Molecular Electronics of DNA Double Helices Using Second-Order Tight-Binding Modeling

Sadeq Malakooti, Eric Hedin, and Yong S. Joe
Center for Computational Nanoscience
Department of Physics and Astronomy
Ball State University
Muncie, IN 47306, USA
E-mail: ysjoe@bsu.edu

***Abstract*—This research deals with molecular electronics of DNA double helices. We consider a 10 base-pair poly(G)-poly(C) double stranded DNA molecule, tilted with respect to the intercontact electric field direction. An advanced tight-binding (TB) model including hopping integrals of the next nearest neighbors (NNN) and DNA helix conformation is implemented. The transport properties, such as single electron transmission spectra and current-voltage characteristics as functions of source-drain voltage and tilt angle, are studied both with and without NNN effects.**

Keywords-quantum transport; molecular electronics; DNA double helix; tight-binding

I. INTRODUCTION

Recent observations have disclosed that under different conditions, DNA molecules can act as insulators [1], semiconductors [2], and also conductors [3], which expresses the immense importance of DNA based electronic systems and devices. Among the theoretical efforts towards interpreting these fascinating experimental results, model-based Hamiltonian methods are of particular interest due to their ease of application and generality [4, 5].

Here the molecule is subjected to a perpendicular gating electric field and so the helix conformation of the strands becomes important [6]. This situation takes place when the trapped molecule is not aligned with the intercontact electric field so that there exists a component of the field perpendicular to the molecular axis (see Fig. 1).

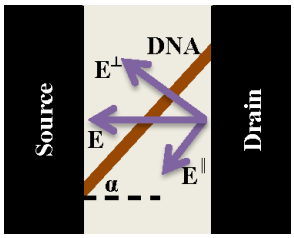

Figure 1. Problem geometry

It is noteworthy that in most of the efforts using TB modeling for DNA charge migration analysis so far, only the hopping strengths between side-by-side sites have been taken into account to capture the pathways of electrons through the DNA structure. In order to produce a more realistic elucidation of possible mechanisms for charge transport in DNA, hopping amplitudes between all the next nearest neighbors (NNN) sites should also be addressed in the modeling.

Accordingly in this work, an advanced TB model including the NNN effects is proposed, and the characteristics of quantum mechanical electron transport through a gated poly(G)-poly(C) ds-DNA molecule are investigated.

II. TIGHT-BINDING MODELING

The planar projection of a DNA duplex connected to two electrode leads is shown schematically in Fig. 2. There are four central conduction branches, linked with one another with interconnected nearest-neighbor sites.

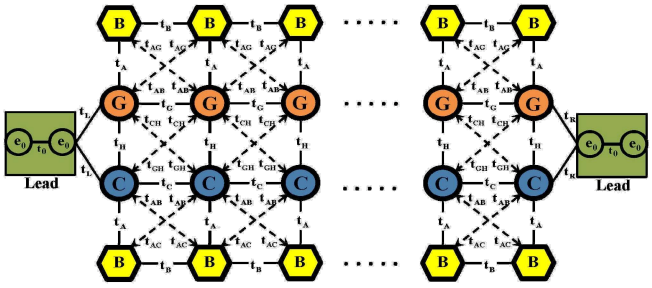

Figure 2. The schematic model of electronic transport through a 10 base-pair, four-channel, poly(G)-poly(C) DNA molecule

Here, we include the helix geometry of the strands in the traditional ladder model. We consider a 10 base-pair full twisted DNA molecule. The on-site energies (ε_i) become (neglecting the difference between major and minor grooves) [6]:

$$\varepsilon_i = \varepsilon_i^0 \pm \frac{d}{2L} V_{\mathrm{sd}} \tan(\alpha) \cos\left(\frac{2\pi i}{10} + \phi_0\right), \qquad (1)$$

where ε_i^0 is on-site energy of the *i-th* base molecule at zero field, V_{sd} is the source-drain voltage, α is the tilted DNA angle, d is the DNA diameter, L is the DNA length, ϕ_0 determines the initial orientation of the DNA molecule, and the positive sign is for the two top DNA strands and the negative sign for the two

bottom strands. Using a two-dimensional TB model, a simple and effective Hamiltonian for charge transport through the ds-DNA between two metallic leads can be written as

$$H_{Total} = H_{DNA} + H_{Lead} + H_{Lead-DNA}. \tag{2}$$

Here, the Hamiltonian for a poly(G)-poly(C) DNA molecule is described by a summation over the N base-pair sites as follows:

$$\begin{aligned} H_{DNA} = & \sum_i \left(\varepsilon_G G_i^\dagger G_i + \varepsilon_C C_i^\dagger C_i + \varepsilon_B B_{i,G}^\dagger B_{i,G} + \varepsilon_B B_{i,C}^\dagger B_{i,C} \right) \\ & - \sum_i \left(t_A G_i^\dagger B_{i,G} + t_H G_i^\dagger C_i + t_A C_i^\dagger B_{i,C} + h.c. \right) \\ & - \sum_i \begin{pmatrix} t_B B_{i,G}^\dagger B_{i+1,G} + t_G G_i^\dagger G_{i+1} + t_C C_i^\dagger C_{i+1} \\ + t_B B_{i,C}^\dagger B_{i+1,C} + h.c. \end{pmatrix} \\ & - H_{NNN}, \end{aligned} \tag{3}$$

where $G_i^\dagger / C_i^\dagger$ (G_i / C_i) and $B_{i,G/C}^\dagger$ ($B_{i,G/C}$) are the creation (annihilation) operators at the *i–th* G/C base sites and the *i-th* upper and lower backbone sites, respectively. $\varepsilon_{G/C}$ and ε_B are the onsite potential energies of the DNA base pair and backbone sites, respectively. t_A , t_B , t_G , t_C and t_H are the hopping amplitudes between backbone and DNA base pairs, between backbone sites, between guanine sites, between cytosine sites, and for guanine-cytosine inter-site hopping, respectively. The last term in Eq. (3), H_{NNN} , is the part of the Hamiltonian related to the NNN sites, which can be written as

$$H_{NNN} = \sum_i \begin{pmatrix} t_{AB} \left[B_{i,G}^\dagger G_{i+1} + B_{i,G}^\dagger G_{i-1} + B_{i,C}^\dagger C_{i+1} + B_{i,C}^\dagger C_{i-1} \right], \\ + t_{AG} \left[G_i^\dagger B_{i+1,G} + G_i^\dagger B_{i-1,G} \right] \\ + t_{GH} \left[G_i^\dagger C_{i+1} + G_i^\dagger C_{i-1} \right] \\ + t_{CH} \left[C_i^\dagger G_{i+1} + C_i^\dagger G_{i-1} \right] \\ + t_{AC} \left[C_i^\dagger B_{i+1,C} + C_i^\dagger B_{i-1,C} \right] \end{pmatrix}, \tag{4}$$

where the coefficients $t_{kl}; k(l) = A, C, G(B, C, G, H)$ are the NNN hopping strengths. The DNA molecule is coupled to two semi-infinite metallic leads by the tunneling Hamiltonian

$$H_{Leads-DNA} = -t_L l_0^\dagger (C_1 + G_1) - t_R l_1^\dagger (C_N + G_N) + h.c., \tag{5}$$

where t_L (t_R) are the hopping strengths between the left (right) lead and the end DNA bases, and $l_i^\dagger$ (l_i) is the creation (annihilation) operator at the *i-th* site of the leads. The leads themselves are modeled by another TB Hamiltonian as

$$H_{Leads} = \varepsilon_0 \sum_i l_i^\dagger l_i - t_0 \sum_i (l_i^\dagger l_{i+1} + h.c.), \tag{6}$$

where ε_0 is the lead onsite energy, and t_0 is the hopping amplitude between sites in the leads.

By discretizing the system spatially with lattice constant *a* and denoting the wave function on site *n* by ψ_n , the Schrödinger equation in the TB approximation can be written as

$$-\sum t_{n,m} \psi_m + \varepsilon_n \psi_n = E \psi_n, \tag{7}$$

where the matrix elements $t_{n,m}$ are hopping integrals (or coupling parameters) between sites *m* and *n* with the single-site potential of site *n*, the sum runs over the nearest (or next-nearest) neighbors of n , E is the electron energy, and ε_n is the on-site energy. The general incoming and outgoing wavefunctions in the leads which form a solution of Eq. (7) may be written as [7, 8]

$$\begin{aligned} \psi_n &= e^{in\theta} + r e^{-in\theta}, \quad n \le 0, \\ \psi_n &= t e^{in\theta}, \qquad n \ge 1, \end{aligned} \tag{8}$$

with $\theta = ka$. Here, k is the wave vector that is connected with the energy by the dispersion relation for the Bloch states $E = -2t_0 \cos ka + \varepsilon_0$, and t and r are the transmission and reflection amplitudes, respectively. The Schrödinger equation for the amplitudes in the two lead sites and the 40 DNA sites (10 G sites, 10 C sites, 20 sugar-phosphate backbone sites) can be written and combined into a matrix form as follows:

$$[\mathbf{M}]_{42\times 42} [\mathbf{\Psi}]_{42\times 1} = [\mathbf{Z}]_{42\times 1} \ , \tag{9}$$

in which

$$\begin{aligned} \bar{\Psi} &= [r \quad \psi_1 \quad \psi_2 \quad \ldots \quad \psi_{39} \quad \psi_{40} \quad t], \\ \bar{\mathbf{Z}} &= [t_0 e^{i\theta} \quad 0 \quad -t_L \quad -t_L \quad 0 \quad 0 \quad \ldots \quad 0], \end{aligned} \tag{10}$$

where $\bar{\Psi}$ and $\bar{\mathbf{Z}}$ are the transpose of $\mathbf{\Psi}$ and $\mathbf{Z}$, respectively, and the matrix M is a banded diagonal matrix formed by hopping amplitudes. Therefore, by solving the matrix equation for the linearized TB Hamiltonian [Eq. (9)] we obtain the transmission amplitude (t) as a function of the incoming electron energy, *E*, and source-drain voltage, V_{sd} . The desired transmission coefficient, $T(E)$ is obtained by taking the square of the transmission amplitude, $|t(E)|^2$. This completes the necessary background for the analysis of the problem. In the next section, we present results for some numerical examples.

III. RESULTS AND DISCUSSION

The DNA is assumed to be connected between two semi-infinite electrodes with an on-site energy of $\varepsilon_0 = 7.75$ eV and a hopping amplitude of t_0 =1 eV between sites. Notice that choosing a different hopping amplitude t_0 in the semi-infinite leads does not alter the main characteristics of electron transport through DNA molecules. All numerical parameters used in the computations, such as DNA hopping probabilities are listed in Table 1.

TABLE I. TIGHT-BINDING MODEL PARAMETERS

Onsite energies (eV)			
$\varepsilon_0 = 7.75$	$\varepsilon_G = 7.75$	$\varepsilon_C = 8.87$	$\varepsilon_B = 8.85$
Hopping amplitudes (eV)			
$t_0 = 1$	$t_L = t_R = 0.5$	$t_A = t_B = 0.1$	$t_{kl} \approx 0.08$
$t_H = t_C = t_G = 0.3$			

Here we study the effects of contact and tilt angle on the quantum transport behavior of the DNA molecule. To do this, first we compute the transmission coefficient, $T(E)$, using Eq. (9). Then we focus on the evaluation of the current-voltage characteristics of the DNA in the system. Accordingly, we assess here the I-V characteristics of the system as a function of the transmission coefficient, using a standard Landauer-Buttiker formula [9-12]:

$$I(V_{sd}) = \frac{2e}{h}\int_{-\infty}^{\infty} T(E,V_{sd})[f_L(E,V_{sd}) - f_R(E,V_{sd})]dE. \qquad (10)$$

Here, $f(E,V_{sd})$ is the Fermi function given by $f_{L/R}(E,V_{sd}) = \left[1 + e^{\beta(E-\mu_{L/R})}\right]^{-1}$, where $\beta = 1/k_BT$ and $\mu_{L/R}$ stands for the electrochemical potential of the left (right) lead, whose value depends on the applied bias voltage. We choose $\mu_L = E_F - (1-\eta)eV_{sd}$ and $\mu_R = E_F + \eta eV_{sd}$, where V_{sd} is the source-drain applied voltage, E_F is the equilibrium Fermi energy, and η is a parameter describing the possible asymmetry of contact to leads, chosen here as E_F = 5.5 eV and η = 0.5, respectively.

A. *Contact effects*

We display the transmission spectra of the DNA as a function of electron energy for selected values of $t_L = t_R$ = 0.1, 0.5 and 0.9 eV in Fig. 3. It is clearly seen that the electrons with the lower energies can be transmitted with the inclusion of NNN effects, which broadens the transmission spectra.

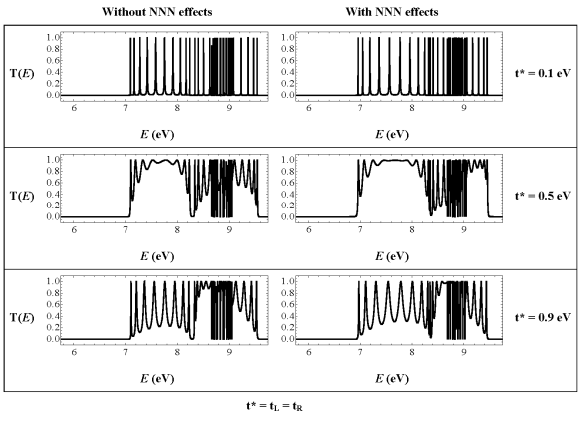

Figure 3. Transmission spectra as a function of electron energy with and without NNN effects for selected contact couplings.

Figure 4 shows the resonant tunneling (RT) current by modulating the voltage (V_{sd}) for three special cases: $t_L = t_R$ = 0.1, 0.5 and 0.9 eV, without and with NNN effects. The highest current is obtained at $t_L = t_R$ = 0.5 eV, with the inclusion of NNN effects. Therefore, in order to achieve maximum current for a given V_{sd} in the system, we should take into account the NNN hopping between the sites.

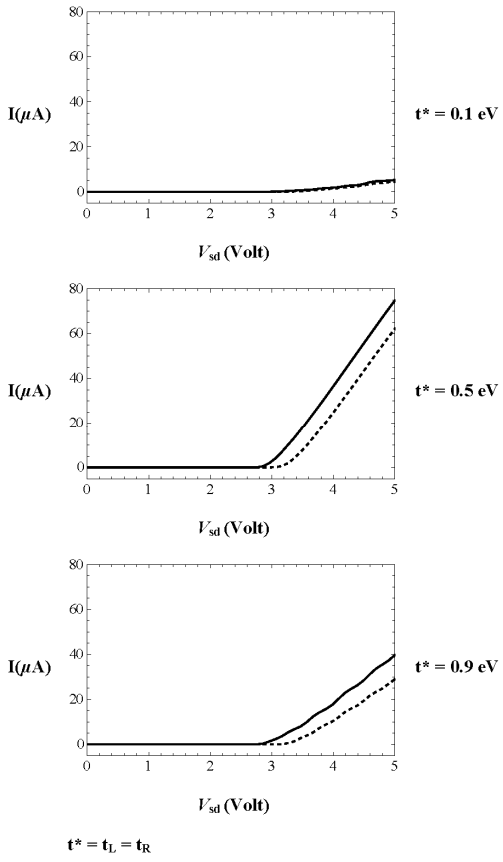

Figure 4. Current as a function of source-drain voltage with (solid) and without (dashed) NNN effects for selected contact couplings.

B. *Tilting effects*

In Fig. 5, we show the transmission spectra of the tilted DNA as a function of electron energy for selected tilt angles (α = 0º, 30º and 60º) and source-drain voltages (V_{sd} = 0, 2 and 4 Volts) with fixed contact hopping strengths ($t_L = t_R$ = 0.5 eV). Spectra become slightly broader in the case with NNN effects which means more electron energies contribute to the transmission. It is clear from (1) that by increasing the tilt angle or the source-drain voltage, the normal electric field component is enhanced. This leads to changes in the surface charge distribution over the DNA strands which regulates the conductivity of the charge carrier in the DNA molecule. This behavior can easily be seen in Fig. 5, which shows that the transmissions are washed out by increasing tilt angle as well as by higher source-drain voltages.

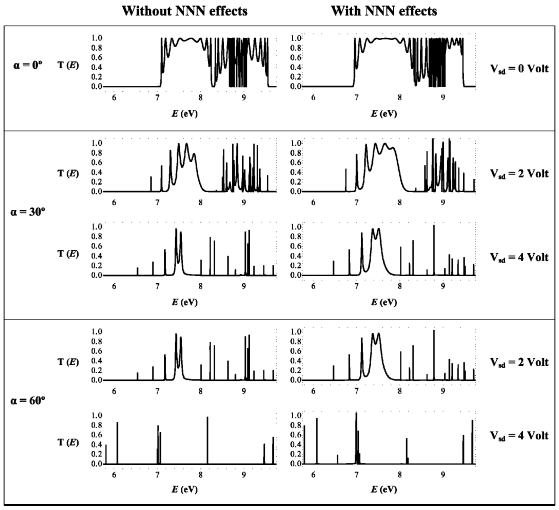

Figure 5. Transmission spectra as a function of electron energy with and without NNN effects for selected tilt angles and source-drain voltages.

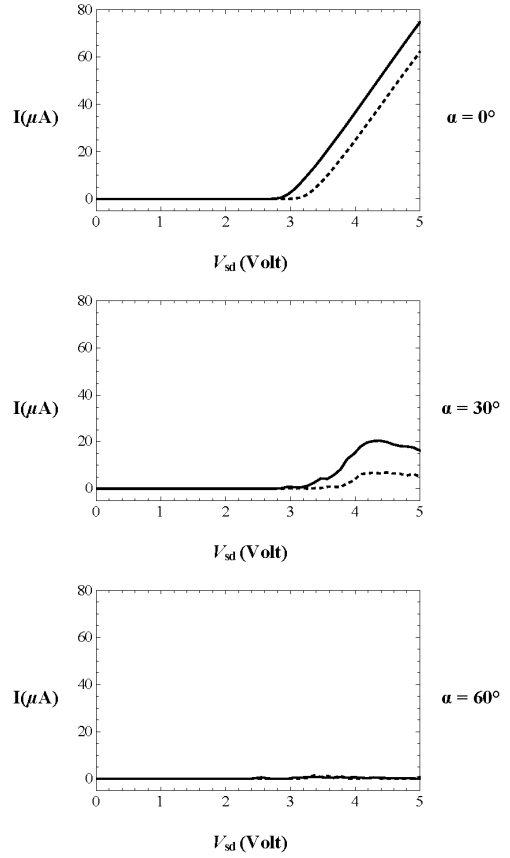

Figure 6. Current as a function of source-drain voltage with (solid) and without (dashed) NNN effects for selected tilt angles.

Figure 6 shows the RT current as a function of voltage (V_{sd}) for selected tilt angles (α = 0º, 30º and 60º) under the symmetrical contact couplings ($t_L = t_R = 0.5$ eV). In agreement with transmission spectra, the current is enhanced in magnitude when the NNN effects are taken into account. In other words, the current gap, which is a typical characteristic of a semiconductor, is decreased by the diagonal electron hopping between the sites. As we discussed before, current is diminished by increasing the tilt angle. It is noticeable that there is a critical voltage which is attributed to the highest current for a tilted DNA molecule.

IV. Conclusions

Herein, we have investigated the electron transport characteristics through ds-DNA molecules using a second-order TB model which considers DNA helical conformation and the NNN effects. We have calculated the transmission and the current-voltage characteristics as a function of the electron energy and source-drain voltage with a variation of the contact coupling between the leads and the DNA molecule and DNA tilt angle. We have found that by considering the NNN effects, higher overall transmission and therefore enhanced current could be obtained. Also, we have presented results showing that the electron transmission and subsequently the current flow are diminished by increasing the tilt angle.

Acknowledgment

We would like to thank Ball State University and IWCE 2012 administrators for their support.

References

[1] E. Braun, Y. Eichen, U. Sivan, and G. Ben-Yoseph, "DNA-templated assembly and electrode attachment of a conducting silver wire," Nature, London, vol. 391, pp. 775-778, 1998.

[2] E. Shapir, H. Cohen, A. Calzolari, C. Cavazzoni, D. A. Ryndyk, G. Cuniberti, A. Kotlyar, R. Di Felice, and D. Porath, "Electronic structure of single DNA molecules resolved by transverse scanning tunnelling spectroscopy," Nature Mater., vol. 7, pp. 68-74, 2008.

[3] H. W. Fink and C. Schönenberger, "Electrical conduction through DNA molecules," Nature, London, vol. 398, pp. 407-410, 1999.

[4] H. Mehrez and M. P. Anantram, "Interbase electronic coupling for transport through DNA," Phys. Rev. B, vol. 71, pp. 115405-115409, 2005.

[5] E. Macia, "Electronic structure and transport properties of double-stranded Fibonacci DNA," Phys. Rev. B, vol. 74, pp. 245105-245114 2006.

[6] A. V. Malyshev, "DNA double helices for single molecule electronics," Phys. Rev. Lett., vol. 98, pp. 096801-096804, 2007.

[7] Y. S. Joe, E. R. Hedin, and A. M. Satanin, "Manipulation of resonances in an open three-terminal interferometer with an embedded quantum dot," Phys. Rev. B, vol. 76, pp. 085419- 085414, 2007.

[8] E. R. Hedin, Y. S. Joe, and A. M. Satanin, "Resonance and phase shift in an open Aharonov–Bohm ring with an embedded quantum dot," J. Phys.: Condens. Matter, vol. 21, pp. 015303-015311, 2009.

[9] R. Landauer, "Electrical resistance of disordered one-dimensional lattices," Philos. Mag., vol. 21, pp. 863-867, 1970.

[10] M. Buttiker, "Voltage fluctuations in small conductors," Phys. Rev. B, vol. 35, pp. 4123-4126, 1987.

[11] D. K Ferry and S. M. Goodnick, *Transport in Nanostructure*, Cambridge University Press, New York, 1997.

[12] S. Datta, *Quantum Transport: Atom to Transistor*, Cambridge University Press, New York, 2005.