Influence of backbone on the charge transport properties of G4-DNA molecules: a model-based calculation



2010 J. Phys.: Condens. Matter 22 065102

(http://iopscience.iop.org/0953-8984/22/6/065102)

J. Phys.: Condens. Matter **22** (2010) 065102 (7pp) doi:10.1088/0953-8984/22/6/065102

# Influence of backbone on the charge transport properties of G4-DNA molecules: a model-based calculation

**Ai-Min Guo, Zhi Yang, Hong-Jun Zhu and Shi-Jie Xiong**

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

Received 8 September 2009, in final form 16 December 2009
Published 21 January 2010
Online at stacks.iop.org/JPhysCM/22/065102

**Abstract**

We put forward a model Hamiltonian to describe the influence of backbone energetics on charge transport through guanine-quadruplex DNA (G4-DNA) molecules. Our analytical results show that an energy gap can be produced in the energy spectrum of G4-DNA by hybridization effects between the backbone and the base and by on-site energy difference of the backbone from the base. The environmental effects are investigated by introducing different types of disorder into the backbone sites. Our numerical results suggest that the localization length of G4-DNA can be significantly enhanced by increasing the backbone disorder degree when the environment-induced disorder is sufficiently large. There exists a backbone disorder-induced semiconducting–metallic transition in short G4-DNA molecules, where G4-DNA behaves as a semiconductor if the backbone disorder is weak and behaves as a conductor if the backbone disorder degree surpasses a critical value.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Double-stranded DNA (dsDNA) and its derivative guanine-quadruplex DNA (G4-DNA) have drawn extensive attention among different scientific communities over the past few decades and have been proposed as building blocks for molecular electronics [1–3]. Many works have focused on investigating the transport properties of the dsDNA molecules [3]. However, in comparison with the dsDNA, the G4-DNA exhibits several advantageous structural traits which are believed to improve the charge transport efficiency of molecular wires. The G4-DNA comprises a large number of stacked G quartets where each G quartet, as sketched in figure 1(a), is a planar aggregate of four hydrogen-bonded G nucleotides arranged in a square-like configuration. The stacking distance of 3.25 Å and the twist angle of 30° between consecutive G quartets are smaller than in the dsDNA, implying a better $\pi$–$\pi$ overlap along the stacking direction of the G4-DNA [4]. Additionally, the quadruple-helical conformation (see figure 1(b)) ensures that the G4-DNA is rather stable under physiological conditions as verified by NMR spectroscopy and x-ray crystallography [5, 6] and indicates higher stiffness and stronger resistance to surface forces than the dsDNA as revealed using atomic force microscopy [7]. On the other hand, the G4-DNA, including the G bases and the sugar-phosphate backbone, where the G base has the lowest ionization potential among the nucleobases, should exhibit efficient long-range charge transport properties [8, 9]. Many G-rich sequences, including telomeres, ribosomal DNA, minisatellites, and immunoglobulin heavy chain switch regions [10, 11], are capable of forming G4-DNA structures in vitro. The G4-DNA can be particularly important in the telomeric regions of all eukaryotic chromosomes as a target for anticancer agents [12, 13], and is an excellent prototype to study self-assembling properties at the supramolecular scale and the design of biomimetic systems [14] (for a review of the physicochemical and biological properties of G4-DNA, see [2]).

Because of the difficulty to synthesize the long G4-DNA samples, only a few studies have been devoted to investigating the electronic properties of the G4-DNA within the nanotechnology research community until now, despite the aforementioned appealing features. It was reported recently that the long monomolecular G4-DNA could be produced from parent poly(G)–poly(C) DNA molecules (C: cytosine) [7]

 

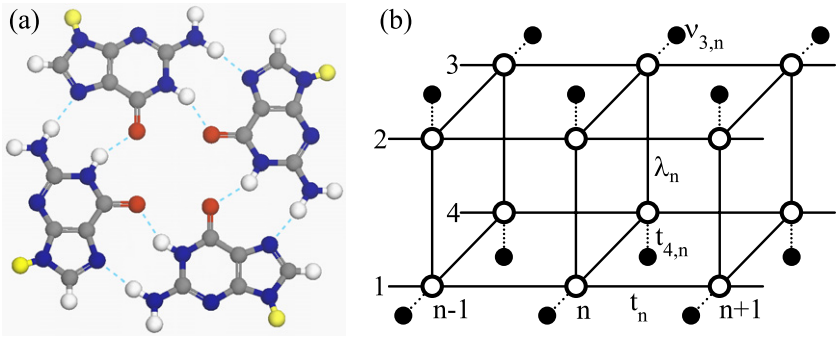


**Figure 1.** (a) Chemical structure of a G quartet which is the planar unit of G4-DNA. The white, gray, blue, and red spheres stand for H, C, N, and O atoms, respectively, while the yellow spheres stand for the sugar-phosphate backbone. The dashed sticks identify the hydrogen bonds. (b) Schematic illustration of G4-DNA. The open and closed circles represent the G base and the sugar-phosphate backbone, respectively.

and its polarizability was demonstrated by electrostatic force microscopy experiments [15]. The latter seems to support the viewpoint that the G4-DNA is better as a conducting molecular wire than the dsDNA [9, 15], since the dsDNA does not exhibit any observable polarizability signal. Theoretically, *ab initio* calculations have provided some valuable information about the electronic properties of the G4-DNA, e.g. the density of states in the presence of $K^+$ ions [16], the strain dependence of the electronic structure [14], and the dependence of the hopping integral on the stacking distance and on the twist angle [4]. However, *ab initio* calculations are currently restricted to rather short DNA molecules and thus a full systematic first principle analysis of their transport properties for realistic molecule length is precluded [14, 16, 17]. Therefore, model-based Hamiltonian methods can provide a complementary way by taking into account the effects of a single factor on charge transport through the G4-DNA at large length scales [9].

It is now widely accepted that to understand the transport properties of DNA molecules one should consider the contributions coming from the backbone system and the environment [18–23]. Accordingly, in this paper we propose an effective tight-binding Hamiltonian, including the sugar-phosphate backbone, to mimic the G4-DNA and explicitly address the influence of backbone energetics on the charge transport properties of the G4-DNA for this model, where each base and backbone site contributes one orbital. Our analytical results show that the homogeneous G4-DNA exhibits semiconducting behavior and the width of the energy gap, separating highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), is very sensitive to the model parameters. When the environmental complications which are simulated by introducing different types of disorder into the backbone sites are considered, we find that the backbone disorder can enhance the charge transport ability of the G4-DNA when the environment-induced disorder is sufficiently large and a new transmission band will appear in the energy gap. A backbone disorder-induced semiconducting–metallic transition is observed in short G4-DNA molecules. These results open perspectives for experimental work which intends to control the charge transport through nanodevices based on synthetic DNA molecules.

The paper is organized as follows. In section 2, an effective tight-binding model containing the backbone sites is introduced to simulate the charge transport through the G4-DNA and the electronic band structure is discussed for this model. In section 3, the transport properties of the G4-DNA are studied in the presence of backbone disorder, while in section 4 the transmission coefficient and the current–voltage ($I$–$V$) characteristics are presented. Finally, the results are summarized in section 5.

## 2. Model and electronic band structure

Our Hamiltonian is an effective tight-binding model, where each base or backbone is treated as a single lattice point and no charge transport is permissible along the backbone sites [19], namely,

$$\mathcal{H} = -\sum_n \left( \sum_j t_n c^\dagger_{j,n} c_{j,n+1} + \sum_{\langle i,j \rangle} \lambda_n c^\dagger_{i,n} c_{j,n} + \text{h.c.} \right) + \sum_{n,j} \nu_{j,n} b^\dagger_{j,n} b_{j,n} - \sum_{n,j} t_{j,n} (b^\dagger_{j,n} c_{j,n} + \text{h.c.}), \quad (1)$$

where the operator $c^\dagger_{j,n}$ ($b^\dagger_{j,n}$) creates a charge at the base (backbone) site with subscript $j \in [1, 4]$ labeling a chain and subscript $n \in [1, N]$ labeling a G quartet and the on-site energy at the base site is taken as the energy reference point. $\langle \cdots \rangle$ stands for a sum over the nearest-neighbor sites. $\nu_{j,n}$ is the on-site energy of the backbone site, $t_n$ ($\lambda_n$) is the intrachain (interchain) hopping integral, and $t_{j,n}$ is the hopping integral between the base and backbone sites. Figure 1(b) shows a schematic illustration of a fragment of the G4-DNA within the dangling backbone model. It is worth mentioning that similar models, including the dangling backbone sites, have been extensively adopted to investigate the transport properties of the dsDNA molecules [18–23], where the obtained results can provide a qualitative even quantitative explanation of the experimental data. We expect that the transport properties of the G4-DNA molecules can be analyzed in great detail within the framework of the effective tight-binding Hamiltonian given by equation (1).

For a homogeneous G4-DNA chain with $\nu_{j,n} = \nu$, $t_n = t$, $\lambda_n = \lambda$, and $t_{j,n} = t_b$, the Hamiltonian of equation (1) can be

diagonalized and the expression for the dispersion relation is obtained analytically:

$$E_1^{\pm}(k) = \frac{\nu}{2} + \lambda - t\cos k \pm \sqrt{\left(\frac{\nu}{2} - \lambda + t\cos k\right)^2 + t_b^2}, \quad (2a)$$

$$E_2^{\pm}(k) = \frac{\nu}{2} - t\cos k \pm \sqrt{\left(\frac{\nu}{2} + t\cos k\right)^2 + t_b^2}, \quad (2b)$$

$$E_3^{\pm}(k) = \frac{\nu}{2} - \lambda - t\cos k \pm \sqrt{\left(\frac{\nu}{2} + \lambda + t\cos k\right)^2 + t_b^2}, \quad (2c)$$

where there exist two superposed energy bands in the energy range determined by equation (2*b*). From equation (2) one realizes that the energy spectrum consists of six isolated subbands provided $\lambda > 2t$. By adopting the critical condition of $\lambda \leqslant 2t$, however, the six subbands are merged into HOMO ($E_-$) and LUMO ($E_+$). In this case, the energy spectrum of the G4-DNA is written as

$$E_{\pm} \in \left[\frac{\nu}{2} - \lambda - t \pm \sqrt{\left(\frac{\nu}{2} + \lambda + t\right)^2 + t_b^2}, \frac{\nu}{2} + \lambda + t \pm \sqrt{\left(\frac{\nu}{2} - \lambda - t\right)^2 + t_b^2}\right], \quad (3)$$

which are separated by an energy gap of width

$$E_g = \sqrt{\left(\frac{\nu}{2} + \lambda + t\right)^2 + t_b^2} + \sqrt{\left(\frac{\nu}{2} - \lambda - t\right)^2 + t_b^2} - 2(\lambda + t). \quad (4)$$

By inspecting equation (4) one notices that the backbone-related factors, including the hybridization between the backbone and the base and the on-site energy difference of the backbone from the base, determine the gap opening in the G4-DNA molecules. For fixed value of $\lambda + t$ the gap width increases with increasing the absolute value of $|t_b|$ or of $|\nu|$, while for fixed values of $t_b$ and $\nu$ it decreases with increasing $\lambda + t$. This provides a qualitative explanation to the gap width variability of the G4-DNA induced by the axial strain [14], because the intrachain hopping integral is very sensitive to the stacking distance and the twist angle between neighboring G quartets [4]. In figure 2, we show the dispersion relation for the homogeneous G4-DNA with backbone and without backbone by employing $\nu = 0$ eV, $\lambda = 2t = 0.4$ eV, and $t_b = 0.7$ eV [18]. The parameters are also consistent with *ab initio* calculations [4, 24] and will be used throughout the paper. As one can see, the backbone can yield an energy gap in the center of the energy spectrum of the G4-DNA and the gap width is smaller than in the poly(G)–poly(C) molecules. Therefore, our analytical results show that the backbone plays a crucial role in the transport properties of the G4-DNA and the homogeneous G4-DNA should exhibit semiconducting behavior. This is consistent with the results reported in [14, 16].

Because of its negatively charged phosphates and its outmost location in the quadruple-helical structure, the backbone will be more easily affected by the environmental conditions than other parts of the G4-DNA. In aqueous buffer solutions, the backbone has a propensity to interact with

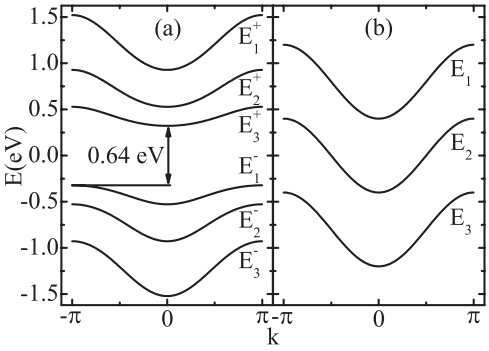


**Figure 2.** Dispersion relation for homogeneous G4-DNA (a) with backbone and (b) without backbone. Here 'without backbone' means that the last two terms should be eliminated from equation (1). The parameters are $\nu = 0$ eV, $\lambda = 2t = 0.4$ eV, and $t_b = 0.7$ eV.

counterions and solute molecules and these interactions can lead to variations in the on-site energies $\nu_{j,n}$ [19, 22, 23, 25]. Even for a dried G4-DNA, the backbone's conformation can be quite different in various experiments because a few counterions and water molecules may still randomly reside on the phosphates of the backbone. Additionally, the backbone can interact with the substrate which may contain impurities on its surface and the on-site energies $\nu_{j,n}$ can be modulated. Different experimental situations will result in different modifications of the backbone's electronic structure, and it may be appropriate to model these by choosing different distribution functions for the on-site energies $\nu_{j,n}$, e.g. uniform disorder $\nu_{j,n} \in [-\frac{W}{2}, \frac{W}{2}]$ or binary disorder $\nu_{j,n} = \pm\frac{W}{2}$ [19, 22, 23]. Here $W$ is the backbone disorder degree and $\langle \nu_{i,m}\nu_{j,n}\rangle = \langle \nu_{j,n}^2\rangle \delta_{i,j}\delta_{m,n}$. We restrict ourselves to static disorder as we consider the low temperature case and neglect the thermal-fluctuation-induced disorder [26, 27]. The transport properties of this quasi-one-dimensional (1D) tight-binding model can be conveniently calculated by using the transfer-matrix method, which allows us to calculate the localization length $\Lambda$ (the inverse of the smallest Lyapunov coefficient $\gamma$) of the G4-DNA. To avoid the terrible overflow of multiplication of transfer matrices, we perform the standard method of Gram–Schmidt reorthonormalization after every ten transfer-matrix multiplications [28]. This method has been widely used to calculate the transport properties of other quasi-1D and two-dimensional (2D) systems [9, 28, 29].

## 3. Effects of backbone disorder

Figure 3(a) shows the localization length $\Lambda$ versus energy $E$ for the G4-DNA with different degrees of binary backbone disorder $W$. As a comparison, figure 3(b) shows $\Lambda$ versus $E$ for the poly(G)–poly(C), which is one of the most conductive dsDNA molecules (other artificial DNA sequences with long-range correlations also exhibit high charge transport efficiency, see [30–33]) and can be simulated by the dangling backbone ladder model with the on-site energies $\varepsilon_G = 0$ eV and $\varepsilon_C = 1.12$ eV [21–23]. Contrary to the localization picture that the conduction of a quantum wire will be further suppressed when the disorder degree is increased, from figure 3 it can be

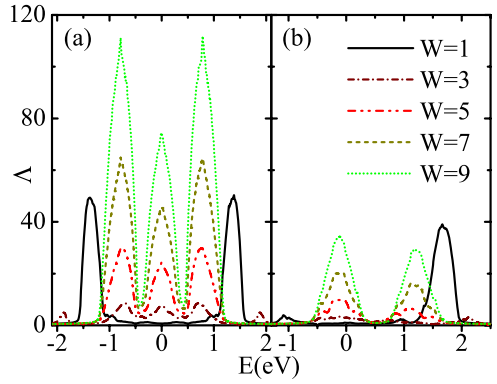


**Figure 3.** Energy-dependent localization length Λ for (a) G4-DNA and for (b) poly(G)–poly(C) in the presence of the binary backbone disorder with different degrees $W$ and length $N = 10^6$.

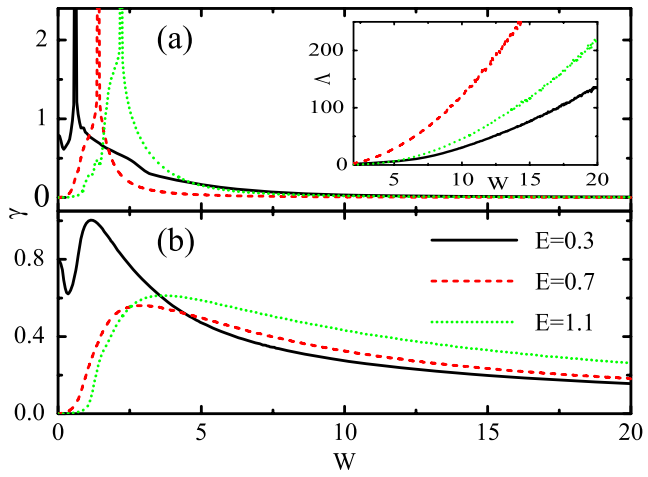


**Figure 4.** Lyapunov coefficient $\gamma$ versus backbone disorder degree $W$ for G4-DNA by considering (a) the binary backbone disorder and (b) the uniform backbone disorder for $E = 0.3$, 0.7, and 1.1 eV. Inset: localization length Λ versus $W$ for G4-DNA by considering the binary backbone disorder. Here $N = 10^6$.

seen that the localization length is significantly enhanced by increasing $W$ in a broad energy range for both DNA molecules. On the other hand, for all values of $W$, the localization length of the G4-DNA is larger than that of the poly(G)–poly(C) over almost the whole energy spectrum, suggesting that the G4-DNA is potentially better as a conducting molecular wire than the dsDNA molecules. This is consistent with the experimental results [15] and the theoretical calculations [9].

In order to further illustrate the effects of backbone disorder on the transport properties of the G4-DNA, in figure 4 we plot the Lyapunov coefficient $\gamma$ versus the backbone disorder degree $W$ for the G4-DNA with $E = 0.3$, 0.7, and 1.1 eV by considering two types of backbone disorder. From figure 4 it can be seen that a nonmonotonous behavior of $\gamma$ versus $W$ is found for the G4-DNA by taking into account either the binary backbone disorder or the uniform backbone disorder. In all curves, there exists a crossover $W_c$ for the backbone disorder degree that the Lyapunov coefficient increases with increasing $W$ for $W < W_c$ and decreases with increasing $W$ for $W > W_c$. Nevertheless, for the energies which are located in the band gap and are close to the boundaries $E = \frac{\nu}{2} \mp (\lambda + t) \pm \sqrt{[\frac{\nu}{2} \pm (\lambda + t)]^2 + t_b^2}$, separating the conducting and nonconducting states for the homogeneous G4-DNA (see equation (3)), we find that the corresponding Lyapunov coefficient is at first attenuated by increasing $W$ and then follows the aforementioned behavior (see the curves with $E = 0.3$ eV in figure 4). This is due to the increasing density of states with $W$ at small $W$ and to the dimensionality effects in the G4-DNA. The crossover $W_c$ is very sensitive to the energy and to types of backbone disorder.

This disorder-induced enhancement of charge transport ability may be understood as follows. By decimation of the backbone sites the effective tight-binding Hamiltonian described in equation (1) can be written as

$$(\varepsilon_{j,n}^{r} - E)\psi_{j,n} = t(\psi_{j,n-1} + \psi_{j,n+1}) + \lambda(\psi_{j-1,n} + \psi_{j+1,n}), \tag{5}$$

where $\psi_{j,n}$ is the amplitude of the wavefunction at the $n$th base site of the $j$th chain and $\varepsilon_{j,n}^{r}$ is the renormalized on-site energy with

$$\varepsilon_{j,n}^{r} = t_b^2/(E - \nu_{j,n}). \tag{6}$$

As a matter of fact, the renormalized sites with on-site energy $\varepsilon_{j,n}^{r}$ act as potential barriers if $\varepsilon_{j,n}^{r} > E$ and as potential wells if $\varepsilon_{j,n}^{r} < E$. By inspecting equations (5) and (6), one realizes that the charge transmission probability can be strongly reduced at the sites with $|\varepsilon_{j,n}^{r}| \gg E$, i.e. the effective localized states that can strongly scatter the conduction states in the G4-DNA should come from disordered backbone sites with $\nu_{j,n}$ in a neighborhood of $E$. We can define this neighborhood as $U(E, \delta) = \{x | E - \delta < x < E + \delta\}$ with the characteristic length $\delta$. As $\nu_{j,n}$ approaches $E$, the renormalized on-site energy $\varepsilon_{j,n}^{r}$ approaches $\infty$ and the electrons (holes) will be completely reflected at site $(j, n)$. This is the so-called antiresonant effect [34, 35]. Accordingly, in view of an electron with eigenenergy $E$ propagating through the G4-DNA, the wavefunction will be effectively cut at the base site which connects the backbone site with $\nu_{j,n}$ locating in a neighborhood of $E$. Therefore, the average distance of two nearest renormalized sites with $\nu_{j,n} \in U(E, \delta)$ gives an approximate estimation of the localization length of the G4-DNA. For $W < 2|E| + 2\delta$, the number of backbone sites with $\nu_{j,n} \in U(E, \delta)$ will be increased by increasing $W$ and leads to the decrease of the localization length at small $W$. In contrast, when the backbone disorder degree is large enough that the energy range of $\varepsilon_{j,n}^{r}$ covers this neighborhood ($W > 2|E| + 2\delta$), the number of backbone sites with $\nu_{j,n} \in U(E, \delta)$ will be reduced by increasing $W$ and can result in the enhancement of the localization length at large $W$. These results suggest that the backbone disorder crossover can be related to the characteristic length by $W_c = 2|E| + 2\delta$ and the charge transport ability of the G4-DNA molecules will increase with increasing $W$ when the environment-induced disorder is sufficiently large. Although it is difficult to determine $\delta$ from equation (6), we expect that the characteristic length may strongly depend upon $E$, $t_b$, and types of backbone disorder, and the dependence of $W_c$ on $E$ can be approximated as $W_c \sim 2|E|$ provided the characteristic length approaches zero.

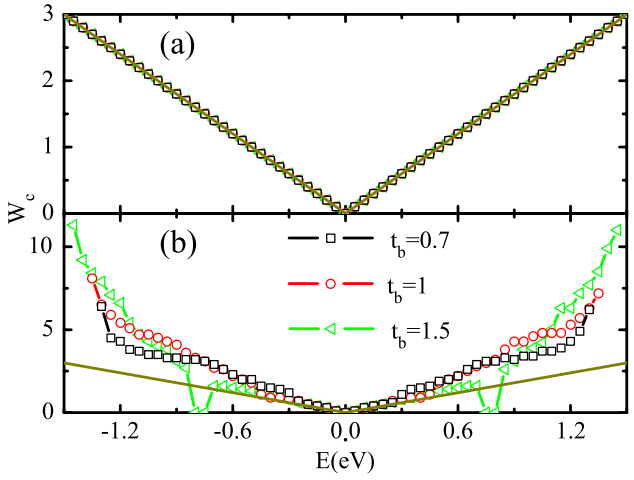


**Figure 5.** Energy-dependent backbone disorder crossover $W_c$ for G4-DNA by considering (a) the binary backbone disorder and (b) the uniform backbone disorder with several values of $t_b$. The solid lines represent the function: $W_c = 2|E|$.

In figure 5, we plot the backbone disorder crossover $W_c$ versus energy $E$ for the G4-DNA with several values of $t_b$ by considering two types of backbone disorder. As we can see, the behavior of $W_c$ versus $E$ exhibits a general '$\vee$' shape for the G4-DNA by taking into account either the binary backbone disorder or the uniform backbone disorder. In the former case, the '$\vee$' shapes superpose with each other and exactly follow the relation $W = 2|E|$ for whatever the value of $t_b$ (figure 5(a)), implying that the characteristic length is $\delta = 0$. In the latter case, however, the '$\vee$' shapes are different for different values of $t_b$ and the crossover $W_c$ will strongly deviate from $2|E|$ if the energy is quite close to the outer band edge, i.e. $E_{+\max}$ and $E_{-\min}$ of equation (3) (figure 5(b)), suggesting that the characteristic length dramatically depends upon $E$ and $t_b$. Therefore, for a given value of Fermi energy, we come to the conclusion that the backbone disorder-induced enhancement of transport may be a generic feature for the G4-DNA by properly tuning the environmental conditions.

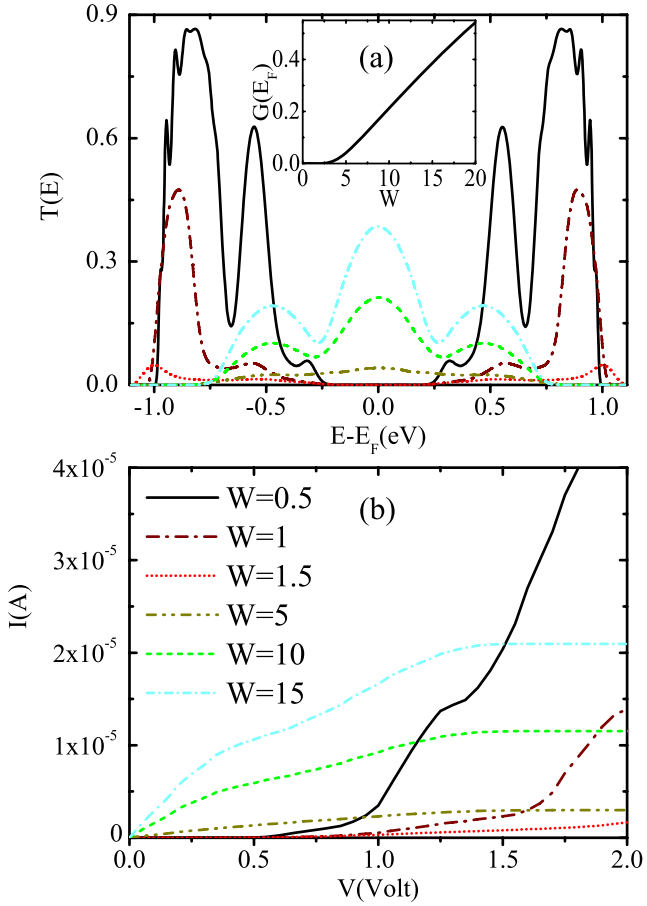


**Figure 6.** (a) Energy-dependent transmission coefficient $T(E)$ and (b) the corresponding current–voltage curves for G4-DNA with different degrees of uniform backbone disorder $W$. The Fermi energy, located in the middle of the band gap for homogeneous G4-DNA, is $E_F = 0$ eV and will not be changed with $W$ because the on-site energy of the backbone is assumed to be randomly distributed around zero. The inset shows the Landauer conductance (in units of $2e^2/h$) versus $W$ at the Fermi energy. Other parameters are $\lambda = 2t = 0.24$ eV, $t_b = 0.5$ eV, and $N = 10$, consistent with *ab initio* calculations [41–43]. The results are averaged over 200 000 configurations of backbone disorder.

## 4. Transmission coefficient and current–voltage characteristics

Since charge transport experiments usually focused on relatively short DNA molecules and measured the $I$–$V$ characteristics [36–38], in this section we numerically calculate the transmission coefficient and the $I$–$V$ characteristics of short G4-DNA molecules. It is reasonable to assume that the ends of the G4-DNA are attached to two semi-infinite quasi-1D electrodes with on-site energies $\varepsilon_m = 0$ eV and hopping integral $t_m = 4$ eV [9]. Then, the $I$–$V$ characteristics can be calculated by using the standard Landauer–Büttiker formula:

$$I = \frac{2e}{h}\int_{-\infty}^{+\infty} T(E)[f_L(E) - f_R(E)]\,\mathrm{d}E, \qquad (7)$$

where $f_{L/R}(E) = \{1 + \exp[(E \mp eV/2 - E_F)/k_BT]\}^{-1}$ is the Fermi distribution function, and $T(E)$ is the transmission coefficient which is related to the Landauer conductance $G(E) = G_0T(E)$ with the quantum conductance $G_0 = 2e^2/h$ [39]. $V$ is the bias voltage, $E_F$ is the equilibrium Fermi energy, and the temperature $T$ is set to 10 K. To minimize the contact effects, we assume an appropriate coupling $\tau = \sqrt{tt_m}$ between the electrodes and the G4-DNA [9, 40].

Figures 6(a) and (b) show the transmission coefficient $T(E)$ and $I$–$V$ curves, respectively, for the short G4-DNA molecules ($N = 10$) with different degrees of uniform backbone disorder $W$ by adopting $\lambda = 2t = 0.24$ eV [41–43] and $t_b = 0.5$ eV [18]. The results are averaged over 200 000 configurations of backbone disorder. By inspecting figure 6(a), one realizes that the transmission spectra of the G4-DNA can be classified into two distinguishable groups for different backbone disorder degrees. (i) In the case of small $W$, there are two transmission bands which are symmetrically distributed around the Fermi energy and are separated by an energy gap. The transmission coefficient,

especially for the states near the energy gap, is decreased by increasing $W$ and the most conducting state in the right (left) transmission band is shifted toward higher (lower) energy. The gap width has little to do with the backbone disorder degree. (ii) In the case of large $W$, the two side transmission bands vanish and a new transmission band emerges around the Fermi energy, suggesting that the environmental effects may induce an additional transport channel in the energy gap. This is consistent with the results obtained from the dsDNA molecules by using *ab initio* calculations [1, 38]. The transmission coefficient gradually increases with increasing $W$. Since electrons around the Fermi energy determine the charge transport properties of the G4-DNA, it would be important to plot the Landauer conductance versus $W$ at the Fermi energy. From the inset of figure 6(a), we can see that the Landauer conductance is approximately proportional to the backbone disorder degree at large $W$. Thus one can observe the backbone disorder-induced semiconducting–metallic transition in short G4-DNA molecules, as is further illustrated in figure 3(b). For small $W$, a voltage gap emerges in the nonlinear $I$–$V$ curves and increases slowly with increasing $W$, while for large $W$, the voltage gap vanishes and the current is dramatically enhanced by increasing $W$. Therefore, our numerical results suggest that the G4-DNA exhibits semiconducting behavior when the environment-induced disorder is weak and shows metallic behavior when the environment-induced disorder is sufficiently large.

## 5. Conclusions

We study the influence of backbone energetics on the charge transport through the G4-DNA molecules based on an effective tight-binding model, where each G base and backbone contributes one orbital. The hybridization between the backbone and the G base and the on-site energy difference of the backbone site from the G base can yield a band gap in the energy spectrum of the G4-DNA and consequently the homogeneous G4-DNA behaves as a semiconductor. We also investigate the environmental effects by introducing different types of disorder into the backbone sites, because the phosphates are negatively charged and the backbone is located in the external region of the G4-DNA. Our numerical results suggest that the backbone disorder plays an important role in the transport properties of the G4-DNA. There exists a crossover $W_c$ for the backbone disorder $W$ that the localization length decreases with increasing $W$ for $W < W_c$ and increases with increasing $W$ for $W > W_c$. Additionally, the localization length of the G4-DNA is larger than that of the poly(G)–poly(C), suggesting that the G4-DNA is a better candidate as a conducting molecular wire than the dsDNA molecules. A backbone disorder-induced semiconducting–metallic transition is observed in short G4-DNA molecules, where the G4-DNA behaves as a semiconductor when the backbone disorder is small and behaves as a conductor when the backbone disorder is sufficiently large. Since the alkali cations are favorable for the formation of the G4-DNA and are small enough to be accommodated at the core of the quadruple-helical structure, we believe that these cations can further enhance the charge transport ability of the G4-DNA molecules. This will be further considered in the future work.

## Acknowledgments

This work was supported by the State Key Programs for Basic Research of China (grant Nos 2005CB623605 and 2006CB921803), and by the National Foundation of Natural Science in China grant Nos 10874071 and 60676056.

## References

[1] Endres R G, Cox D L and Singh R R P 2004 *Rev. Mod. Phys.* **76** 195
[2] Davis J T 2004 *Angew. Chem. Int. Edn* **43** 688
[3] Chakraborty T (ed) 2007 *Charge Migration in DNA: Perspectives from Physics, Chemistry and Biology* (Berlin: Springer)
[4] Kubař T, Woiczikowski P B, Cuniberti G and Elstner M 2008 *J. Phys. Chem.* B **112** 7937
[5] Smith F W and Feigon J 1992 *Nature* **356** 164
[6] Aboul-ela F, Murchie A I H and Lilley D M J 1992 *Nature* **360** 280
[7] Kotlyar A B, Borovok N, Molotsky T, Cohen H, Shapir E and Porath D 2005 *Adv. Mater.* **17** 1901
[8] Delaney S and Barton J K 2003 *Biochemistry* **42** 14159
[9] Guo A-M and Xiong S-J 2009 *Phys. Rev.* B **80** 035115
[10] Kee K, Niu L and Henderson E 1998 *Biochemistry* **37** 4224
[11] Hershman S G, Chen Q, Lee J Y, Kozak M L, Yue P, Wang L S and Johnson F B 2007 *Nucleic Acids Res.* **36** 144
[12] Črnugelj M, Hud N V and Plavec J 2002 *J. Mol. Biol.* **320** 911
[13] Lee J Y, Okumus B, Kim D S and Ha T 2005 *Proc. Natl Acad. Sci. USA* **102** 18938
[14] Di Felice R, Calzolari A, Garbesi A, Alexandre S S and Soler J M 2005 *J. Phys. Chem.* B **109** 22301
[15] Cohen H, Sapir T, Borovok N, Molotsky T, Di Felice R, Kotlyar A B and Porath D 2007 *Nano Lett.* **7** 981
[16] Calzolari A, Di Felice R, Molinari E and Garbesi A 2002 *Appl. Phys. Lett.* **80** 3331
[17] Tsukamoto T, Ishikawa Y, Sengoku Y and Kurita N 2009 *Chem. Phys. Lett.* **474** 362
[18] Cuniberti G, Craco L, Porath D and Dekker C 2002 *Phys. Rev.* B **65** 241314(R)
[19] Klotsa D, Römer R A and Turner M S 2005 *Biophys. J.* **89** 2187
[20] Maciá E and Roche S 2006 *Nanotechnology* **17** 3002
[21] Shih C-T, Roche S and Römer R A 2008 *Phys. Rev. Lett.* **100** 018105
[22] Díaz E 2008 *J. Chem. Phys.* **128** 175101
[23] Guo A-M, Xiong S-J, Yang Z and Zhu H-J 2008 *Phys. Rev.* E **78** 061922
[24] Yan Y J and Zhang H Y 2002 *J. Theor. Comput. Chem.* **1** 225
[25] Barnett R N, Cleveland C L, Joy A, Landman U and Schuster G B 2001 *Science* **294** 567
[26] Kornyshev A A, Lee D J, Leikin S and Wynveen A 2007 *Rev. Mod. Phys.* **79** 943
[27] Wynveen A, Lee D J, Kornyshev A A and Leikin S 2008 *Nucleic Acids Res.* **36** 5540
[28] MacKinnon A and Kramer B 1983 *Z. Phys.* B **53** 1
[29] Slevin K, Asada Y and Deych L I 2004 *Phys. Rev.* B **70** 054201
[30] Carpena P, Bernaola-Galván P, Ivanov P Ch and Stanley H E 2002 *Nature* **418** 955
[31] Roche S, Bicout D, Maciá E and Kats E 2003 *Phys. Rev. Lett.* **91** 228101
[32] Albuquerque E L, Vasconcelos M S, Lyra M L and de Moura F A B F 2005 *Phys. Rev.* E **71** 021910
[33] Guo A-M 2007 *Phys. Rev.* E **75** 061915

[34] Wang X R, Wang Y and Sun Z Z 2002 *Phys. Rev.* B **65** 193402
[35] Xiong G 2007 *Phys. Rev.* B **76** 153303
[36] Xu B, Zhang P, Li X and Tao N 2004 *Nano Lett.* **4** 1105
[37] Cohen H, Nogues C, Naaman R and Porath D 2005 *Proc. Natl Acad. Sci. USA* **102** 11589
[38] Shapir E, Cohen H, Calzolari A, Cavazzoni C, Ryndyk D A, Cuniberti G, Kotlyar A, Di Felice R and Porath D 2008 *Nat. Mater.* **7** 68
[39] Büttiker M, Imry Y, Landauer R and Pinhas S 1985 *Phys. Rev.* B **31** 6207
[40] Maciá E, Triozon F and Roche S 2005 *Phys. Rev.* B **71** 113106
[41] Voityuk A A, Jortner J, Bixon M and Rösch N 2001 *J. Chem. Phys.* **114** 5614
[42] Mehrez H and Anantram M P 2005 *Phys. Rev.* B **71** 115405
[43] Senthilkumar K, Grozema F C, Guerra C F, Bickelhaupt F M, Lewis F D, Berlin Y A, Ratner M A and Siebbeles L D A 2005 *J. Am. Chem. Soc.* **127** 14894