IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 075109 (7pp) doi:10.1088/0953-8984/20/7/075109

Electronic transport in poly(CG) and poly(CT) DNA segments with diluted base pairing

F A B F de Moura[1], M L Lyra[1] and E L Albuquerque[2]

[1] Instituto de Física, Universidade Federal de Alagoas 57072-970 Maceió-AL, Brazil
[2] Departamento de Física, Universidade Federal do Rio Grande do Norte 59072-970 Natal-RN, Brazil

Received 2 October 2007, in final form 20 December 2007
Published 28 January 2008
Online at stacks.iop.org/JPhysCM/20/075109

Abstract

We present a model for describing electrical conductivity along poly(CG) and poly(CT) DNA segments with diluted base pairing within a tight-binding Hamiltonian approach. The base pairing is restricted to occurring at a fraction p of the cytosine (C) nucleotides at which a guanine (G) nucleotide is attached. We show that the Schrödinger equation can be mapped exactly onto that of the one-dimensional Anderson model with diluted disorder. Using a Green function formalism as well as exact diagonalization of the full one-dimensional Hamiltonian of finite segments, we compute the density of states, the wavefunction of all energy eigenstates and their corresponding localization lengths. We show that the effective disorder introduced by the diluted base pairing is much stronger in poly(CG) than in poly(CT) segments, with significant consequences for the electronic transport properties. The electronic wavepacket remains localized in the poly(CT) case, while it acquires a diffusive spread for the poly(CG)-based sequence.

1. Introduction

There has been tremendous interest in recent years in developing concepts and approaches for self-assembled systems, searching for their electronic and optical applications [1, 2]. Biology can provide models and mechanisms for advancing this approach, but there is no straightforward way to apply them in electronics since biological molecules are essentially electrically insulating [3]. However, exquisite molecular recognition of various natural biological materials can be used to form a complex network of potentially useful particles for a variety of optical, electronic, and sensing applications [4]. For instance, investigations of electrical junctions, in which single molecules or small molecular assemblies operate as conductors connecting traditional electrical components, such as metal or semiconductor contacts, constitute a major part of what is nowadays known as molecular electronics [5]. Their diversity, versatility, and amenability to control and manipulation make them potentially important components in nanoelectronic devices [6].

The first pioneering experiments were performed demonstrating that individual molecules can operate as switches one thousand times smaller than those on conventional microchips [7]. In particular, the ability to choose the sequence of nucleotides and hence provide addressability during the self-assembly processes makes DNA an ideal molecule for these applications, with the potential of having profound impact in this field. Despite Nature's impressive ability to manufacture and assemble complex molecules, like DNA and proteins, the design of DNA-based devices for molecular nanoelectronics is not yet an easy task since they are crucially dependent upon elucidation of the mechanism and dynamics of electrons and hole transport in them [8]. Besides, unlike proteins, DNA does not primarily present an electron/hole-transfer problem, and its suitability as a potential building block for molecular devices may not depend only on long-distance transfer of electrons and holes through the molecule. The reason for that lies in the mechanism itself: it fails to explain the persistence of efficient charge transfer when the transfer rates do not decrease rapidly with the transfer distance [9]. Fortunately, its π-stacked array of base pairs does indeed provide an appropriate pathway for long-range charge transport [10], although the mechanisms for long-range transport and short-range transfer may differ entirely [11]. Strong stacking interactions result in the fastest electron-transfer kinetics, whereas dynamical motion of

the base pairs and reactant energetics also modulate the distance dependence of DNA-mediated charge transport, reducing its efficiency [12]. The possible influence of disorder in the DNA sequence on its electronic transport properties has also been a subject of recent investigations [13–18].

Hereditary information is encoded in the chemical language of DNA and reproduced in all cells of living organisms. The double-stranded helical structure of the DNA is a key to its use in self-assembly applications. Each strand of the DNA is about 2 nm wide and is composed of a linear chain of four possible bases, namely adenine (A), cytosine (C), guanine (G), and thymine (T), on a backbone of alternating sugar molecules and phosphate ions. Each unit of a phosphate, a sugar molecule, and a base is called a nucleotide. Each nucleotide is about 0.34 nm long. The specific binding through hydrogen bonds between adenine and thymine, and cytosine and guanine can result in the joining of two complementary single-stranded DNA entities to form a double-stranded DNA.

Due to their potential applications in nanoelectronics, there has been a growing interest both in the synthesis and characterization of DNA-based molecules with periodic nucleotide sequences, and in the theoretical prediction of the electronic properties of model molecular structures [19, 20, 22–24, 21]. Among these, molecules with binary periodic sequences have attracted a lot of attention due to their special electronic band structure composed of two main bands of allowed states separated by an energy gap. Such band structure is similar to those of solid-state semiconductors. At half-filling the presence of the energy gap gives to these molecules an intrinsic insulator character. The introduction of defects may generate states within the gap and substantially improve the conductance, especially of finite molecules. In single-strand molecules, defects may be originated within their own nucleotide sequences or by laterally attaching new structures at random. However, disorder modifies profoundly the nature of the electronic states in 1D systems. All states usually become exponentially localized for any amount of disorder [25]. Such exponential localization competes with the above improvement of the conductance associated with the presence of states within the gap. Therefore, schemes for introducing defects that minimize the tendency of exponential localization of the electronic states are essential for tailoring the electronic transport properties of DNA-based structures.

Within the above context, we report in this work an analytical as well as numerical investigation of the one-electron states in single-strand binary DNA-based segments with diluted base pairing. Our opting for considering single-strand molecules was mainly motivated by the fact that these are known to be poorer conductors than double-stranded molecules. It was not motivated by the simplicity of the numerical and mathematical treatment, making use, for example, of a renormalization scheme as in [26], since similar techniques can be used in either case. Our main intention was to reinforce that the resonance mechanism reported in our paper leads to an anomalous wavepacket dynamics, even in the worse case of strong localization in single-strand molecules. Specifically, we will consider poly(CG) and poly(CT) segments at which guanine bases (G) are attached laterally at a fraction of the cytosine (C) bases. Within a tight-binding description, we will compute the density of states and eigenfunctions of the one-electron states. We will show that the model Hamiltonian for this system can be mapped onto that of the Anderson chain with diluted disorder. We will explore the influence of the effective disorder on the nature of the one-electron states as well as on the wavepacket dynamics. In particular, we will show that in segments formed with complementary units (as in poly(CG)), base pairing dilution does indeed lead to a complete exponential localization of all one-electron states. On the other hand, in chains with non-complementary units (as in poly(CT)), a resonant state is not affected by the disorder and remains extended. In the presence of such a resonant state, the wavepacket develops a diffusive dynamics.

2. Model Hamiltonian

In what follows, we will work within a tight-binding approach. We will consider an effective Hamiltonian describing one electron moving in a geometry composed of a periodic chain of alternating bases (CG or CT sequences). Our model Hamiltonian is constructed considering the essential ingredients responsible for the quite distinct electronic transport properties of the poly(CG) and poly(CT) molecules with diluted base pairing. Additional contributions will play similar roles in poly(CG) and poly(CT) molecules. In the tight-binding Hamiltonian model of electronic transport, the main information taken from the underlying complex structure is the HOMO level of its building blocks and the transfer integrals. Previous tight-binding studies have correctly captured several features of the electronic transport of DNA-based molecules [27–29].

Recent results showed that more sophisticated effective Hamiltonians are in order to capture some features of the electronic transport in DNA. For example, the hybridization of the overlapping p orbital in the base pair stack coupled to the backbone is sufficient to predict the existence of a gap in the nonequilibrium current–voltage characteristics with a minimal number of parameters [30]. Environment effects would effectively act as a source of disorder while the backbone promotes the emergence of a band gap of the order of the hopping integral connecting it to the nucleobases [31]. The inclusion of additional terms to take into account the presence of the sugar–phosphate backbone mainly affects the structure of the density of states. Electrostatic interactions between base pairs also play an important hole in the charge localization properties of DNA [32]. These terms have no direct impact on the resonance mechanism that we intend to describe here, which is responsible for the emergence of a delocalized state and for the diffusive wavepacket spread in poly(CT) molecules with diluted base pairing.

We assume that G bases are laterally attached to the C sites at random, with probability p (see figure 1). We consider just a single orbital per site and nearest-neighbor transfer integrals V (along the main chain) and V' (among paired bases). The corresponding time-independent Schrödinger equation for a

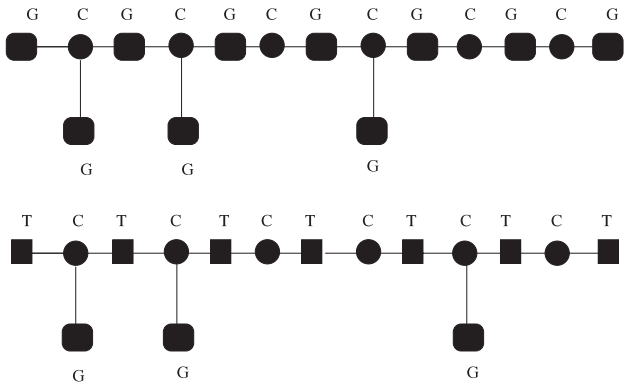

Figure 1. Schematic representation of the single-strand DNA molecule showing the main periodic chains of alternating bases (CG and CT sequences) with diluted base pairing. Guanine (G) bases are laterally attached at random to a fraction p of the cytosine (C) sites.

poly(CG) sequence is given by [33]

$$E\psi_j^{\mathrm{G}} = V(\psi_{j-1}^{\mathrm{C}} + \psi_{j+1}^{\mathrm{C}}) + \epsilon_{\mathrm{G}}\psi_j^{\mathrm{G}} \qquad \text{for odd } j, \tag{1}$$

$$E\psi_j^{\mathrm{C}} = V(\psi_{j-1}^{\mathrm{G}} + \psi_{j+1}^{\mathrm{G}}) + V'\beta_j\psi_j^{\mathrm{G}} + \epsilon_C\psi_j^{\mathrm{C}}, \text{ for even } j. \tag{2}$$

For a poly(CT) sequence one just has to replace G by T. ϵ_α (α = G, T or C) represents the on-site potential at the bases G, T or C and ψ_j^α is the wavefunction coefficient in the single-orbital basis, defined by

$$|\Psi\rangle = \sum_{(j,\alpha)} \psi_j^\alpha |j,\alpha\rangle, \tag{3}$$

where (j,α) runs over all base units. Also, $\beta_j = 1$ with probability p and $\beta_j = 0$ with probability $1-p$, where p is the concentration of G sites attached to the single-stranded main periodic chain. At the sites where $\beta_j = 1$, we have an additional equation:

$$E\psi_j^{\mathrm{G}} = V'\psi_j^{\mathrm{C}} + \epsilon_{\mathrm{G}}\psi_j^{\mathrm{G}}, \qquad \text{for even } j \quad \text{and} \quad \beta_j = 1. \tag{4}$$

A clear picture of the nature of the electronic states on the above model can be achieved by performing a procedure of decimation of the attached base units. The above tight-binding model for a DNA-based molecule can be mapped onto an effective one-dimensional diluted Anderson model [34–37]. Such a model contains diagonal disorder diluted by an underlying periodicity. The resulting sequence is composed of two inter-penetrating sub-lattices, one composed of random potentials (the Anderson chain), the other having non-random segments.

The degrees of freedom associated with the lateral DNA bases appearing in the above equations can be removed by substituting [38]

$$\psi_j^{\mathrm{G}} = [V'/(E-\epsilon_{\mathrm{G}})]\psi_j^{\mathrm{C}}, \qquad \text{for even } j, \tag{5}$$

into the equation for the coefficients ψ_j^{C}, yielding

$$E\psi_j^{\mathrm{C}} = \epsilon_{\mathrm{C}}^*\psi_j^{\mathrm{C}} + V(\psi_{j-1}^{\mathrm{G}} + \psi_{n+1}^{\mathrm{G}}), \tag{6}$$

where

$$\epsilon_{\mathrm{C}}^* = \epsilon_{\mathrm{C}} + [V'^2/(E-\epsilon_{\mathrm{G}})] \tag{7}$$

is the renormalized potential at the cytosine sites at which the G bases are laterally attached. For those cytosine bases with no lateral attachment, the potential remains the bare one.

Therefore, after having eliminated the coefficients associated with the lateral G bases, the remaining set of equations expresses an alternating sequence of CG (or CT). Most importantly, the C sites have now two possible values for the on-site potential, namely ϵ_{C}^* with probability p or ϵ_{C} with probability $1-p$, respectively. The remaining bases of the periodic sequence all have the same potential: ϵ_{G} for poly(CG) or ϵ_{T} for poly(CT). The random character of the diluted base pairing is reflected in a random sequence for the effective on-site energies of the cytosine sites. This kind of sequence is similar to the structure so-called diluted Anderson model. It consists of two inter-penetrating sequences: a periodic sequence containing the guanine or thymine sites, for poly(CG) or poly(CT) respectively, and a random sequence containing bare and renormalized cytosine sites. Due to the periodicity of the non-random sub-lattice, a special resonance energy E_0 appears with vanishing wavefunction amplitudes on the random sub-lattice [34–37]. Therefore, this mode is mainly insensitive to the presence of disorder and may lead to a possible mechanism for inducing conductance in such DNA-based molecules. For the poly(CT) molecule, the resonance energy is $E_0 = \epsilon_{\mathrm{T}}$. At this energy, the renormalized cytosine potential remains finite, and a divergence of the localization length of the one-electron eigenmodes as the resonance energy is approached can be anticipated [34, 36]. On the other hand, the resonance energy for poly(CG) molecules is $E_0 = \epsilon_{\mathrm{G}}$. At this energy, the renormalized cytosine potential diverges. This case corresponds to an effectively infinite disorder which counteracts the delocalization effect. With such reasoning, one expects diluted base pairing to induce a stronger localization of the one-electron eigenfunctions in poly(CG) than in poly(CT) chains.

3. Numerical results

In order to illustrate numerically the above described features, we compute the Lyapunov exponent $\gamma(E)$ (which is the inverse of the localization length Λ) of long DNA segments, by means of the following equation:

$$\gamma(E) = 1/\Lambda(E) = (1/2N)\ln\left[\mathrm{Tr}\left|G_{1,N+1}^{N+1}\right|^2\right], \tag{8}$$

where $G_{1,N+1}^{N+1}$ denotes the Green's function operator between the first and the $(N+1)$ th sites. To compute this operator, we use a standard recursion method (see [39] for details). For extended states, $1/\Lambda(E)$ vanishes in the thermodynamic limit.

In the following numerical study, we will take $V' = V$, although base pair couplings are weaker than the intra-strand coupling [40]. Further, in most of the following calculations, we consider $V = 1$ eV which is somewhat larger than previously reported estimates of intra-strand transfer integrals [41, 42]. However, the resonance effect that we

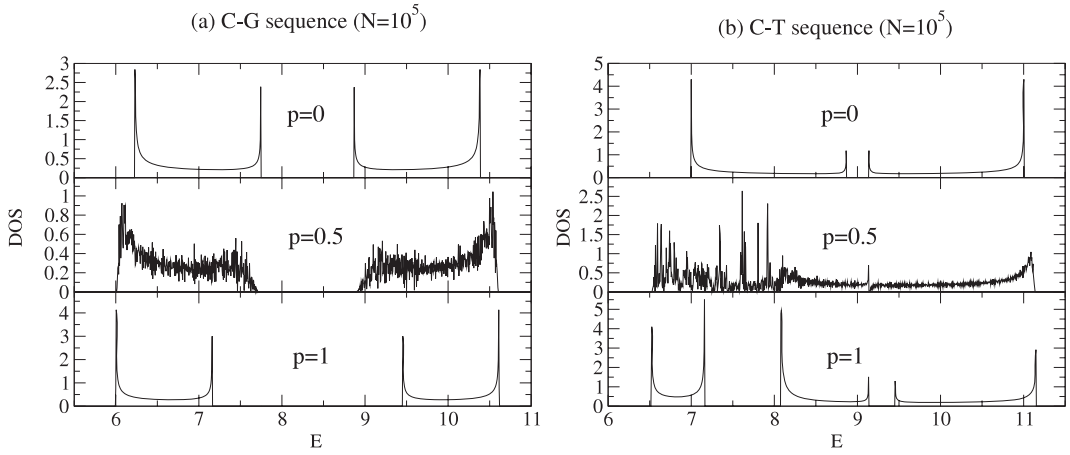

Figure 2. Plot of the electronic density of states (DOS) versus the reduced energy E (in units of eV), for the particular cases of transfer integral $V = 1$ eV. (a) Poly(CG)-based DNA sequences. The band gap persists for poly(CG) chains with diluted base pairing and all van Hopf singularities are rounded off. (b) Poly(CT)-based DNA sequences. The bands coalesce for base pair diluted poly(CT) before splitting in three bands. Disorder does not affect the van Hopf singularity at $E = \epsilon_T$. The gapless band structure, together with the non-localization of the resonance state, favors the electronic transport in this case.

are going to explore is robust with respect to distinct transfer integral values and can be more clearly analyzed without considering the additional energy scale associated with distinct intra-strand and inter-strand transfer integrals. Estimates for the values of the tight-binding on-site potentials of the nucleobases are quite spread in the literature and depend on the molecular environment [31, 42, 43]. Here, we will consider the ionization potentials of nucleobase monomers reported in [44] as a typical set of parameter values ($\epsilon_T = 9.14$, $\epsilon_G = 7.75$ and $\epsilon_C = 8.87$, all units in eV). In addition, we apply an exact diagonalization of the complete tight-binding Hamiltonian, given by equations (1)–(3), to compute explicitly the participation number of all eigenstates.

We start by using the recursion Dean method to obtain the electronic density of states (DOS). In figure 2, we show our results for three representative values of the concentration of paired cytosine bases, namely:

(i) $p = 0$, corresponding to pure poly(CG) and poly(CT) chains;
(ii) $p = 1$, describing the poly(CG) and poly(CT) chains with guanine bases laterally attached to all cytosine bases;
(iii) $p = 0.5$ representing a typical sequence of diluted base pairing.

In figure 2(a) we display our results for the poly(CG) sequences with $V = 1$ eV. As one can see, the electronic density of states has two main bands, which is typical of binary sequences, with the gap for $p = 1$ being larger than for $p = 0$. Such enhancement of the energy gap is a direct consequence of the base pairing. For $p = 0.5$ one notices that all van Hopf singularities at the band edges are rounded off by the presence of disorder. The fluctuations in the DOS have been exploited in the literature to identify the nature of the states [45, 46]. The variance in the number of states in a given energy window will scale linearly with the system size for localized states while having just a slow logarithmic scaling for extended states. These two regimes reflect the distinct level spacing statistics of localized and extended states. As a result, much smaller fluctuations are attained in the normalized DOS when extended states are present as compared to the fluctuations observed in the energy range corresponding to localized states. These fluctuations are of the same magnitude in the two bands, which indicates that these bands are equally affected by disorder.

The DOS for poly(CT)-based chains are depicted in figure 2(b). For these molecules, one can observe a series of relevant features not found in the previous case. Firstly, one sees that the two-band structure of the binary $p = 0$ case evolves to a three-band structure at $p = 1$, as expected for a periodic structure with three distinct sites in the unit cell. It is important to stress that, although after renormalization the poly(CT) has just two sites per unit cell at $p = 1$, the energy dependence of the renormalized cytosine potential takes into account the original three-site structure. It is interesting to notice that the bottom of the upper band at $p = 0$ coincides with the top of the middle band at $p = 1$. This energy corresponds exactly to $E_0 = \epsilon_T$. When the concentration of the attached guanine bases increases, the two-band structure firstly coalesces into a single band, before splitting into three bands, as shown for the particular case of $p = 0.5$. Further, the van Hopf singularities are rounded off, except the one located at E_0 which corresponds to the resonance state insensitive to disorder. Therefore, diluted base pairing produces a gapless band structure while keeping the states around E_0 extended, an ideal scenario for electronic transport. Additionally, the DOS exhibits stronger fluctuations at the bottom than at the top of the energy band, indicating that the low-energy states are more strongly localized than the high-energy states.

By computing the Lyapunov exponent $\gamma = 1/\Lambda$, one can directly measure the disorder effect on the nature of the electronic eigenstates. In figure 3(a), the spectrum of the Lyapunov exponent for the base pair diluted poly(CG) molecule with $p = 0.5$ is shown. Notice that, for the hopping amplitude $V = 1$ eV, the Lyapunov exponent achieves a minimum value of the order of 10^{-2} in both energy bands. Therefore, the maximum localization length in this chain is of the order of 100 sites, i.e., no delocalized

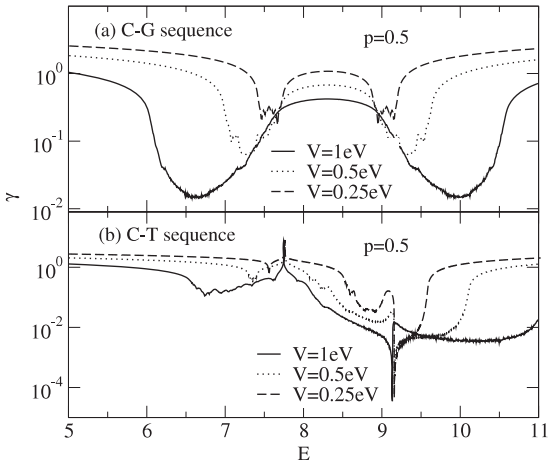

Figure 3. (a) Lyapunov exponent $\gamma(E)$ versus energy E (in units of eV) for a poly(CG) DNA sequence with $p = 0.5$ diluted base pairing. All states are exponentially localized, with the maximum localization length being of the order of 10^2 sites for $V = 1$ eV and decreasing as $1/V^2$. (b) Same as in (a) but for a poly(CT) DNA sequence. For $E = \epsilon_G$ one observes a strong localization as the renormalized energy ϵ_C^* diverges. At the resonance energy $E = E_0 = \epsilon_T$ the mode is not affected by disorder and keeps its Bloch-like character. Data for different values of the transfer integral V confirm that the resonance mechanism is robust with respect to this energy scale.

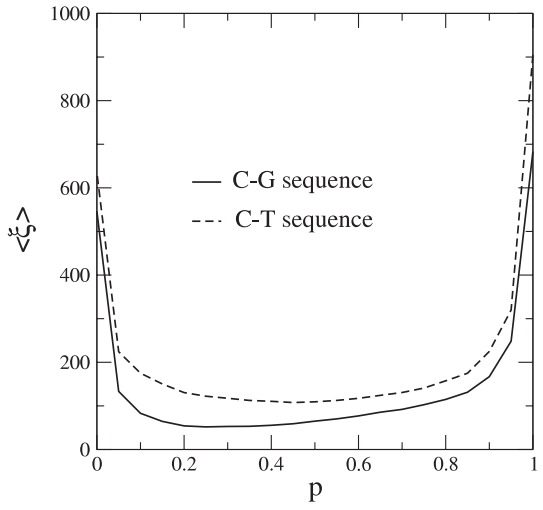

Figure 4. Mean participation number $\langle\xi\rangle$ versus the concentration p of laterally attached guanine bases for both poly(CG) and poly(CT) DNA sequences with transfer integral $V = 1$ eV. Due to the presence of an extended resonance mode, the base pair diluted poly(CT) molecule shows a larger average localization length than the poly(CG) one. The asymmetric dilution effect in poly(CG) is a consequence of the joint effects of Anderson localization and band gap enhancement.

mode survives to diluted base pairing in binary periodic DNA sequences of corresponding bases, such as poly(CG). The average localization length scales as $1/V^2$. Further, this kind of disorder affects the two bands in a similar way, as already pointed out through the analysis of the DOS fluctuations. Figure 3(b) shows the corresponding Lyapunov exponent spectrum for a poly(CT) chain with $p = 0.5$ diluted base pairing. Here, one can observe the presence of two singularities. The first one is at $E = \epsilon_G$ which corresponds to the energy at which the renormalized ϵ_C^* diverges, thus leading to an effective infinite disorder. At this energy the one-electron mode is strongly localized. The second singularity is at $E = E_0 = \epsilon_T$. This corresponds to the energy mode not affected by the disorder. This mode has a Bloch-like character [34, 36]. In addition, we observe explicitly that the low-energy modes are more localized than the high-energy ones, in agreement with the observation that these regions depict distinct DOS fluctuations. In figure 3 we also show the spectra of Lyapunov exponents computed considering chains with weaker hopping amplitudes ($V = 0.5$ and 0.25). These also display the same resonances, thus corroborating the anticipated robustness of the resonance mechanism with regard to distinct energy scales of the transfer integrals.

In order to characterize the overall dependence of the localization length of the one-electron eigenstates on the concentration p of laterally attached bases, we performed an exact diagonalization of the Hamiltonian of chains with 10^3 sites in the main periodic structure. As a representative measure of the localization length of each mode, we computed the participation number defined as $\xi = 1/\sum_{j,\alpha} \psi_{j,\alpha}^4$.

Figure 4 depicts the average participation number $\langle\xi\rangle$ of all eigenstates as a function of the concentration p for base pair diluted poly(CG) and poly(CT) chains with $V = 1$ eV. In the limits of $p = 0$ and $p = 1$, $\langle\xi\rangle$ becomes of the order of the chain size due to the absence of disorder. At finite concentrations, the average participation number of the base pair diluted poly(CG) is always smaller than that for poly(CT). Further, the dilution effect on poly(CG) is quite asymmetric, with the localization being more pronounced at small concentrations of attached bases than at large concentrations. For poly(CT), the minimum in the average participation number occurs at maximum disorder (dilution concentration $p = 0.5$), corresponding to the regime in which the energy bands are superposed.

The quite distinct effects caused by diluted base pairing in poly(CG) and poly(CT) will have a significant impact on the electronic transport. To illustrate this, we solved the time-dependent Schrödinger equation to investigate the time evolution of a wavepacket initially localized at the central guanine (thymine) base of the main periodic poly(CG) (poly(CT)) sequence. The initial wavepacket has a wide spectral distribution and, therefore, its time evolution contains contributions coming from all eigenmodes. In the calculations, we considered chains with 80 000 sites in the main periodic sequence and integrated the Schrödinger equations numerically. The integration time was long enough to allow the wavepacket to spread and reach the asymptotic regime before touching the chain boundaries.

The time evolution of the wavepacket root mean square deviation is shown in figure 5, considering the time measured in units of $\mathrm{eV}/\hbar \simeq 6.58 \times 10^{-16}$ s. For the poly(CG) chain with diluted base pairing, the wavepacket exhibits an initial transient after which its width saturates. The saturation wavepacket width is of the order of the average localization length of the one-electron eigenmodes. The saturation time

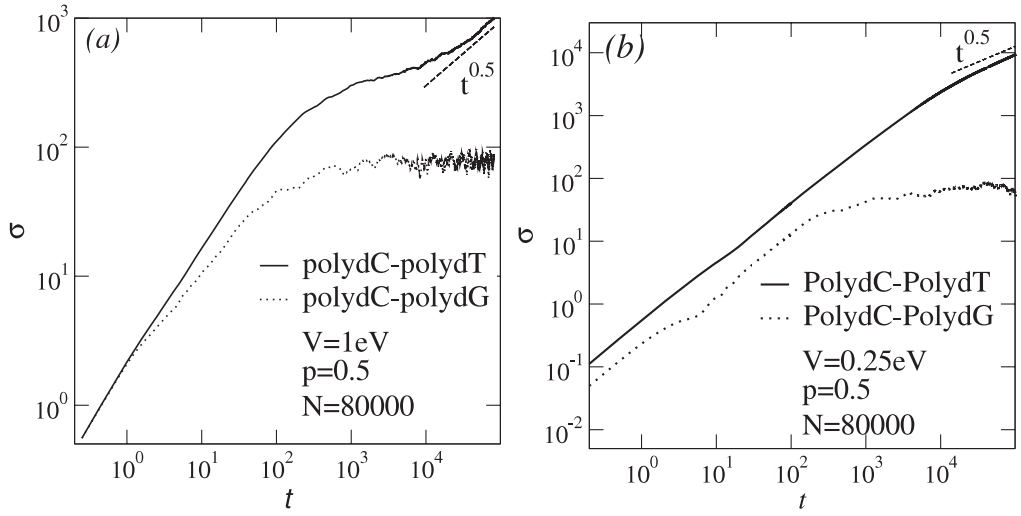

Figure 5. The wavepacket root mean square deviation σ as a function of time (in units of eV/$\hbar$) for (a) $V = 1$ eV and (b) $V = 0.25$ eV. For poly(CG) with diluted base pairing, the wavepacket width saturates after an initial transient time on the scale of picoseconds, irrespective to the transfer integral. On the other hand, the saturation is interrupted for the poly(CT) molecule when $V = 1$ eV (a). The wavepacket develops an asymptotic diffusive spread due to the contributions coming from the effectively extended state. In the weak coupling regime (b), the intermediate regime is suppressed and the asymptotic diffusive spread sets up after the initial transient.

is on the scale of picoseconds, after which the wavepacket remains trapped in a finite segment. The saturation wavepacket width for the diluted poly(CG) chain is roughly independent of the transfer integral. For the poly(CT) chain with diluted base pairing, the wavepacket exhibits a similar initial transient. For hopping integral $V = 1$ eV (figure 5(a)), the saturation of the wavepacket width, which starts to occur on the same timescale as for poly(CG), is interrupted by a crossover to an asymptotic diffusive spread. In this regime, the wavepacket dynamics is governed by the contributions coming from the effectively extended states located near the resonance energy. This asymptotic diffusive regime sets up for timescales larger than 10 ps. For weaker transfer integrals, as shown in figure 5(b), the intermediate dynamical regime is suppressed. The initial transient lasts longer due to the effective weakening of the disorder mediated by the coupling of the main chain to the guanine lateral bases. The asymptotic regime remains diffusive. Therefore, the influence of the resonance mode in the wavepacket dynamics becomes stronger in the weak coupling regime.

4. Summary and conclusions

In summary, we investigated the nature of the one-electron eigenstates within a tight-binding model of DNA-based poly(CG) and poly(CT) molecules with diluted base pairing. The model considers that guanine nucleotides are allowed to attach laterally to the cytosine bases of the main chain with probability p. We demonstrated that this model can be exactly mapped on the diluted Anderson model, consisting of two inter-penetrating chains. One of these chains is composed of non-random units: G sites for poly(CG) or T sites for poly(CT). The second chain is a random sequence of bare cytosine sites with on-site potential ϵ_C and renormalized cytosine sites with effective on-site potential given by $\epsilon_C^* = \epsilon_C + V'^2/(E - \epsilon_G)$.

By employing a recursion method to compute the electronic density of states as well as the Lyapunov exponent, and solving the time-dependent Schrödinger equation to follow the time evolution of an initially localized wavepacket, we found qualitatively distinct influences of diluted base pairing in each chain model. For the poly(CG) case, the disorder introduced by the diluted base pairing promotes the exponential localization of all one-electron states. Furthermore, it enhances the gap between the two main bands of allowed energy states. These two factors reinforce the insulator character of this molecule. On the other hand, for poly(CT) molecules, there is a resonant mode with energy $E_0 = \epsilon_T$ which is not affected by the disorder and remains extended with a Bloch-like character. Besides, the two energy bands, typical of the pure poly(CT) molecule, coalesce into a single band for intermediate dilution before splitting into three bands. Therefore, when the Fermi energy coincides with the resonance energy, we have a typical scenario favoring electronic transport: a gapless density of states with extended states near the Fermi level. As one approaches the resonance energy from below, the localization length of the one-electron modes diverges. Above E_0 the localization length remains finite. This feature implies that hole transport will predominate over electron transport.

We presented also the dynamics of a one-electron wavepacket and found that the wavepacket width in poly(CG) with diluted base pairing saturates after an initial transient on a scale of a picosecond. For poly(CT), the wavepacket dynamics develops a crossover to an asymptotic diffusive spread due to contributions coming from the effectively extended states. The presence of a resonance state and the consequent diffusive one-electron dynamics found in poly(CT) with diluted base pairing will also be present in other DNA-based periodic sequences with random base pairing. The essential ingredient is that the laterally attached nucleobase must be distinct from the base

unit of the main sequence at which no base pairing is allowed. In our model, we just considered the case of clean DNA molecules and did not take into account the possible effect of the environment. The presence of water molecules and counterions [47] is known to introduce additional disorder and thus enhance the Anderson localization. Further, geometrical distortions may also strongly affect the electron transport by introducing disorder. In particular, it is known that the terms for coupling between nucleobases undergo large fluctuations under structural distortions [48]. These effects will affect similarly the poly(CG) and poly(CT) molecules with diluted base pairing. As a result, the average localization length will be reduced by the disorder due to the environment and geometric distortions. Besides, the poly(CT)-based molecule will still be able to transport electrons over distances much longer than those for its poly(CG) counterpart due to the resonance mechanism that we reported. This mechanism is quite robust and is expected to sustain the resonance state even in extended models that consider the transfer integral of paired bases smaller than that along the main strand, as well as additional orbitals representing the sugar–phosphate backbone. We hope that the present findings described in this work will stimulate further developments in the synthesis and characterization of new DNA-based molecules with potential applications in nanobioelectronics.

Acknowledgments

We would like to thank for partial financial support FINEP, CAPES and CNPq-Rede Nanobioestruturas (Brazilian Research Agencies) as well as FAPEAL (Alagoas State Research Agency).

References

[1] Luryi S, Xu J M and Zaslavsky A (ed) 1999 *Future Trends in Microelectronics: the Road Ahead* (New York: Wiley)
[2] Endres R G, Cox D L and Singh R R P 2004 *Rev. Mod. Phys.* **76** 195
[3] Braun E and Keren K 2004 *Adv. Phys.* **53** 441
[4] Nicoloni C 1996 *Molecular Bioelectronics* (Singapore: World Scientific)
[5] Braun E, Eichen Y, Sivan U and Ben-Yoseph G 1998 *Nature* **391** 775
Cai L T, Tabata H and Kawai T 2000 *Appl. Phys. Lett.* **77** 3105
Kasumov A Y *et al* 2001 *Science* **291** 280
Taniguchi M and Kawai T 2004 *Phys. Rev.* E **70** 11913
Hipps K W 2001 *Science* **294** 536
[6] Park J, Pasupathy A N, Goldsmith J I, Chang C, Yaish Y, Petta J R, Rinkoski M, Sethna J P, Abruna H D, McEuen P L and Ralph D C 2002 *Nature* **417** 722
Liang W J, Shores M P, Bockrath M, Long J R and Park H 2002 *Nature* **417** 725
[7] Reed M A, Chen J, Rawlett A M, Price D W and Tour J M 2001 *Appl. Phys. Lett.* **78** 3735
[8] Lewis F D, Liu X Y, Liu J Q, Miller S E, Hayes R T and Wasielewski M R 2000 *Nature* **406** 51
[9] Giese B, Amaudrut J, Kohler A K, Spormann M and Wessely S 2001 *Nature* **412** 318
[10] Roche S 2003 *Phys. Rev. Lett.* **91** 108101
Roche S, Bicout D, Maciá E and Kats E 2003 *Phys. Rev. Lett.* **91** 228101
Roche S, Bicout D, Maciá E and Kats E 2004 *Phys. Rev. Lett.* **92** 109901 (erratum)
[11] Porath D, Bezryadin A, de Vries S and Dekker C 2000 *Nature* **403** 635
Fink H W and Schonenberger C 1999 *Nature* **398** 407
[12] Kelley S O and Barton J K 1999 *Science* **283** 375
[13] Komineas S, Kalosakas G and Bishop A R 2002 *Phys. Rev.* E **65** 061905
[14] Carpena P, Galván P B, Ivanov P Ch and Stanley H E 2002 *Nature* **418** 955
Carpena P, Galván P B, Ivanov P Ch and Stanley H E 2003 *Nature* **421** 764
[15] Caetano R A and Schulz P A 2005 *Phys. Rev. Lett.* **95** 126601
[16] Albuquerque E L, Vasconcelos M S, Lyra M L and de Moura F A B F 2005 *Phys. Rev.* E **71** 021910
[17] Diaz E, Sedrakyan A, Sedrakyan D and Dominguez-Adame F 2007 *Phys. Rev.* B **75** 014201
[18] Albuquerque E L, Lyra M L and de Moura F A B F 2006 *Physica* A **370** 625
[19] Tippin D B, Ramakrishnan B and Sundaralingam M 1997 *J. Mol. Biol.* **270** 247
[20] Taniguchi M and Kawai T 2004 *Phys. Rev.* E **70** 011913
[21] Taniguchi M and Kawai T 2006 *Physica* E **33** 1
[22] Yoo K H, Ha D H, Lee J O, Park J W, Kim J, Kim J J, Lee H Y, Kawai T and Choi H Y 2001 *Phys. Rev. Lett.* **87** 198102
[23] Guttiérrez R, Mandal S and Cuniberti G 2005 *Nano Lett.* **5** 1093
[24] Malyshev A V 2007 *Phys. Rev. Lett.* **98** 096801
[25] Abrahams E, Anderson P W, Licciardello D C and Ramakrishnan T V 1979 *Phys. Rev. Lett.* **42** 673
[26] Maciá E 2006 *Phys. Rev.* B **74** 245105
Maciá E and Roche S 2006 *Nanotechnology* **17** 3002
[27] Nitzan A 2001 *Annu. Rev. Phys. Chem.* **52** 681 and references there in
[28] O'Neill P, Parker A W, Plumb M A and Siebbeles L D A 2001 *J. Phys. Chem.* B **105** 5283
[29] Wei J H and Chan K S 2007 *J. Phys.: Condens. Matter* **19** 286101
[30] Cuniberti G, Craco L, Porath D and Dekker C 2002 *Phys. Rev.* B **65** 241314(R)
[31] Klotsa D, Römer R A and Turner M S 2005 *Biophys. J.* **89** 2187
[32] Brunaud G, Castet F, Fritsch A and Ducasse L 2003 *Phys. Chem. Chem. Phys.* **5** 2104
[33] Kohmoto M, Kadanoff L P and Tang C 1983 *Phys. Rev. Lett.* **50** 1870
[34] Hilke M 1997 *J. Phys. A: Math. Gen.* **30** L367
[35] Lazo E and Onell M E 2001 *Physica* B **299** 173
Lazo E and Onell M E 2001 *Phys. Lett.* A **283** 376
[36] de Moura F A B F *et al* 2003 *Eur. Phys. J.* B **36** 81
[37] Hilke M 2003 *Phys. Rev. Lett.* **91** 226403
[38] Yamada H 2004 *Phys. Lett.* A **332** 65
[39] MacKinnon A and Kramer B 1981 *Phys. Rev. Lett.* **47** 1546
Mookerjee A, Dasgupta I and Saha T 1995 *Int. J. Mod. Phys.* B **9** 2989
[40] Voityuc A A, Jortner J, Bixon M and Rösch N 2001 *J. Chem. Phys.* **114** 5614
[41] Natsume T, Dedachi K, Tanaka S, Higuchi T and Kurita N 2005 *Chem. Phys. Lett.* **408** 381
[42] Mehrez H and Anantram M P 2005 *Phys. Rev.* B **71** 115405
[43] Rakhmanova S V and Conwell E M 2001 *J. Phys. Chem.* B **105** 2056
Roche S and Maciá E 2004 *Mod. Phys. Lett.* B **18** 847
[44] Sugiyama H and Saito I 1996 *J. Am. Chem. Soc.* **118** 7063
[45] Altshuler B L 1987 *Jpn. J. Appl. Phys.* **26** (Suppl.) 1938
[46] Evangelou S N 1994 *Prog. Theor. Phys. Suppl. (Japan)* **116** 319
Evangelou S N and Argyrakis P 1995 *Phys. Rev.* B **51** 3489
[47] Voityuk A A 2005 *J. Chem. Phys.* **122** 204904
[48] Troisi A and Orlandi G 2002 *J. Phys. Chem.* B **106** 2093