Electronic Transport in DNA — the Disorder Perspective

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Abstract. We are studying the electronic properties of DNA by looking at a tight-binding model and four DNA sequences. The charge transfer is studied in terms of localisation lengths as a function of Fermi energy and backbone disorder. Onsite potentials and different types of disorder account for different real environments. We have performed calculations on poly(dG)-poly(dC), telomeric-DNA, random-ATGC DNA and λ-DNA. We find that random and λ DNA have localization lengths allowing for electron motion among a few dozen base pairs only. However, an enhancement of localisation lengths is observed at particular energies for an increasing binary backbone disorder.

The question on whether DNA can conduct electricity, and if so how this can be utilized, has been a subject of discussion particularly since direct experimental results became available [1]. Part of the motivation for such studies is the potential use of DNA in nanotechnology and also the possibility of DNA damage-repair mechanisms via electron transfer [2]. Various experiments, models and ideas exist that aim to describe its electronic transport properties and these have recently been reviewed in Refs. [3, 4]. Despite the enhanced activity in both experimental and theoretical studies, the complexity of DNA is still preventing us from forming a consistent understanding.

In most models [5, 6] it has been assumed that electronic transport takes place along the long axis of the DNA molecule and that the conduction path is due to π-orbital overlap between consecutive bases; density-functional calculations [7] have shown that the bases, especially Guanine, are rich in π-orbitals. Quantum mechanical approaches to the problem use standard one-dimensional (1D) tight-binding models [8]. Of particular interest to us is a 1D model [5] which includes the backbone structure of DNA explicitly and exhibits a semiconducting gap.

In this paper, we extend this 1D model to a biologically more relevant ladder structure, as shown in Fig. 1 and study its electronic properties for various DNA sequences, including poly(dG)-poly(dC), telomeric, random-ATGC and λ- (bacteriophage) DNA. Our approach uses standard transfer-matrix techniques [9] which give estimates of the localisation lengths of a single electronic excitation averaged over the DNA strand at zero temperature. The ladder model is a planar projection of the structure of the DNA-the helix being unwound. There are two connected central branches with sites that represent the DNA bases. These central branches are the

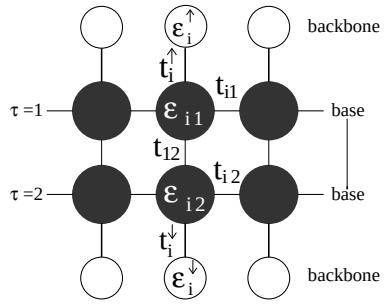

FIGURE 1. Ladder model of DNA corresponding to the Hamiltonian (1).

π-orbital conduction pathways for the electrons and their sites are additionally linked to upper and lower sites corresponding to the upper and lower backbones; backbone sites are not interconnected. The Hamiltonian for the ladder model is given by:

$$\begin{aligned} H &= \sum_{i=1}^{L} \Bigg(\sum_{\tau=1,2} t_{i,\tau} |i,\tau\rangle\langle i+1,\tau| + \varepsilon_{i,\tau} |i,\tau\rangle\langle i,\tau| \\ &\quad + \sum_{q=\uparrow,\downarrow} t_i^q |i\rangle\langle i,q_i| + t_{1,2} |i,1\rangle\langle i,2| + \varepsilon_i^q |i,q\rangle\langle i,q| \Bigg) \\ &\quad + h.c. \end{aligned} \tag{1}$$

where $t_{i,\tau}, \tau = 1,2$, is the hopping amplitude along the τ-branch, t_i^q gives the hopping to the upper ($q = \uparrow$) and lower ($q = \downarrow$) backbone, $t_{1,2}$ represents the hopping between the two central branches; $\varepsilon_{i,\tau}$ is the onsite potential energy on each site along the two central branches and ε_i^q gives the onsite energy at the sites of the backbone.

In Ref. [5], it has been argued that $t_{i,\tau} \approx t_i^q/2 \sim 0.5$eV can describe experimental results in poly(dG)-poly(dC) DNA for a simplified one-chain version of the ladder

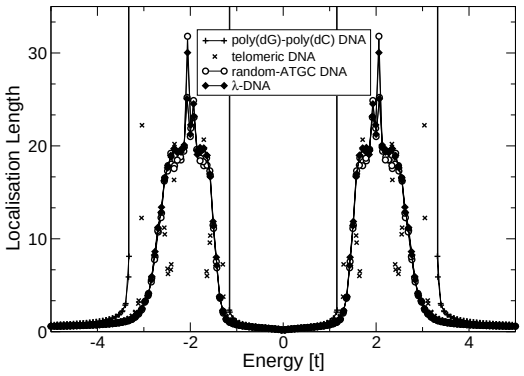

FIGURE 2. Localisation lengths as a fucntion of energy for poly(dG)-poly(dC), telomeric, random-ATGC, and λ-DNA as described in the text. The energy is measured in units of hopping strength between like base pairs. The spectrum is symmetric in energy. Lines are guides to the eye only.

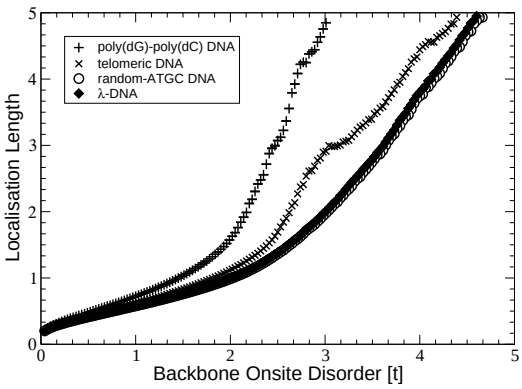

FIGURE 3. Localisation lengths as a function of binary backbone disorder for poly(dG)-poly(dC), telomeric, random-ATGC, and λ-DNA at energy $E = 0$. The disorder corresponds to a situation when 50% of all backbone sites are occupied, e.g., by a salt ion.

model. Semi-empirical calculations on DNA base pairs using the SPARTAN package have shown that the wavefunction overlap between a base pair is weak and therefore we take it to be $t_{1,2} = t_{i,\tau}/10$. We make the further assumption that the wavefunction overlap between consecutive bases along the DNA strand is weaker between unlike and non-matching bases, for which we thus choose $t_{i,\tau} = t_i^q/4$, whereas $t_{i,\tau} = t_i^q/2$ between identical and matching bases (i.e. AT/TA, GC/CG, AA, TT, GG, CC). Initially, all small onsite potential fluctuations due to differences in base-ionization energies are ignored. In Fig. 2, the energy dependence of the localisation lengths computed using model (1) is shown for four different sequences of DNA, namely, poly(dG)-poly(dC) DNA with 10,000 base pairs, a telomeric DNA (repetitions of pattern TTAGGG truncated at 6000 base pairs), random-ATGC DNA with 10,000 bases and λ-DNA (bacteriophage) with 48,502 bases. As expected, poly(dG)-poly(dC) and telomeric DNA give rise to perfect conductivity, due to their periodic electronic structure, within small minibands centered around $E = 0$. On the other hand, random-ATGC and λ-DNA give two bands with finite localisation lengths in the energy regions $(-4,-1)$ and $(1,4)$. The localisation lengths, which roughly equal the average distance an electron would be able to travel (conduct), are close to the distance of 20 bases within the band, with a maximum of ~ 30 bases at the centre of each band.

In vivo and most experimental situations, DNA is exposed to diverse environments. The solution, the thermal effects and the available space (causing the DNA to bend) are factors that alter the structure and properties that one is measuring [10, 11]. Here, we model this by introducing various types of disorder into the hopping (t) and onsite-energy parameters (ε). In general, this leads to a reduction of the localisation lengths and a gradual filling of the gap. A particularly intriguing result emerges when using *binary* onsite disorder at the backbone, in order to model the random adhesion of saline solvents [11]. In Fig. 3, we show that at energy $E = 0$, the localisation length increases with increasing disorder. This is also true for the model of Ref. [5]. Thus, it appears that adding binary disorder leads to *partial delocalisation*.

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