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Polaronic transport through DNA molecules

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We present results of theoretical studies on polaronic and incoherent transport through a DNA-based junction. Decoherence itself is modelled through the use of an imaginary dephasing potential. Non-perturbative computational scheme, used in this work, is based on Green's functions within the framework of the so-called polaron transformation (GFT-PT). This method maps exactly the many-body hole –phonon interaction problem into a one-body multi-channel scattering problem, where the availability of particular conduction channels is determined by an appropriate weight factor. The results obtained for poly(dG)-poly(dC) DNA molecule reveal saturation effect of the current at high voltages, where for short chains we establish an exponential DNA length dependence. Besides, we document strong coupling and exponential dephasing dependences of the maximum current.

Key words: *polaronic transport; DNA-based device; DNA electronics; decoherence*

1. Introduction

Recent advances in nanofabrication allow us to fabricate devices composed of individual DNA molecules connected to metallic electrodes and to measure current-voltage (*I*–*V*) characteristics of such junctions [1–4]. The actual magnitude of DNA conductivity and its physical mechanism is still under debate [5, 6]. In particular, long DNA oligomers are expected to be true insulators, while short biomolecules are rather semiconductors with a relatively large HOMO-LUMO gap. Since the residence time of the charge carrier on guanine G (nucleobase with lower oxidation potential) is long in comparison with characteristic time associated with molecular vibrations, the hole-type (positive ion) conduction is treated as incoherent. This means that the charge carrier is temporarily localized on guanine, losing its phase and exchanging energy with the biomolecule.

Since nucleobases involved in the conduction process are thermally activated to vibrations (phonon modes are excited) and vibrational coupling parameter is suffi-

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ciently strong, charge carriers are locally coupled to phonons, leading to polaron formation. The main purpose of this work is to study the polaronic and incoherent transport through short poly(dG)-poly(dC) DNA treated as a linear chain of quantum dots, where only one HOMO level on each guanine is taken into consideration, as shown in Fig. 1.

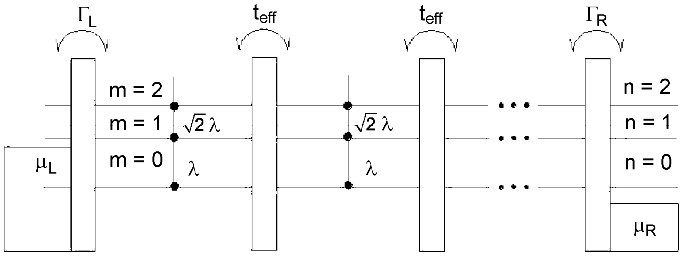

Fig. 1. A schematic representation of the inelastic scattering problem for the device composed of a series of molecular quantum dots connected to metals

Decoherence itself is modelled trough the use of an imaginary (optical) dephasing potential, where all the phase-breaking processes are included [7, 8]. This potential has the sense of the coupling with external environment. It should be also noted that recently polaron hopping was suggested as a possible mechanism to explain the transport found on DNA stacks [9–12].

2. The model and method

In modelling the process of charge transfer through DNA, we consider the nucleotide sequence as a system of N sites, in which each site corresponds to a GC base pair. In this chain, a hole travels along energetically appropriate HOMO levels of guanine bases, since their oxidation potential is lower than that of cytosine nucleotides. Let us write down a simplified Hamiltonian of the whole system in the form:

$$\begin{aligned} H = &\sum_j \left[(\varepsilon_j - i\phi_j) - \lambda(d_j + d_j^+) \right] c_j^+ c_j - \sum_j \left[t_{eff} c_j^+ c_{j+1} + \text{h.c.} \right] \\ &+ \sum_j \Omega d_j^+ d_j + \sum_{k\in\alpha} \varepsilon_k c_k^+ c_k + \sum_{k\in\alpha, j} \left[\gamma_k c_k^+ c_j + h.c. \right] \end{aligned} \tag{1}$$

where: ε_j and ε_k are the energies of holes on the jth site of the molecule and in the reservoirs with momentum k, ϕ_j is the on-site dephasing potential, λ is the electron –phonon interaction parameter, t_{eff} denotes the hopping integral between two neighbouring sites (guanines), Ω is the phonon energy, γ_k is the strength of the molecule–reservoir coupling. Furthermore, c_k, c_j, d_j and their adjoints are annihilation and creation operators for holes in the reservoirs, at the molecular sites, and for the primary on-site phonons, respectively.

To proceed, we apply the so-called polaron transformation [13–16], where the electron states are expanded into the direct product states composed of single-electron states and m-phonon Fock states:

$$|j,m\rangle = c_j^+(d_j^+)^m|0\rangle/\sqrt{m!}, \qquad |k,m\rangle = c_k^+(d_j^+)^m|0\rangle/\sqrt{m!}$$

where $|0\rangle$ denotes the vacuum state. This method maps exactly the many-body hole –phonon interaction problem into a one-body multi-channel scattering problem. After eliminating the reservoir degrees of freedom, we can present the effective Hamiltonian of the reduced molecular system as:

$$\begin{aligned} H_{\text{eff}} = & \sum_{j,m,\alpha}\left(\varepsilon_j - i\phi_j^m + m\Omega + \Sigma_\alpha^m\right)|j,m\rangle\langle j,m| \\ & -\sum_{j,m} t_{eff}^m\left(|j,m\rangle\langle j+1,m| + |j+1,m\rangle\langle j,m|\right) \\ & -\sum_{j,m}\lambda\sqrt{m+1}\left(|j,m\rangle\langle j,m+1| + |j,m+1\rangle\langle j,m|\right) \end{aligned} \tag{2}$$

where: $\Sigma_\alpha^m = -i\Gamma_\alpha^m/2$ is the self-energy in the wide-band approximation, while $\Gamma_\alpha^m = 2\pi|\gamma_k^m|^2\rho_\alpha$ is the so-called linewidth function with ρ_α as the density of states related to the α electrode. Index m numbers the particular channels and their accessibility before scattering is determined by an appropriate weight factor: $P_m = [1-\exp(-\beta\Omega)]\exp(-m\beta\Omega)$, where $\beta = 1/k_B\theta$, while θ is the device working temperature. In practice, the maximum amount of phonon quanta excited on each site is restricted to a finite number $m = m_{\max}$ because of the numerical efficiency.

Choosing an appropriate matrix element of the molecular Green function defined as: $F(\varepsilon) = (J\varepsilon - H_{\text{eff}})^{-1}$, where J is the unit matrix, we can define the transmission probability of each possible transition, where hole incoming from channel m is scattered on the DNA molecule, and then outgoing to channel n:

$$T_{m,n}(\varepsilon) = \Gamma_L^m\Gamma_R^n|F_{m+1,\bar{n}+1}(\varepsilon)|^2$$

where $\bar{n} = n + (N-1)m_{\max}$. The electrical current flowing through the system is given by the following relation:

$$I = \frac{e}{\pi\hbar}\int_{-\infty}^{+\infty} d\varepsilon \sum_{m,n} T_{m,n}(\varepsilon)\left[P_m f_L^m(\varepsilon)\left(1-f_R^n(\varepsilon)\right) - P_n f_R^n(\varepsilon)\left(1-f_L^m(\varepsilon)\right)\right] \tag{3}$$

where:

$$f_\alpha^m(\varepsilon) = \frac{1}{1+\exp\left[\beta(\varepsilon + m\Omega - \mu_\alpha)\right]}$$

is the Fermi function, while the electrochemical potentials are defined as: $\mu_L = \varepsilon_F + eV/2$, $\mu_R = \varepsilon_F - eV/2$, ε_F denoting the Fermi energy and V being the applied bias.

3. Numerical results and discussion

A difficult part of the calculations of polaron properties is associated with choosing parameters for DNA. Here, we take the following energy parameters (given in eV): $\Gamma_L^m = \Gamma_R^m = 0.2$ (the case of weak molecule-metal contacts), $\varepsilon_j = 0$ (the reference energy of the HOMO level of guanine), $\varepsilon_F = -1.73$ (as deduced from the experimentally obtained conductivity gap), $\lambda = 0.3$ (as estimated from the reorganization energy), $\phi_j^m = 0.185$ (the fitting parameter), $\Omega = 0.13$, $t_{\text{eff}}^m = 0.6$ (as obtained from ab initio calculations of the two energy levels for a pair of overlapped guanine bases). Temperature θ is set at 300 K ($\beta = 0.025$/eV), while maximum amount of phonon quanta $m_{\max} = 10$ is chosen to give fully converged results with the accuracy better than 1%.

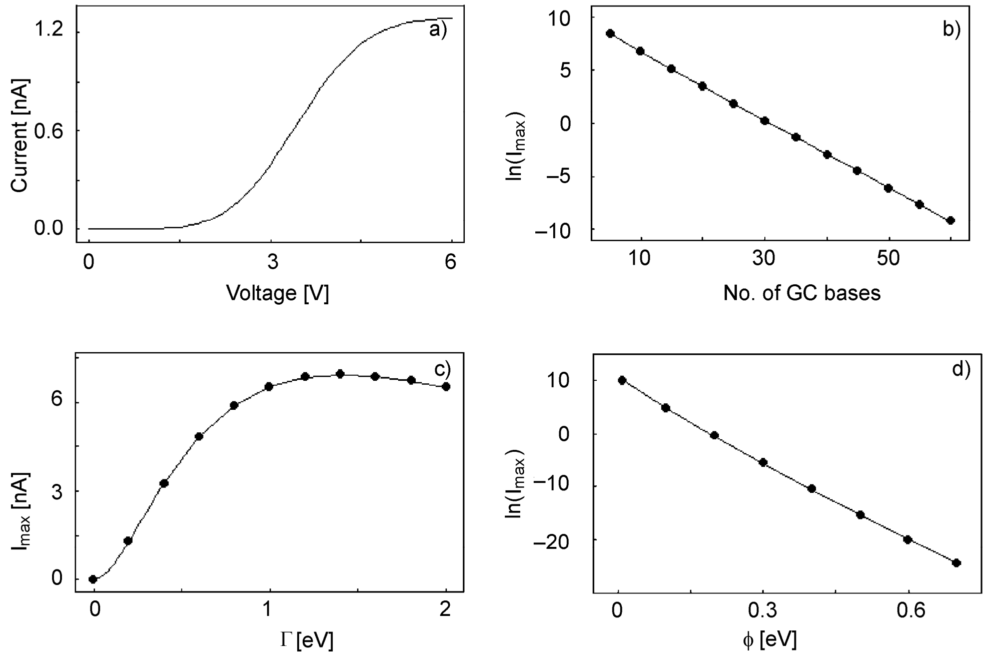

Fig. 2. Current-voltage dependence for $N = 30$ pair poly(dG)-poly(dC) DNA (a); maximum value of the current as a function of the number of GC bases in the logarithmic scale (b); maximum current as a function of the coupling strength parameter for $N = 30$ (c); maximum value of the current as a function of dephasing potential in the logarithmic scale for $N = 30$ (d)

The calculated I–V characteristics for a double-stranded 30-base pair poly(dG) -poly(dC) DNA molecule connected to two metallic electrodes is demonstrated in

Fig. 2a, where all the model parameters were reasonably chosen to quantitatively reproduce the experimental data (cf. Porath et al. [2]). Here, we observe the saturation effect at high voltages after the smoothing increase of the current, where we have $dI/dV = 0$. Our calculations indicate that the magnitude of the current flow exponentially depends on the DNA length: $\ln(I_{\max}) \approx 9.91 - 0.32N$ (as shown in Fig. 2b), the maximal current given in μA can thus be estimated from the following relation: $(I_{\max}) \approx 20.13\exp(-0.32N)$. This conclusion is in contradiction to the previous rate-equation calculations indicating the algebraic length dependence [17, 18]. The shape of the I–V curve does not change significantly upon changes in a wide range of model parameters, but the magnitude of the current flow is very different. Figure 2c shows that the maximum current smoothly increases with the increase of the coupling parameter $\Gamma = \Gamma_L^m = \Gamma_R^m$. Interestingly enough, for extremely strong coupling ($\Gamma > 1.4$) we observe the opposite trend. The strength of the DNA-electrode coupling can be controlled by changing the distance between them. Furthermore, the magnitude of the current flow exponentially decreases with the increase of the dephasing potential: $\ln(I_{\max}) \approx 9.7 - 50\phi$, so the maximum current given in μA can be estimated from the following relation: $(I_{\max}) \approx 16.3\exp(-50\phi)$.

4. A brief summary

We have studied the polaronic and incoherent transport through DNA molecule (treated as a linear chain of quantum dots) using non-perturbative computational scheme (based on Green's functions theory within the framework of polaron transformation), where decoherence is modelled through the use of an imaginary dephasing potential. It was shown that, with the model, we can reproduce experimental data by fitting the model parameters. According to our calculations, at high voltages we observe the saturation effect after the smoothing increase of the current. Here we found the exponential dependence of the saturation current vs. the length of the molecular bridge, so the transport through DNA does not have a purely hopping character. It was also shown that the maximum current smoothly increases with the increase of the coupling parameter until some critical point ($\Gamma = 1.4$) and then it starts decreasing. Besides, our predictions indicate the exponential decrease of the current flow with the increase of the dephasing potential.

Acknowledgements

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