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Charge transport in polyguanine–polycytosine DNA molecules

J H Wei^{1,2} and K S Chan¹

¹ Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China

² Department of Physics, Shangdong University, Shangdong, People's Republic of China

E-mail: apkschan@cityu.edu.hk

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Abstract

A double chain tight-binding model is proposed to interpret the experimental I – V curves for polyguanine–polycytosine DNA molecules reported in Porath *et al* (2000 *Nature* **493** 635). The proposed model includes the salient features of existing transport models of DNA molecules. The proposed double chain model fits excellently with the experimental I – V curves and provides a theoretical interpretation of features found in the I – V curves, which so far do not have a satisfactory explanation. Steps in the I – V curves are explained as the result of transmission gaps caused by hybridization with reservoirs and inter-chain coupling. Variations in I – V curves are due to the variation of inter-chain and intra-chain hopping parameters caused by structural changes in the DNA molecules.

1. Introduction

DNA molecules are the subject of intense research, not only as important molecules of life but also as basic building blocks in molecular electronics [1]. The chemical behaviour of DNA molecules offers the potential of their use as assembly templates in nano-circuit fabrication [2]. The capability of conducting charges through DNA molecules makes it attractive to use DNA molecules as circuit components with self-assembly capability. As a result, a number of experimental [3–7] and theoretical studies [8–15] have been carried out on the charge transport properties of DNA molecules. Despite these extensive efforts, there are still controversies and unexplained features due to the complexity of the subject, such as sensitivity to environment and structural stability of the molecule. An experimental study carried out by Porath *et al* [3] shows that polyguanine–polycytosine DNA has an electronic structure like a semiconductor as there is a voltage gap in the current–voltage (I – V) characteristics. The widely accepted explanation for the observed I – V curves of DNA molecules is coherent transport through hybridized π orbitals of the bases. However, existing theoretical models used to interpret the

experiments disagree in some important aspects, such as the π orbitals involved in charge conduction and the energy alignment of the orbitals. Below we will discuss in more detail the differences between these models. For these controversies, it is hard to claim at this stage that there is a complete picture of charge transport in DNA molecules. To advance our understanding of this problem, it is necessary to have a model which does not have the drawbacks of the other models. Most importantly, the model should be able to fit experiments and extract useful information about the transport mechanism for comparison between experiments or *ab initio* calculations. The objective of the present study is to propose such a model and analyse some experimental results reported in Porath *et al* [3].

Before we discuss our model, it is useful to review the important features of models which have been used to explain the experimental results of Porath *et al* [3]. Li and Yan [8] consider a one-dimensional tight-binding model for the hybridized molecular orbitals of the G–C base pairs. The molecular orbital of a G–C base pair responsible for charge transport is represented by one tight-binding orbital in the model. The effect of scattering is included in the model by attaching reservoirs to the sites. The voltage gap in the I – V curve is explained by the energy separation between the metal lead Fermi level and the hybridized molecular levels. Hjort and Stafstrom [9] include the π orbitals of both G and C bases in a tight-binding model and attribute some step-like features in the I – V curves to the energy difference between these two hybridized π orbitals. In this double chain model, the π orbitals of the G and C bases are not coupled to each other and there are two independent conduction channels formed by these orbitals. The voltage gap found experimentally is explained by the separation between the metal lead Fermi level and the hybridized G π orbitals. Cuniberti *et al* [10] proposed a model in which the G π orbitals not only hybridize among themselves but also with other structural units in the molecule, for example, the sugar groups in the backbone. They explain the voltage gap as the result of the hybridization of the G π orbitals with the backbone sugar groups and the inter-chain hybridization with C base molecular orbitals. To agree with experiment, they assume the metal Fermi level is in the middle of the gap opened up by hybridization with backbone groups and C bases. This assumption does not agree with other models which assume that the metal Fermi level lies above the hybridized π orbitals of G bases. Iguchi [11] proposed a double chain tight-binding model in which inter-chain hopping is possible between the orbitals of G and C bases bonded by hydrogen bonding. All these models agree in some aspects of the transport mechanism and disagree in other aspects. They can explain some important features of the experimental results with different points of view. Recently, the effect of counterions on the properties of DNA molecules has been investigated in [16–18]. The counterions can modify the DNA properties, shift the on-site potential of the π stack or form an additional conduction channel.

In view of these controversies between different theoretical models, we therefore propose a double chain tight-binding model, which includes the salient features of these models and uses parameters in agreement with existing experimental and theoretical studies. In this tight-binding model, both the G and C π orbitals are included as conduction channels and the metal Fermi level lies above the G orbital. G–C π orbital hybridization, backbone hybridization, scattering effect due to the environment and possible charge transfer to the environment (i.e. the counterions), which are described in the last paragraph, are also included in the model. In the present model, the variation of the molecular energy levels and the metal Fermi level is limited to certain ranges which are in agreement with those values obtained in other studies. Other parameters which depend on the experimental conditions, such as the hybridization strength, are then varied to fit with experimental results. With such a modelling scheme one can extract useful information about the hybridization strengths and the electronic structure of the molecule from the experimental results, which is an important step in understanding the important factors

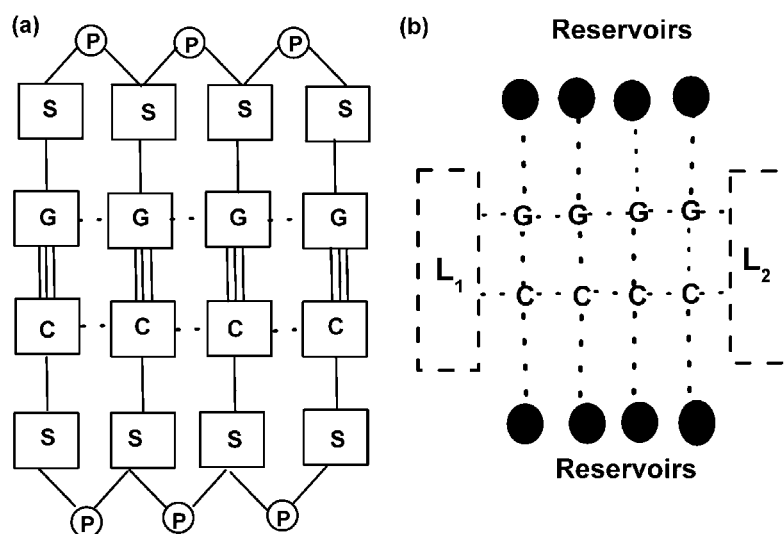


Figure 1. (a) Schematic diagram of the structure of a polyguanine-polycytosine DNA molecule. G (C) denotes guanine (cytosine) groups and S (P) denotes sugar (phosphate) groups. (b) Schematic diagram for the coupling (represented by dotted lines) between π orbitals, metal contact and hybridization reservoirs. G (C) denotes a π orbital on the guanine (cytosine) group. The black ovals denote the reservoirs. L_1 and L_2 are the metal contacts.

that influence the charge transport in DNA. The organization of this paper is as follows. In section 2, we discuss in detail the model and the calculation method. In section 3, the fitting results are discussed and interpreted. The paper is concluded in section 4.

2. Model

DNA is a normally double stranded macromolecule consisting of two polynucleotide chains held together by weak thermodynamic forces [19]. The coupling between the bases of a DNA double helix is as follows: A couples to T on the opposite strand through two hydrogen bonds and G couples to C on the opposite strand with three hydrogen bonds. Through this pairing arrangement the famous DNA double helix structure is formed. Instead of natural DNA molecules, Porath *et al* [3] studied experimentally polyguanine-polycytosine DNA molecules consisting of 30 consecutive GC base pairs. According to the theoretical point of view discussed in the introduction, we should start with a theoretical model which includes all the bonding and hopping coupling in the molecule and then fit the model with experimental results to extract useful information about charge transport in DNA molecules. Therefore it is more reasonable to treat a poly(G)–poly(C) DNA molecule as two one-dimensional base chains bonded to each other through hydrogen bonding, as schematically shown in figure 1(a), instead of treating the two chains of base molecules as two isolating chains conducting electrical current independently. In figure 1(a), the G bases are bonded to the corresponding C bases of another chain by hydrogen bonding. All the G and C bases are held in place by covalent bonding to the backbone sugar and phosphate groups. The dotted line joining the neighbouring G or C bases represents the hopping coupling, by which electrons can travel from one orbital to another.

In figure 1(b), a schematic diagram is given of the π orbitals of the bases participating in charge transport and how they interact with neighbouring π orbitals through hopping coupling

(represented by dotted line in the figure) in our proposed model. We include the hopping coupling between two chains as the bases of two chains are bonded to each other by hydrogen bonding and it is possible for electrons to hop from one chain to another. At the moment, there is limited information about the inter-chain hopping strength available in the literature. We believe that by fitting our model to experiments we can find the inter-chain hopping strength. The coupling strength between neighbouring orbitals of the same chain is different from the coupling strength between orbitals on different chains owing to the differences in distances separating these orbitals. In our proposed model, the orbitals are also coupled to reservoirs as described in Li and Yan [8], to account for the hybridization interaction with the backbone sugar groups as considered in [10] as well as the environmental effects. According to Cuniberti *et al* [10] the G and C bases are also coupled to the backbone sugar groups (in [10] it is referred to as hybridization coupling), which are modelled by attaching to each base a single tight-binding site by a hopping coupling term. For DNA molecules in dielectric surroundings the environment effect may not be negligible; for example, in a solvent, the polarizable and/or counterion surroundings are crucial for their stability and may have effects on the charge transport and other properties. The polarizable solvent environment also has an effect on electron transfer dynamics in some biological processes, which have been studied in [20, 21]. Some studies of the effects of counterions on DNA molecules have been reported in [16–18]. Even under dry conditions, there are still some counterions left from the synthesizing procedure and their scattering effects, as well as other environmental scattering effects, and these can be included by a reservoir term in the model. We notice that, mathematically, the hybridization coupling to the backbone sugar group is equivalent to a semi-infinite tight-binding chain with the intra-chain hopping term equal to zero. When the intra-chain hopping term is small, the semi-infinite tight-binding chain has more than one energy level distributed in a narrow energy range and this enables the term to describe the hybridization with a group of energy levels. Hereafter, to simplify the discussion, we refer to this term as the hybridization term and the semi-infinite chains as reservoirs. One of the important features of the present model is the use of this hybridization term to represent the effects of these three mechanisms so that the model can be used to fit experiments to extract useful information about these mechanisms. Although our knowledge of the hybridization interactions is limited, the existence of these interactions is indirectly confirmed by the variations in the experimental I – V curves. A possible approach to finding their strengths is *ab initio* calculation, but not much progress has been made in this direction, possibly due to the problem's computational complexity. So, we can only extract the strength of hybridization by fitting to experiments and use the values to correlate different experiments. In the model, the DNA molecule is also connected to two metal nanoelectrodes L_1 and L_2 , which allows charges to flow in and out from the molecule. The metal electrodes are represented by two one-dimensional tight-binding chains coupled together by hopping interactions.

The Hamiltonian describing the coupling of the orbitals and interaction with the hybridization reservoirs and the metal leads is given as,

$$H = H_{\text{mol}} + H_{\text{res}} + H_{\text{lead}} + H_{\text{coup}}, \quad (1)$$

where H_{mol} is the Hamiltonian of the π orbitals of the poly(G)–poly(C) DNA molecule given by,

$$H_{\text{mol}} = \sum_i \varepsilon_G c_{G,i}^\dagger c_{G,i} - \sum_i t_G (c_{G,i}^\dagger c_{G,i+1} + \text{h.c.}) + \sum_i \varepsilon_C c_{C,i}^\dagger c_{C,i} - \sum_i t_C (c_{C,i}^\dagger c_{C,i+1} + \text{h.c.}) - \sum_i t_\perp (c_{G,i}^\dagger c_{C,i} + \text{h.c.}), \quad (2)$$

where $c_{G,i}^\dagger$ and $c_{C,i}^\dagger$ are the creation operators for an electron in the orbital of G and C base

site i , t_G (t_C) is the nearest-neighbour electron hopping interaction along the G (C) chain, t_\perp denotes the hopping interaction between G and C bases, and ε_G (ε_C) is on-site energy of the G (C) orbital. Here we neglect the spin index to simplify the notation although the spin degree of freedom is included in the calculation. $i = 1, 2, \dots, N$ denotes the site location on the G and C chains. There are in total $N = 30$ sites on each chain, which equals the number of base pairs of the molecules studied in [3]. Endres *et al* [22] have obtained the energy difference between the G and C orbitals using *ab initio* calculations as $\varepsilon_G - \varepsilon_C \approx 0.6$ eV. H_{lead} and H_{hyb} are the Hamiltonians of the metal electrodes (left and right leads) and the hybridization reservoirs, respectively. The Hamiltonian of the left (L) electrode is given by

$$H_L = \sum_{i,j} \chi_{L,j} a_{L,i,j}^\dagger a_{L,i,j} + \rho_L \sum_{i,j} (a_{L,i,j}^\dagger a_{L,i+1,j} + a_{L,i,j}^\dagger a_{L,i,j+1} + \text{h.c.}),$$

where $a_{L,i,j}^\dagger$ and $a_{L,i,j}$ are respectively the creation and annihilation operators of site i, j of the left lead. $\chi_{L,j}$ is the site energy of the left lead and ρ_L is the hopping strength of the left lead. We choose the site energies of the lead matching those of the DNA molecule to be $\chi_{L,1} = \chi_{R,1} = \varepsilon_G$ and $\chi_{L,2} = \chi_{R,2} = \varepsilon_C$ so that there is no potential step at the interfaces between the leads and the DNA molecule. Index i denotes the site location along the longitudinal direction and $j = 1, 2$ is the transverse site index. A similar expression can also be obtained for the right lead by replacing L by R in the expression. The Hamiltonian of the reservoir attached to site i of the DNA tight-binding chain is a semi-infinite one-dimensional tight-binding chain given by $H_{\text{Res},i} = \sum_l \xi_i b_{i,l}^\dagger b_{i,l} + \gamma_i \sum_l (b_{i,l}^\dagger b_{i,l+1} + \text{h.c.})$, where l denotes the site location along the linear chain representing the reservoir. The site energy of the reservoir is assumed equal to the site energy to which the reservoir is attached. For example, a reservoir attached to the i th G site has $\xi_i = \varepsilon_G$. For a reservoir attached to the i th C site, $\xi_i = \varepsilon_C$. We also assume all reservoirs have the same hopping parameter, $\gamma_i = \gamma$. H_{coup} represents the coupling between the DNA molecule and electrodes and the coupling between the molecule and reservoirs. The coupling between the molecule and the left (right) lead is given by $\lambda_L (a_{L,1,1}^\dagger c_{G,1} + a_{L,1,2}^\dagger c_{C,1} + \text{h.c.}) + \lambda_R (a_{R,1,1}^\dagger c_{G,N} + a_{R,1,2}^\dagger c_{C,N} + \text{h.c.})$ and we assume $\lambda_R = \lambda_L$. The coupling between the i th G base with the i th reservoir is given by $\lambda_G (b_{i,1}^\dagger c_{G,i} + \text{h.c.})$. A similar expression for the coupling for the i th C base to the i th reservoir can be obtained by replacing G by C in the expression. The coupling parameters between the bases and the reservoir attached to each base chain are not assumed identical $\lambda_G \neq \lambda_C$ in the present study. As discussed in Roche [12], DNA molecules can be torsionally distorted and have torsional vibrations, which reduce the transmission coefficients and hence the current. Here in our one-electron model, this effect is not included and therefore could have effects on the accuracy of some parameters, such as the coupling parameter between the molecule and the metal electrodes.

The current passing through the DNA molecule can be calculated according to the Landauer–Buttiker theory [23], if the transmission is known, as follows.

$$I = \frac{2e}{h} \int T(E) [f(E - \mu_L) - f(E - \mu_R)] dE, \quad (3)$$

where $f(E - \mu) = 1/\{1 + \exp[(E - \mu)/k_B T]\}$ is the Fermi function, μ ($= \mu_L$ and μ_R) is the chemical potential of metal leads (left and right ones), $\mu_L = E_f - \eta$ eV; $\mu_R = E_f + (1 - \eta)$ eV, where η is the factor that characterized how the applied voltage V is divided between the two contact junctions between the molecule and the leads [24], and E_f is the equilibrium Fermi energy. The transmission function $T(E)$ can be determined from the lattice Green's function (LGF) according to the Fisher–Lee relation as [23, 25]

$$T(E) = \text{Tr}[\Gamma_L G^R(E) \Gamma_R G^A(E)], \quad (4)$$

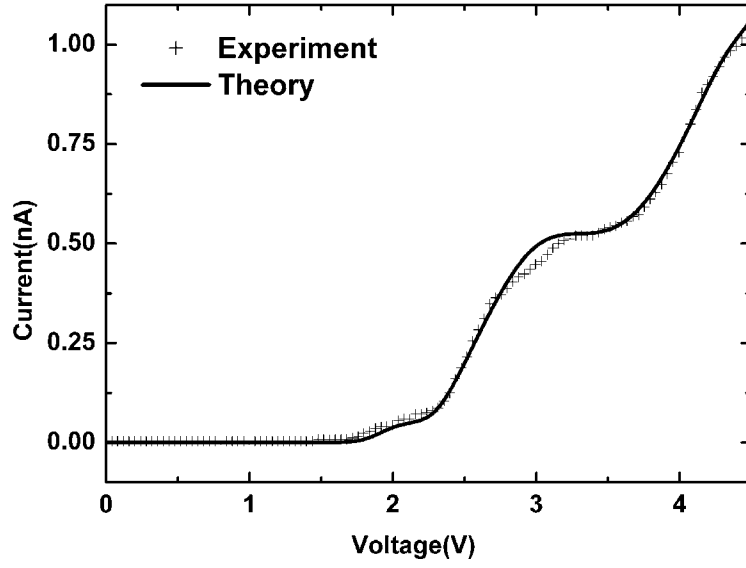


Figure 2. The fitting of the theoretical model with the experimental I - V curve reported in figure 2 of Porath *et al* [3]. The parameters used in the theoretical model are shown in column I in table 1.

where $\Gamma_p = i[\Sigma_p^R - \Sigma_p^A]$, where $p = L, R$, is the lead spectral density and $\Sigma_p^{R(A)}$ is the retarded (advanced) self-energy of lead p . The lattice Green's function can be expressed as,

$$G^R = (E_c I - H_{\text{mol}} - \Sigma_L - \Sigma_R - \Sigma_{\text{res}})^{-1}, \quad (5)$$

where I denotes the identity operator and Σ_L , Σ_R and Σ_{res} are the self-energy operators due to coupling to the left and right leads and the reservoirs. In the tight-binding formulation, the operators can be easily represented by matrices. The LGF can be calculated by inverting the matrix of the operator $E_c I - H_{\text{mol}} - \Sigma_L - \Sigma_R - \Sigma_{\text{res}}$. According to Li and Yan [8], in the presence of reservoir scattering, the transmission function $T(E)$ given above should be replaced by the total effective transmission coefficient $T_{\text{eff}}(E)$, which can be constructed from the transmission function between sites μ and ν , $T_{\mu\nu}$. Here the indices μ and ν denote all the sites in the DNA molecule and also the sites of the leads which are directly coupled to the DNA molecule. The expression for $T_{\text{eff}}(E)$ is given by [8]

$$T_{\text{eff}}(E) = T_{LR} + \sum_{\mu, \nu=1}^N K_{\mu}^{(L)} W_{\mu, \nu}^{-1} K_{\nu}^{(R)}, \quad (6)$$

where $K_{\mu}^{(L)} = T_{L\mu}$ and $K_{\nu}^{(R)} = T_{\nu R}$. W^{-1} is the inverse of the matrix W defined in terms of the matrix elements $T_{\mu\nu}$ as $W_{\mu\nu} = \delta_{\mu\nu} \sum_{\mu \neq \nu} T_{\mu\nu} - T_{\mu\nu}(1 - \delta_{\mu\nu})$. The first term in equation (6) is the coherent contribution and the second term is the incoherent contribution.

3. Results and discussion

By choosing appropriate parameters, we first fit the I - V curve reported in figure 2 of Porath *et al* [3], which shows the typical semiconducting feature of a voltage gap at about 1.75 V. The parameters used are summarized in column I of table 1. Column II in table 1 shows another set of parameters which we use to fit another experimental I - V curve reported in Porath *et al* [3], which we will discuss below. Before a detailed discussion of the fitting results, it is useful

Table 1. Tight-binding model parameters used in the present study.

Parameters	I	II
ε_G (eV)	0.6	0.6
ε_C (eV)	0	0
t_G (eV)	0.18	0.50
t_C (eV)	0.20	0.55
t_\perp (eV)	0.32	0.50
E_f (eV)	1.96	1.90
η	0.5	0.5
λ_L (eV)	0.0096	0.0117
λ_G (eV)	0.02	0.02
λ_C (eV)	0.006	0.006
ρ_L (eV)	0.7	0.7
γ (eV)	0.04	0.04

to discuss here how the parameters are chosen. The values of ε_G and ε_C equal values obtained from *ab initio* calculations and are fixed throughout our study. We believe that ε_G and ε_C are least affected by the environment and should remain constant. Another parameter which has limited variability is the Fermi level in the metal lead E_F . The Fermi level of the lead lies above ε_G according to Endres *et al* [22], who give an estimate of 2.3 eV above ε_G ; Li and Yan [8] obtained an estimate of 1.73 eV above ε_G from the experimental voltage gap of the I - V curves. We therefore limit the variation of E_f to approximately this range to fit the experiment. The other parameters in table 1 can be varied with greater flexibility to fit the experimental results. However, the values of these parameters used in other works are taken into account in our choice of parameters. Eventually, we found that the final values of these parameters obtained in the present study by fitting are similar to those used in other works. Without losing generality, the zero point of energy is set at ε_C and ε_G equals 0.6 eV, which is the value obtained by Endres *et al* [22]. The π - π -stacking interaction between nearest neighbour G (C) sites t_G (t_C) is chosen to be 0.18 (0.20) eV, which is in good agreement with the values obtained in *ab initio* calculations (~ 0.1 – 0.4 eV) [26]. λ_L is the coupling between the leads and the DNA molecule and $\lambda_L \sim 0.01$ eV is used in the present work. Increasing λ_L can push up the current but does not change the shape of the I - V curve. The hybridization strength is characterized by the coupling parameters λ_G and λ_C . One should note that in our calculations, the parameters, ε_G , t_G and λ_G , are different from ε_C , t_C and λ_C respectively. It means that the structure of the guanine chain is asymmetric with respect to the cytosine chain. Therefore, without any inter-chain coupling, the π electron energy band of the DNA molecule should consist of a C π -band at lower energy and a G π band at higher energy. With inter-chain coupling these two bands are mixed together. When fitting with the experiment, the parameters, ε_G , t_G , ε_C , and t_C , are not allowed to deviate very much from the values reported in the literature, while other parameters are allowed to vary with higher flexibility. By doing this, the model can be used to determine other parameters such as inter-chain hopping strength from existing experimental data and obtain some physical insight into the nature of charge transport in the molecule.

The theoretical I - V characteristics at room temperature, together with the experimental data taken from Porath *et al* [3] are shown in figure 2. Our theoretical results are in quantitative agreement with the measured data in a wide bias voltage range from zero to 4.5 V. Although a single chain tight-binding model [8, 10] has been used to explain the wide voltage gap, as well as the increasing trend of the I - V curve, the single chain model fails to reproduce all the features such as the steps between 1.75 and 3.5 V. We also notice a rapid increase in current starting at about 2.2 V, which so far does not have any proper explanation.

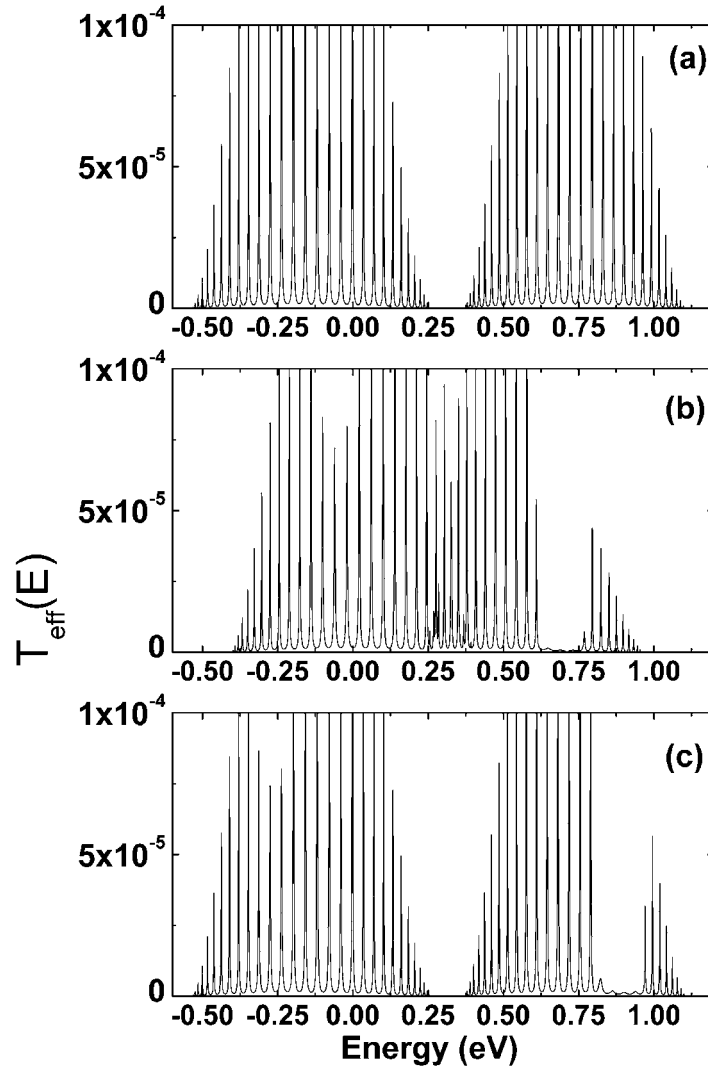


Figure 3. Effective transmission coefficient (T_{eff}) as a function of incident energy for three different sets of parameters: (a) including perpendicular inter-chain coupling but no hybridization-coupling ($t_{\perp} \neq 0, \lambda_G = \lambda_C = 0$), (b) including hybridization coupling but no perpendicular inter-chain coupling ($t_{\perp} = 0, \lambda_G, \lambda_C \neq 0$), (c) including both perpendicular inter-chain coupling and hybridization coupling.

In order to explain the physical origin of these features, we plot in figure 3 the energy dependence of the total effective transmission coefficients $T_{\text{eff}}(E)$ as a function of incident energy for the following three cases: (1) including perpendicular inter-chain coupling but no hybridization coupling ($t_{\perp} \neq 0, \lambda_G = \lambda_C = 0$), (2) including hybridization coupling but no perpendicular inter-chain coupling ($t_{\perp} = 0, \lambda_G, \lambda_C \neq 0$), (3) including both perpendicular inter-chain coupling and hybridization. In case (1), the inter-chain coupling opens a gap in the transmission at energies 0.25–0.375 eV. In case (2), the hybridization coupling opens a gap in the transmission at energies 0.625–0.75 eV. In case (3), which corresponds to the parameters which we use to fit the experimental results, there are two gaps in the transmission, one due to

the interchain coupling and one due to the hybridization coupling. The gap due to hybridization coupling is shifted to energies 0.8–0.95 eV in comparison to the gap found in case (2). Below we will explain the step features of the experimental I – V curves in Porath *et al* [3] in terms of these two gaps in the transmission coefficient.

In figure 2, we notice the following important features in the experimental I – V curve of Porath *et al* [3]: (a) the current starts to rise at a voltage of 1.75 V, (b) a small step at 2 V (c) a larger step from 3 to 3.5 V and (d) rapid increases in current from 2.3 to 3 V and from 3.5 to 4 V. These features can all be explained by the transmission coefficients shown for case (3) in figure 3. First of all, feature (a) can be explained by the onset of transmission at energy 1 eV and a metal lead Fermi level at 1.96 eV. When the bias voltage is small, both the guanine and cytosine molecular orbitals are below the left and right lead Fermi levels and there is no charge conduction through the molecular orbitals. When the bias voltage equals 1.75 V, the Fermi level of the right lead (assuming the left lead Fermi level is higher than the right one under forward bias) is below some guanine molecular orbitals and a conduction channel is set up. At this bias voltage the current starts to increase with voltage. This increase in current is slowed down when the right lead Fermi level is in the gap of the transmission coefficient between 0.8 and 1.0 eV. At these bias voltages, the current does not increase significantly with bias voltage and a current step is formed (feature (b) described above). When the bias voltage is further increased, the right Fermi level is in the transmission band between 0.325 and 0.8 eV and the current increases rapidly with the bias voltage (the rapid increase in current from 2.3 to 3 V described in feature (d)). The current step described in feature (c) can be explained by having the right lead Fermi level lying in the transmission gap between 0.25 and 0.325 eV. The rapid increase in current for a bias voltage >3.5 V is due to the conduction through molecular orbitals with energy between -0.5 and 0.25 eV.

One point worth noting is that the hopping parameter γ of the hybridization reservoirs used in the present model, which equals 0.04 eV, is relatively small in comparison with the value of 1.25 eV used in Li and Yan [8]. As a result, the spread of the energy levels of the hybridization reservoirs is $4\gamma = 0.16$ eV, which is not very large. As we point out in section 2, the hybridization term can be used to represent the backbone hybridization effect if a very narrow spread of energy levels is used in the model. Here, our fitting result shows that one of the current steps in the experimental I – V curve can be explained as the result of a transmission gap opened by an hybridization term with a narrow spread of energy levels (from the point of view of an electron in the base, the effect of this term resembles a single energy level with a finite life-time, and hence resembles a backbone hybridization effect). This indicates that backbone hybridization could be the cause of current steps found in experimental I – V curves.

In order to further verify the double chain tight-binding model, we fit another I – V curve reported in Porath *et al*'s [3] experiments with the model by changing some parameters as shown in column II of table 1. Once again, the experimental results agree very well with the theoretical curve calculated using the double chain model as shown in figure 4. In the I – V curve, there is a voltage gap at a bias of 0.5 V, much smaller than the bias of 1.75 V shown in figure 2. Instead of two current steps, there is only one current step spanning from 2.4 to 2.8 V. These features are properly reproduced in the theoretical curve. In order to find the physical explanation of these features, we show the effective transmission coefficients $T_{\text{eff}}(E)$ in figure 5. We notice that the transmission coefficients are spread over a wider range of energies from -1.5 to 2 eV, while, in figure 3, the spread is only from -0.5 to 1 eV. This explains why the first increase in current starts at a much lower voltage (0.5 V instead of 1.75 V). We also see one gap in the transmission in figure 5, which explains why there is only one current step in the experimental I – V curve. Comparing the parameters used for case I and case II, we notice that case II has stronger inter-chain and intra-chain hopping coupling between molecular orbitals.

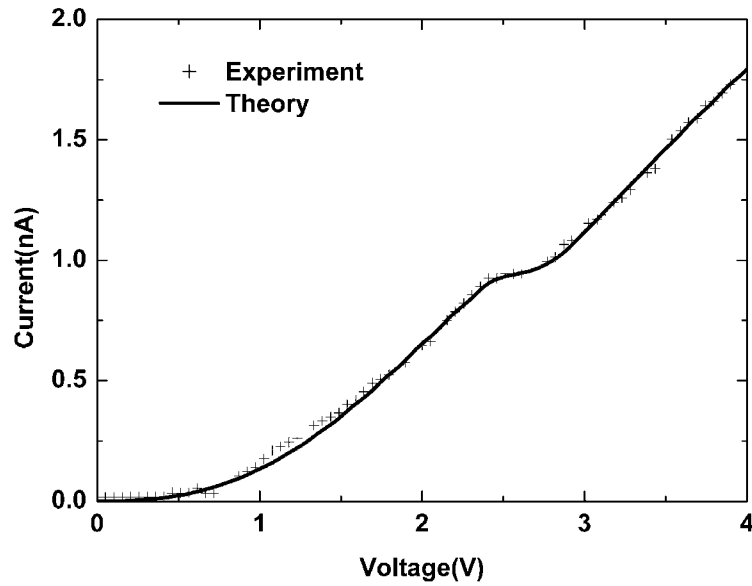


Figure 4. The fitting of the theoretical model with an experimental I - V curve reported in Porath *et al* [3]. The parameters used in the theoretical model are shown in column II in table 1.

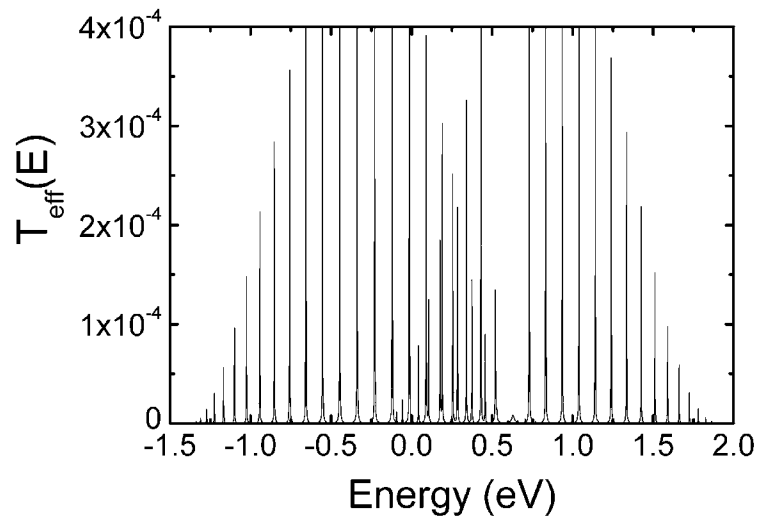


Figure 5. Effective transmission coefficient (T_{eff}) as a function of incident energy for parameters shown in column II in table 1. The theoretical I - V curve obtained with these parameters is shown in figure 4.

A stronger intra-chain coupling can destroy the gap opening phenomenon due to hybridization coupling and only the gap opened by inter-chain coupling remains. Although the intra-chain coupling strength is increased in the second fit, they are still in agreement with values obtained by *ab initio* calculation. The changes in the inter- and intra-chain coupling strength could be due to structural distortion in the molecule.

4. Conclusion

We propose a double chain model, which includes both inter-chain and intra-chain hopping coupling between molecular orbitals as well as hybridization effects due to both backbone hybridization and the environment, to explain the experimental I - V curves measured by Porath *et al* [3]. The theoretical I - V curves obtained from the double chain model agree well with the experimental I - V curves. In Porath *et al*'s [3] measurement, several different I - V curves have been measured under the same experimental condition. Although these I - V curves look similar, there are variations in some features such as the widths of the voltage gaps and the widths of the current steps. So far, there is no consistent and satisfactory explanation of all these important features and their variations. In the present study, we have demonstrated that a double chain model, which includes inter-chain coupling, can be used to explain these features and the variations found in experimental I - V curves. The variations in the I - V curves are explained as being the result of the variation of the inter-chain and intra-chain hopping parameters. This indicates that although the I - V measurements are carried out in the same experimental conditions, there are still some structural distortions or variations in the DNA molecules, which modify these important transport parameters and hence produce different I - V curves. These structural changes could easily happen in DNA molecules as the base pairs are not strongly bonded in fixed positions in the double chain structure as discussed in Endres *et al* [22].

The agreement between the theoretical and experimental results is not merely the consequence of skillful curve fitting, but is due to the fact that the proposed model captures the salient features of charge transport in the DNA molecule. The reason for this conclusion is that the number of experimental data points is much larger than the number of fitted parameters used in the study. In the present study, the most flexible parameters are t_{\perp} and λ_L . The other parameters that can be varied in a restricted range (values around the values published in literature) are t_G , t_C , and E_F . On the other hand, in the experimental curve, the number of data points is in the range of hundreds, which is significantly larger than the number of most flexible parameters, which is 2, and the number of fitted parameters, which is 5. For this mismatch in the numbers of data points and parameters, it is very unlikely that we can obtain agreement between theory and experiment if the model is not an accurate description of the physical phenomenon.

One important result of the present study is the importance of the inter-chain coupling. According to our model, the inter-chain coupling is strong, which agrees with the numerical estimation obtained by Zhang *et al* [26]. As a result, G and C conduction channels are mixed together and the resulting conduction channels would have hopping parameters different from the pure G and pure C conduction channels. This implies that in the design of the molecular device, the contact between metal electrode and the molecule must be chosen carefully, taking into consideration this modification of hopping parameters. According to Macia *et al* [15], an efficient injection contact can be obtained when the contact-molecule coupling matches the hopping parameter of the conduction channel. Since the inter-chain coupling can modify the hopping parameters, one must carefully include this effect in the design of efficient injection contacts.

We also notice the following points from the results which will be useful in further investigations in this field:

- (i) Some steps in the I - V curves are consequences of the transmission gaps opened by the hybridization interaction. The term used in the present model resembles a backbone hybridization term as it has a narrow spread of energy levels. This indicates that backbone hybridization, or other scatterers similar in nature, could be the cause of current steps in the

I – V curves. Further experimental studies are needed on the positions of these current steps as well as the step sizes and how the preparation environment affects these characteristics in order to understand the physical or chemical nature of the scatterers. The appearance or disappearance of these current steps should be studied in conjunction with the size of the voltage gap, for reasons discussed in point (ii) below.

- (ii) The widths of current steps in the I – V curves are reduced, making the current steps less prominent, by an increase in the intra-chain hopping parameters t_C and t_G . At the same time, when these parameters increase, the voltage gap in the I – V curves is reduced. This indicates that when the intra-chain hopping coupling is the main cause of the variations in the I – V curves the sizes of the voltage gap and the current steps are correlated (increased or decreased simultaneously). To have a better understanding of charge transport physics in DNA, future investigation should be focused on the relation between the sizes of the voltage gap and current steps. The preparation and measuring of environmental factors that caused these variations should also be investigated to find the factors that change the intra-chain hopping coupling.

The tight-binding model developed in the present study with the fitted parameters is very useful in other studies of DNA's transport properties. For example, the model can be used to investigate in detail the effects of the contacts or used to predict the performance of DNA molecular devices. At the moment, the development of a complete *ab initio* model for charge transport in DNA is infeasible as the problem is computationally too complicated. The present model, combining some *ab initio* results with fitted parameters, provides a reliable description of the I – V curve in good agreement with experiments, which will be very useful in the study of using DNA molecules as nano-electronic building block.

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References

- [1] Joachim C, Gimzewski J K and Aviram A 2000 *Nature* **408** 541
- [2] Luryi S, Xu J and Zaslavsky A 1999 *Future Trends in Microelectronics: the Road Ahead* (New York: Wiley)
- [3] Porath D, Bezryadin A, de Vries S and Dekker C 2000 *Nature* **403** 635
- [4] Fink H W and Schonenberger C 1999 *Nature* **398** 407
- [5] Kasumov A Y *et al* 2001 *Science* **291** 280
- [6] Zhang Y *et al* 2002 *Phys. Rev. Lett.* **89** 198102
- [7] De Pablo P J *et al* 2000 *Phys. Rev. Lett.* **85** 4992
- [8] Li X Q and Yan Y J 2001 *Appl. Phys. Lett.* **79** 2190
- [9] Hjort M and Stafstrom S 2001 *Phys. Rev. Lett.* **87** 228101
- [10] Cuniberti G, Craco L, Porath D and Dekker C 2002 *Phys. Rev. B* **65** 241314
- [11] Iguchi K 2001 *J. Phys. Soc. Japan* **70** 593
- [12] Iguchi K 1997 *Int. J. Mod. Phys. B* **11** 2405
- [13] Roche S 2003 *Phys. Rev. Lett.* **91** 108101
- [14] Roche S and Macia E 2004 *Mod. Phys. Lett. B* **18** 847
- [15] Zhu Y, Kaun C C and Guo H 2004 *Phys. Rev. B* **69** 245112
- [16] Macia E, Triozon F and Roche S 2005 *Phys. Rev. B* **71** 113106
- [17] Adessi Ch, Walch S and Anantram M P 2003 *Phys. Rev. B* **67** 081405
- [18] Gervasio F L, Carloni P and Parrinello M 2002 *Phys. Rev. Lett.* **89** 108102
- [19] Hübsch A, Endres R G, Cox D L and Singh R R P 2005 *Phys. Rev. Lett.* **94** 178102
- [20] Watson J and Crick F 1953 *Nature* **171** 737

- [20] Onuchic J N and Wolynes P G 1993 *J. Chem. Phys.* **98** 2218
- [21] Leite V B P, Alonso L C P, Newton M and Wang J 2005 *Phys. Rev. Lett.* **95** 118301
- [22] Endres R G, Cox D L and Singh R R P 2004 *Rev. Mod. Phys.* **76** 195
- [23] Datta S 1995 *Electronic Transport in Mesoscopic Systems* (Cambridge: Cambridge University Press)
- [24] Datta S, Tian W, Hong S, Reifenberger R, Henderson J I and Kubiak C P 1997 *Phys. Rev. Lett.* **79** 2530
- [25] Ferry D and Goodnick S M 1997 *Transport in Nanostructures* (Cambridge: Cambridge University Press) chapter 3, and references therein
- [26] Zhang H *et al* 2002 *J. Chem. Phys.* **117** 4578
- Voityuk A A *et al* 2001 *J. Chem. Phys.* **114** 5614
- Sugiyama H and Saito I 1996 *J. Am. Chem. Soc.* **118** 7063