and included to all orders in $\mathbf{G}$. We denote in what follows $t(E)$ as a transmission, though it is not directly related to the usual Landauer transmission function due to the presence of the dissipative bath in the wire propagator.

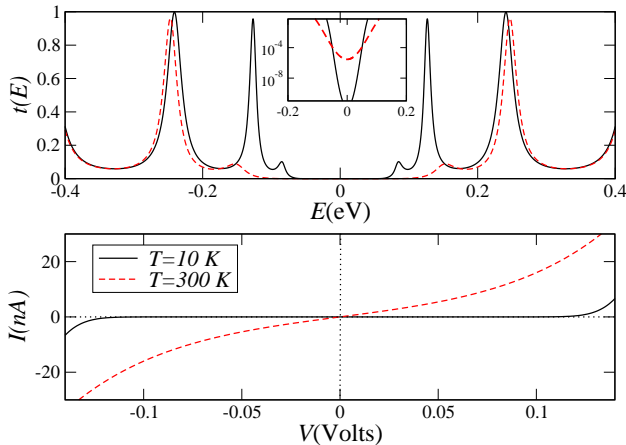The Green function $\mathbf{G}$ can be calculated using equation

FIG. 2: Upper panel: The function $t(E)$ for two different temperatures; the inset is a log-plot around $E = 0$ showing the strong temperature dependence of the pseudo-gap. Lower panel: I-V characteristics. Parameters: $N = 20$, $J_0/\omega_c = 20$, $t_{||} = 0.6\,eV$, $t_\perp/t_{||} = 0.2$, $\Gamma_{L/R}/t_{||} = 0.16$.

of motion techniques. One finds to lowest order in $t_\perp$: [20]

$$\mathbf{G}^{-1}(E) = E\mathbf{1} - \mathcal{H}_C - \mathbf{\Sigma}(E) - t_\perp^2\mathbf{P}(E), \qquad (2)$$

$$P_{\ell j}(E) = \delta_{\ell j}\int_0^\infty dt\, e^{i(E+i0^+)t}\, G_c^0(t)\, e^{-\Phi(t)},$$

where $\mathbf{\Sigma}(E) = \mathbf{\Sigma}_L(E) + \mathbf{\Sigma}_R(E)$, $e^{-\Phi(t)} = \langle\mathcal{X}(t)\mathcal{X}^\dagger(0)\rangle_B$ is a dynamical bath correlation function and $\mathcal{X} = \exp\left[\sum_\alpha(\lambda_\alpha/\Omega_\alpha)(B_\alpha - B_\alpha^\dagger)\right]$. The electrode selfenergies $\mathbf{\Sigma}_{L/R}$ are calculated in the wide-band limit, $\Sigma_{L,\ell j}(E) = -i\Gamma_L\delta_{1\ell}\delta_{1j}$ and $\Sigma_{R,\ell j}(E) = -i\Gamma_R\delta_{N\ell}\delta_{Nj}$, i.e. ignoring their energy dependence. Note that the function $P(E)$ containing the free electron Green function $G_c^0(t)$ of the side chain and the bath correlator $\exp(-\Phi(t))$, act as an additional selfenergy for the central chain propagator.

In the weak-coupling regime to the bath, no relevant physical effects were found [20]. In the following, we discuss the strong-coupling limit $J_0/\omega_c > 1$, where an appreciable modification of the electronic spectrum occurs. Recent estimates [22] of the latter parameter using the classical Onsager model for molecule-solvent interactions suggest that this regime can be realized in a water environment.

In Fig. 2 the transmission $t(E)$ and the corresponding current are shown. A strong temperature dependent gap in the electronic transmission spectrum $t(E)$ is found, its magnitude increasing with temperature. The low-voltage I-V characteristics evolve from a "semiconducting" behavior at low temperatures (zero current around $V = 0$) to a "metallic" behavior (nonzero slope near $V = 0$) with increasing temperature. The reason is that in the strong dissipative regime a *pseudo-gap* rather than a gap in the electronic spectrum is induced by the bath dynamics. An analysis of the real and imaginary parts of $P(E)$, Eq. (2), at low energies helps to understand this. One can show that (i) $\mathrm{Re}\, P(E) \sim E$ for $E \sim 0$ and (ii)

$\mathrm{Im}\, P(E)$ is peaked at $E = 0$. For comparison, in the absence of the bath $\mathrm{Re}\, P(E)$ would display a $1/E$ behavior around $E = 0$ [16]. It follows from (i) that additional low energy poles of the wire Green function $\mathbf{G}(E)$ might emerge symmetrically placed around the Fermi energy, building a third electronic manifold. These states can show up as resonances in the transmission spectrum inside the gap, see Fig. 1, and form a polaronic band. We stress that they are neither present for $\lambda_\alpha = 0$ nor in the weak-coupling limit. We would then have three electronic manifolds. It turns out, however, that the non-vanishing $\mathrm{Im}\, P(E)$ (the "frictional" part) has a dramatic influence on these states. Since they are located in an energy region where $\mathrm{Im}\, P(E)$ is appreciably different from zero, no well-defined resonances manifest in the low-energy sector of the transmission. Nevertheless, these bath-induced states *do* contribute with a temperature dependent incoherent background and eventually lead to an increase in the density of states near $E = 0$ when the temperature grows. Hence, the current may be enhanced at low voltages with increasing temperature. We thus interpret the central manifold as an incoherent polaronic band that supports activated hopping at high temperatures. This is farther reflected in the temperature dependence of the transmission at the Fermi energy, which displays an Arrhenius-like law, see Fig. 3. We note in passing that a qualitative similar effect is found in the so called spin-polaron problem. [23]

A controversial issue in transport through DNA-based systems is the actual length dependence of the electron transfer rates or correspondingly, of the linear conductance [24, 25, 26]. Different functional dependences have been found in charge transfer experiments ranging from strong exponential behavior related to superexchange mediated electron transfer [25] to algebraic dependences typical of thermal activated hopping [24, 26]. As far as transport experiments are concerned, Xu et al. [9] reported an algebraic length dependence of the conductance for poly(GC) oligomers in solution. Theory has shown that a transition between different regimes may happen as a function of the wire length [27]. We have investigated the length dependence of $t(E_F)$ and found different scaling laws dependent on the strength of the electron-bath coupling. For $J_0/\omega_c > 1$, an exponential law for energies close to E_F was found, $t(E_F) \sim \exp(-\gamma L)$, see Fig. 3, middel panel. Here, $L = Na_0$, $a_0 \sim 3.4\,\text{Å}$ being the average inter-base separation. At the first sight, this might be not surprising since a gap in the spectrum does exist. Indeed, in the absence of the bath, i.e. with an intrinsic electronic gap, we get decay lengths γ_{coh} of the order of 2 Å^{-1}. However, as soon as the interaction with the bath is included, we find values of γ much smaller than expected for virtual tunneling, ranging from $0.15\,\text{Å}^{-1}$ to $0.4\,\text{Å}^{-1}$. Additionally, γ is strongly dependent on the strength of the electron-bath coupling as well as on temperature; γ is reduced when J_0/ω_c or k_BT increase, see Fig. 3, since in both cases the density of states within the pseudo-gap increases. These results
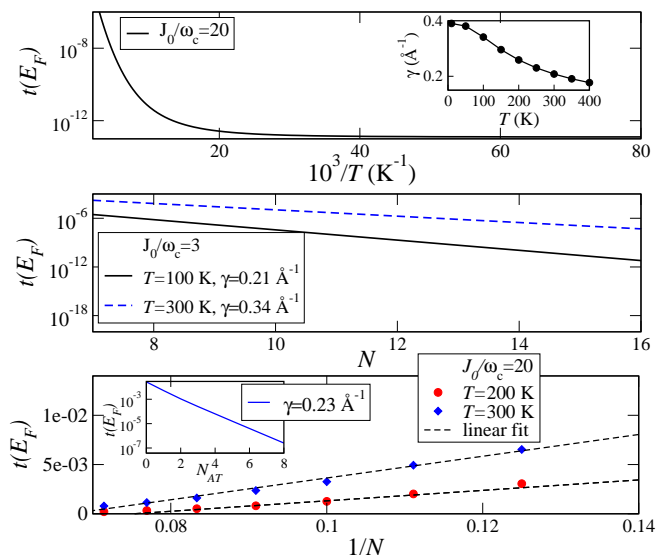
FIG. 3: Upper panel: Arrhenius plot for $t(E_F)$. Parameters: $N = 20$, $t_{||} = 0.6\,eV$, $t_{\perp}/t_{||} = 0.2$, $\Gamma_{L/R}/t_{||} = 0.16$. Inset: temperature dependence of the exponential decay length γ (see text). Middle and lower panels: Length dependence of $t(E_F)$ at different temperatures for two different strengths of the electron-bath coupling J_0/ω_c. The electronic coupling parameters are the same as in the upper panel. The inset in the lower panel shows the effect of introducing tunnel barriers to simulate the insertion of N_{AT} A-T base pairs in an otherwise homogeneous chain of length N (T=300 K). The algebraic lenght dependence goes over onto an exponential one. For this, the onsite energies along a finite segment of the wire were shifted by $\epsilon_b = -1.5\,eV$, see Eq. (1). The number of unperturbed sites N_{GC} in a sequence like $N_{GC} - N_{AT} - N_{GC}$ was kept constant ($N_{GC} = 4$) while varying $N_{AT} = 1 \cdots 8$.

clearly indicate that the bath does strongly determine the effective decay length in a way which we can quantify by extracting a γ_{env} term such that $\gamma = \gamma_{coh} - \gamma_{env}$. The first contribution γ_{coh} is purely determined by the intrinsic electronic structure of the wire and can be obtained, *e.g.* by means of complex band structure approaches [14, 28]. A γ_{coh} of the order of $1.5\,\text{Å}^{-1}$ has been recently calculated for poly(GC) [14], which compares well with our estimated γ_{coh}. The dependences on

J_0 and $k_B T$ are hence contained in the bath-induced contribution γ_{env}. Remarkably, in the regime $J_0/\omega_c \gg 1$ the weak exponential length dependence goes over onto an algebraic dependence, see Fig. 3, lower panel. The introduction of a tunnel barrier induced by the insertion of A−T base pairs in the poly(GC) oligomer [9], can be simulated in the simplest way by a shift of the onsite energies along a finite segment of the wire. In this case, the exponential dependence is recovered (see the inset of Fig. 3, lower panel).

In conclusion, we have investigated the influence of a dissipative environment on charge transport along a molecular wire in a model that mimics basic features of the electronic structure of poly(GC) oligomers. We found a strong modification of the low-energy electronic structure of the wire in the strong dissipative regime. Indeed, a *pseudo-gap* is formed which induces a temperature dependent background around the Fermi energy. The resulting non-vanishing low-bias current at room temperature as well as the algebraic dependence of the conductance on the wire length found in our model suggests that the striking results of Xu *et al.* transport experiments [9] may be related to the presence of an aqueous environment. The interplay with other dynamical degrees of freedom like internal molecular vibrations has, of course, to be further clarified. We note that the inclusion of randomness in the base pair distribution (as is the case of e.g. λ-DNA) does not qualitatively change the above picture [20]. Disorder mainly washes out the side bands in the transmission without essentially changing the behavior around the Fermi level.

Finally, we remark that a close estimation of the physically relevant model parameters, especially of the electron-bath interaction strengths, requires a detailed analysis of first principle calculations of DNA oligomers in solution, eventually including vibrational degrees of freedom. This goes, however, not only beyond the scope of this investigation, but also beyond the actual capabilities of most *ab initio* approaches.

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