# Sequence Dependent DNA-Mediated Conduction

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We report on coherent charge transport studies in periodic Poly(dG)-Poly(dC) and aperiodic $\lambda$-phage DNA sequences. The extent and efficiency of charge transfer is discussed as a function of sequence dependent energetics, of temperature dependent base-base couplings, and in relation with experiments.

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The ability of DNA to convey charge carriers over large distances has become a challenging debate, owing to the envisioned impact of charge transfer in molecular (bio)electronics [1] as well as for the understanding and engineering of biological processes (such as damage recognition processes and nanoscale sensors for mutations or protein binding) [2]. Actually, unlike proteins, a $\pi$-stacked array of base pairs [made from four different nucleotides: guanine (G), adenine (A), cytosine (C), thymine (T)] provides a natural "highway" to promote long range charge migration. However, dynamical motions of the base pairs within the molecular stack, as well as sequence dependent inhomogeneities in energetics and base-base couplings are also expected to jeopardize a "metalliclike" molecular conduction. Photoexcitation experiments have demonstrated that charge excitations could be promoted from a donor metallointercalator to the DNA-bridge states, preferentially injected through the guanine highest occupied molecular orbitals (G-HOMO), and transmitted to a tethered acceptor [2,3].

Electronic transfer has been widely investigated in Poly(dG)-Poly(dC) and $\lambda$-bacteriophage DNA sequences. Notwithstanding, the wealth of available experimental results does not yet yield a consensus. Indeed, the many experiments performed with $\lambda$-phage DNA have suggested the material to be anything from a metallic wire [4], superconducting [5] at low temperature to an insulating medium [6]. Semiconducting [7] and insulating behaviors [8] have also been reported for Poly(dG)-Poly(dC). Temperature effects in DNA are important but have so far been poorly addressed theoretically [9]

Actually, periodicity in the energetics of Poly(dG)-Poly(dC) [10] should favor electronic delocalization over a certain energy range. The electronic transmission coefficients, related to the Landauer resistance, should then appear roughly length independent, contrary to aperiodic sequences (such as the $\lambda$-phage) for which hole transport should experience an increasing contribution of backscattering owing to the increasing number of C, T, A potential barriers with sequence length. Despite such argument, little is known about the intrinsic conduction mechanism in $\lambda$-phage, especially in regards to the energetic profile of the DNA sequence. In this Letter, we report on a numerical study of electronic conduction in both Poly(dG)-Poly(dC) and $\lambda$-phage sequences that highlights the critical effects of energetics and fluctuating base-base couplings in understanding the electrical transport.

Our Hamiltonian is an effective tight-binding model that describes the site energies of a hole located at nucleotide $n$ [11–13]

$$\mathcal{H} = \sum_n - t_{\mathrm{DNA}} \cos(\theta_{n,n+1})(c_n^\dagger c_{n+1} + \mathrm{H.c.}) + \varepsilon_n c_n^\dagger c_n,$$

where $c_n^\dagger$ ($c_n$) is the creation (annihilation) operator of a hole at site $n$. The variables $\varepsilon_n$ describe the energy of the hole at site $n$, and will be given by the ionization potentials of respective bases, taken as $\varepsilon_{\mathrm{A}} = 8.24$ eV, $\varepsilon_{\mathrm{T}} = 9.14$ eV, $\varepsilon_{\mathrm{C}} = 8.87$ eV, $\varepsilon_{\mathrm{G}} = 7.75$ eV [13], while $t_{\mathrm{DNA}}$ stands as the hopping integral between adjacent nucleotides. Such coupling describes the $\pi-\pi$-stacking interaction between base pairs. *Ab initio* calculations find that between two interacting nucleotides, $t_{\mathrm{DNA}}$ are in order of $\sim$0.1–0.4 eV [13], and it has been shown [11,12] that the effective tight-binding Hamiltonian for the Poly(dG)-Poly(dC) with $t_{\mathrm{DNA}} = 0.4$ eV reproduces *ab initio* results [13] and experiments [7]. As discussed afterwards, when connecting the DNA chains to external leads, the case $t_{\mathrm{DNA}} \sim t_m$ ($t_m$ the hopping term for the metallic contacts) will allow a better characterization of intrinsic conduction properties (such as resistivity). Finally $\theta_{n,n+1}$ is the relative twist angle deviated from its equilibrium value between sites $n$ and $n+1$, because of temperature [9]. Each $\theta_{n,n+1}$ is an independent random variable that follows a Gaussian distribution with average $\langle\theta_{n,n+1}\rangle = 0$, whereas the variance is taken according to the equipartition law, i.e., $\langle\theta_{n,n+1}^2\rangle = k_B T/I\Omega^2$, where $I$ is the reduced moment of inertia for the relative rotation of the two adjacent bases and $\Omega$ is the oscillator frequency of the mode ($I\Omega^2 = 250$ K). Following [9], we take $t_{\mathrm{DNA}} \cos(\theta_{n,n+1}) \sim t_{\mathrm{DNA}}(1 - \theta_{n,n+1}^2/2)$.

The current measured through a DNA macromolecule connecting two metallic electrodes results from the injection of carriers onto the stack of bases together with the intrinsic conduction along the DNA sequence. At low voltage, the main contribution to the resistance comes from the metal-DNA junction potential mismatch,

  

whereas at sufficiently higher bias, once the electrode Fermi level and the G-HOMO states of the molecule are lined up, the resistance of the junction is controlled by the DNA-mediated transfer rather than the injection process efficiency. Accordingly, the observed gap in a $I(V)$ measurement is somehow related to the energy difference between the metallic work function and the energy of the G-HOMO [12].

In the following, our DNA sequences are assumed to be connected to two semi-infinite electrodes described by another tight-binding Hamiltonian with site energies $\varepsilon_m = \varepsilon_G = 7.75$ eV, whereas the hopping integral is taken as $t_m = 1$ eV. Such choices for modeling the external leads allow us to scan the transmission profile of a given DNA sequence over a spectrum with width $[\varepsilon_m - 2t_m, \varepsilon_m + 2t_m]$. An important issue is then related to the absolute value of $t_{\mathrm{DNA}}/t_m$. Indeed, if $t_{\mathrm{DNA}}/t_m \sim 1$ the potential barrier at the contact interface is small, allowing for a better investigation of intrinsic scattering properties inside the DNA, whereas for $t_{\mathrm{DNA}}/t_m \ll 1$, strong backscattering at the interface might dominate the behavior of the transmission coefficient and screen its intrinsic features (such as the typical resistivity). This motivates our choice to consider $t_{\mathrm{DNA}}$ within the range $[0.4, 1]$ eV.

To compute the transmission coefficient, a standard transfer matrix formalism is used [14]. Projecting the time independent Schrödinger equation into the localized basis yields

$$\begin{pmatrix} \psi_{n+2} \\ \psi_{n+1} \end{pmatrix} = \mathcal{M}_n \begin{pmatrix} \psi_{n+1} \\ \psi_n \end{pmatrix} = \mathcal{M}_n \mathcal{M}_{n-1} \ldots \mathcal{M}_1 \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix} = \mathcal{P}_n \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix}$$

with $\psi_n$ the component of the wave function for energy $E$ at site $n$,

$$\mathcal{M}_n = \begin{pmatrix} \frac{E-\varepsilon_n}{t_{n+1}} & -\frac{t_n}{t_{n+1}} \\ 1 & 0 \end{pmatrix}, \quad \text{and} \quad \mathcal{P}_n = \prod_{i=n}^{1} \mathcal{M}_i.$$

A transmission study between metallic electrodes is then performed to evaluate the energy-dependent transmission coefficient $T(E)$ which gives the fraction of tunneling electrons transmitted through the DNA, and that is related to the Landauer resistance $h/2e^2[1 - T(E)]/T(E)$ ($h/2e^2$ the quantum resistance). $T(E)$ can be analytically expressed as [14]

$$T(E) = \frac{(4 - \frac{(E-\varepsilon_m)^2}{t_m^2})}{2 + \sum_{i,j=1,2} \mathcal{P}_{ij}^2 + \frac{(E-\varepsilon_m)}{t_m}(\mathcal{P}_{11} - \mathcal{P}_{22})(\mathcal{P}_{12} - \mathcal{P}_{21}) - \frac{(E-\varepsilon_m)^2}{t_m^2}(\mathcal{P}_{12}\mathcal{P}_{21} + 1)}.$$

The electronic transmission properties are first studied for a periodic 20 nm long Poly(dG)-Poly(dC). Such kinds of sequences can be engineered artificially [10] and provide macromolecules that should display fast charge transfer properties. Band resonant tunneling has been demonstrated using *ab initio* methods [15]. From our tight-binding calculation (Fig. 1, top frame), whatever the value of $t_{\mathrm{DNA}}/t_m$, two bands are found separated by an energy gap $\simeq 1.12$ eV which is slightly underestimated in regards to *ab initio* calculations [16] since electronic correlations are neglected. Within the bands, a certain number of resonances $[T(E) = 1]$ are found due to the finite size of our chain. The bandwidth for transmission is proportional to $t_{\mathrm{DNA}}/t_m$ [see Fig. 1, inset (a)] and the number of resonant energies at which transmission is ballistic is length dependent.

From the calculation it appears that by using a third gate electrode a strong switching efficiency should be found. Indeed, at a negative gate bias (exploring the energy range below the Fermi level which is $= 7.75$ eV at half filling), a good conduction is expected, whereas a positive gate bias will yield full depletion of current (due to the absence of transmitting states). This tends to support the experimental observations [7,8]. Our temperature study (Fig. 1, bottom frame) demonstrates that thermal fluctuations of $\pi$-$\pi$ interaction progressively reduces coherent transmission, while the average transmission remains nearly independent of $t_{\mathrm{DNA}}/t_m$.

Let us now discuss the measurement of intrinsic resistivity of DNA molecules. Theoretically, intrinsic electronic resistivity should not depend on external leads and writes

$$\rho \sim \frac{h}{2e^2} \frac{1 - T(E)}{T(E)} \frac{S_{\mathrm{DNA}}}{L_{\mathrm{DNA}}}$$

with $L_{\mathrm{DNA}}$ the length of the chain, $S_{\mathrm{DNA}} = 3 \times 10^{-18}$ m$^2$ the average cross section, and $h/2e^2 = 12$ k$\Omega$ the quantum resistance. Meaningless in the ballistic regime $[T(E) = 1]$, a resistivity can be deduced from transmission coefficient as soon as $T(E) \ll 1$. For Poly(dG)-Poly(dC), whatever the value of $t_{\mathrm{DNA}}/t_m$, we find that the most conducting states roughly correspond to $T(E) \sim 1.510^{-2}$ at $T = 240$ K for the 20 nm long chain. From this, one deduces $\rho \simeq 0.012\ \Omega$ cm which turns out to be in good agreement with the experimental measurement [7].

We now turn to $\lambda$-phage sequences which present a larger complexity due to an aperiodic distribution of A, T, C, G bases [17], which, however, cannot be considered as random, because of long range correlations [18]. The complete $\lambda$-phage DNA contains 48 502 base pairs corresponding to a length of $\simeq 16\ \mu$m.

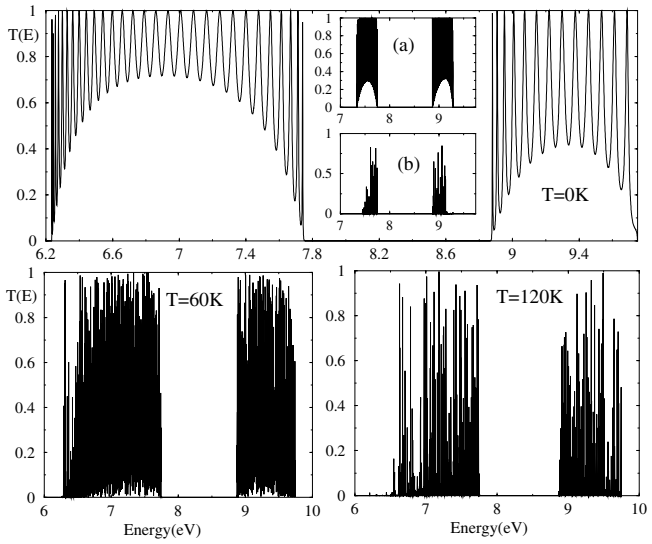


FIG. 1. Energy dependent transmission coefficient for a Poly(dG)-Poly(dC) (60 bp) sequence for several temperatures. Top panel (main frame): results for $t_{\mathrm{DNA}}/t_m = 1$ at zero temperature; insets: (a) $t_{\mathrm{DNA}}/t_m = 0.4$ at zero temperature, (b) $t_{\mathrm{DNA}}/t_m = 0.4$, at $T = 120$ K. Bottom panel: results for $t_{\mathrm{DNA}}/t_m = 1$ at different temperatures.

In Fig. 2 (top and bottom left panels), we show for $t_{\mathrm{DNA}}/t_m = 1$, the behaviors of $T(E)$ for short sequences of the chain but with an increasing number of base pairs (bp), corresponding to systems from 20 to 80 nm long. The starting sequence with 60 bp is $\lambda_1$-gggcggcgacctcgcgggttttcgctatttatgaaaattttccggtttaaggcgtttccg, while larger sequences are constructed from $\lambda_1$ adding successively the next 60 bp of the complete sequence. Different from the Poly(dG)-Poly(dC) chains, the transmission pattern strongly depends on the chain length. Indeed, in our situation, any A, T, C base acts as a potential barrier that reduces coherent quantum tunneling. As the number of corresponding bases increases, fewer states will present good transmission ability, and for lengths above $\sim$100 nm, almost all states are strongly backscattered by the energetic profile. Different parts of the $\lambda$-phage sequence have also been investigated and point out that the exact details of a given transmission pattern substantially depend on the internal structure of the sequence. For instance, taking the 20 nm long sequences corresponding to $\lambda_2$-ttcttcttcgtcataacttaatgttttttatttaaaatacccctctgaaaagaaaggaaacg, $\lambda_3$-acaggtgctgaaagcgaggctttttggcctctgtcgtttcctttctctgtttttgtccgt, $\lambda_4$-ggaatgaacaatggaagtcaacaaaaagcagctggctgacattttcggtgcgagtatccg, $\lambda_5$-taccattcagaactggcaggaacagggaatgcccgttctgcgaggcggtggcaagggtaa (constructed by translating an integer number of 60 bp from $\lambda_1$ within the complete sequence), large fluctuations in the transmission patterns are obtained (Fig. 3).

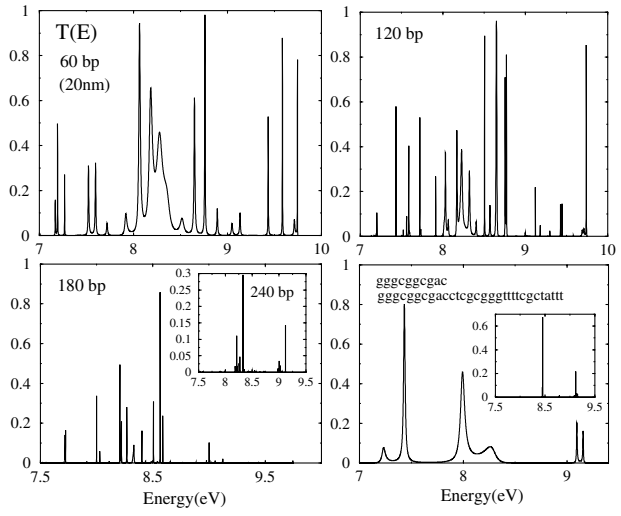


FIG. 2. Top and bottom left panels: transmission coefficients for $\lambda$-phage sequences ($t_{\mathrm{DNA}}/t_{\mathrm{m}} = 1$) with an increasing number of base pairs from 60 bp (20 nm) to 240 bp (80 nm). Bottom right panel: $T(E)(t_{\mathrm{DNA}}/t_m = 0.4)$ for chains with 10 and 30 bp (inset).

The temperature dependence of the transmission coefficients for the $\lambda_1$ chain are reported on Fig. 4. In our model, temperature yields misorientations of adjacent bases that result in temperature dependent base-base hoppings. At low temperature (see the case $T = 60$ K), the transmission spectrum presents a higher number of transmitting states, due to a breaking of level degeneracy. At higher temperatures, the number of transmitting states decreases, but interestingly there persist many states with high transmission coefficients at temperatures as high as $\sim$140 K. We have also studied the behavior of the Lyapunov coefficient $\gamma(E)$ that is directly related to the transmission coefficient through $\gamma(E) = \frac{1}{2N}\ln T(E)$ for a DNA sequence with $N$ sites (its inverse gives the localization length in disordered systems) [19]. The Lyapunov

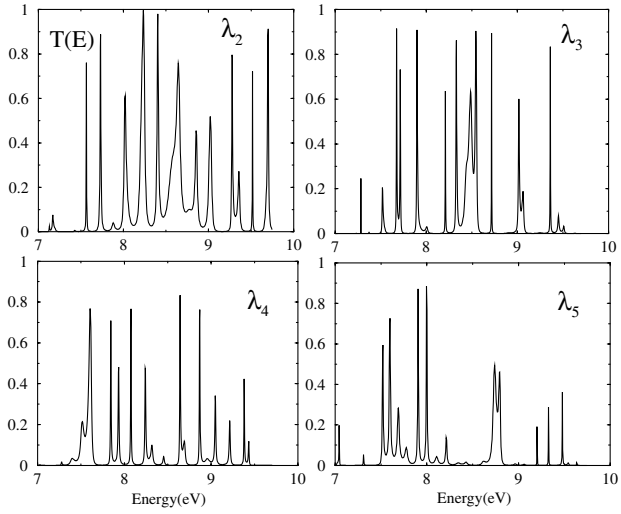


FIG. 3. Energy dependent transmission coefficient ($t_{\mathrm{DNA}}/t_m = 1$) for several $\lambda$-phage based sequences (see text).

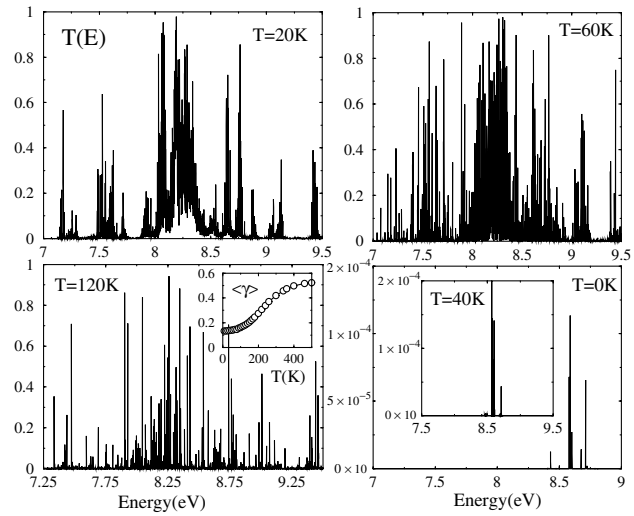


FIG. 4. Top bottom left panels: Temperature dependence of $T(E)$ ($t_{\mathrm{DNA}}/t_m = 1$) for the $\lambda_1$ sequence. Bottom left panel, inset: temperature dependent behavior of the averaged Lyapunov coefficient. Bottom right panel: $T(E)$ for $\lambda_3$ ($t_{\mathrm{DNA}}/t_m = 0.4$) at zero temperature (main frame) and $T =$ 40 K (inset).

coefficient $\langle\gamma\rangle$ is averaged over the whole spectrum and followed as a function of temperature (displayed in Fig. 4, bottom panel, left inset). Interestingly, the obtained behavior is in good agreement with previous theoretical calculations [9] that has further elucidated the temperature dependent conductivity in the hopping regime.

On Fig. 2 (bottom right panel), the case $t_{\mathrm{DNA}}/t_m = 0.4$ for chains with 10 bp ( $\sim 3$ nm) and 30 bp (10 nm) are shown. The backscattering is here found to be much stronger, and chains with lengths $\gtrsim 20$ nm have vanishingly small transmission coefficients at zero temperature. The temperature patterns follow the same trends, as shown for the $\lambda_3$ chain (Fig. 4, bottom right panel). $T(E)$ is occasionally enhanced by temperature at some particular energies, but a chain 20 nm long becomes quickly transmissionless with the increase of thermal fluctuations. Consequently, searching for the intrinsic resistivity of the $\lambda$-phage becomes more problematic. Indeed, if the $T(E)$ are of similar order as those of the Poly(dG)-Poly(dC) for the case $t_{\mathrm{DNA}}/t_m = 1$ (that would agree with the estimate of Fink and Schönenberger [4]), by reducing $t_{\mathrm{DNA}}/t_m$ to 0.4, 20 nm long $\lambda$ chains are found to be transmissionless, and such complete backscattering points to an insulating behavior [6]. All this demonstrates that backscattering in aperiodic $\lambda$-DNA is strongly sensitive to the length and temperature of the chain, but the nature of the contact between the DNA and the substrate or the electrodes is also likely to have a major contribution to the measured insulating behavior [8,20].

To date, although chemical or mesoscopic measurements have been made on similar DNA sequences, few studies have compared the consistency of charge transfer results. From a theoretical viewpoint, a relation can be drawn between the electronic transfer rate $k_{\mathrm{DA}}$ [21] between metallic intercalators tethered to the DNA and the resistance that is measured from a mesoscopic probe experiment. Following the arguments of Nitzan [22], the conductance reads $\sim e^2/\pi\hbar \times [10^{-13} k_{\mathrm{DA}}(\mathrm{ps}^{-1})]$ from which we find that for Poly(dG)-Poly(dC) with transmission coefficient $T(E) \sim 1.510^{-2}$ ($L_{\mathrm{DNA}} =$ 20 nm), a corresponding electronic transfer would be in order of $k_{\mathrm{DA}} \sim 0.2\ \mathrm{ps}^{-1}$ (for $t_{\mathrm{DNA}} = 1$ eV). By taking $t_{\mathrm{DNA}} = 0.4$ eV closer to *ab initio* predictions, $k_{\mathrm{DA}} \sim 0.032\ \mathrm{ps}^{-1}$ which is in the order of the transfer rate estimated with photochemical experiments, on smaller DNA sequences but in a water environment [23].


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