ELECTRON TRANSPORT THROUGH
ONE AND FOUR-CHANNEL DNA MODELS

A THESIS
SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE
MASTER OF SCIENCE
BY
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JULY, 2010
To my Father
ABSTRACT

DNA molecules possess high density genetic information in living beings, as well as self-assembly and self-recognition properties that make them excellent candidates for many scientific areas, from medicine to nanotechnology. The process of electron transport through DNA is important because DNA repair occurs spontaneously via the process that restores mismatches and lesions, and furthermore, DNA-based molecular electronics in nano-bioelectronics can be possible through the process. In this thesis, we study theoretically the transport properties through a one-dimensional one-channel DNA model, a quasi-one-dimensional one-channel DNA model, and a two-dimensional four-channel DNA model by using the Tight-Binding Hamiltonian method. We show graphical outputs of the transmission, overall contour plots of transmission, localization lengths, the Lyapunov exponent, and current-voltage characteristics as a function of incoming electron energy and magnetic flux which are obtained using Mathematica run on the CSH Beowulf Cluster. Our results show that the semiconductor behavior can be observed in the I-V characteristics. The current through a quasi-one-dimensional one-channel DNA model starts to flow after the breakdown voltage and remains constant after threshold voltage. The variations of the temperature make the fluctuations of the system. As the temperature increases, the sharp transmission resonances are smeared out and the localization lengths are also decreased. Due to a magnetic field penetrating at the center of the two-dimensional DNA model, the Aharonov-Bohm (AB) oscillations can be observed.
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Yong Joe, for his help, advice, support, and work with me during the research process. I really appreciate his patient instruction and enthusiasm in thinking of problems and solutions, which inspired me in the following study and research. I would also like to thank both Dr. Yong Joe and Dr. Eric Hedin for their assistance throughout my research and their suggestions for preparing presentations at conferences. I also want to express my appreciation to my thesis committee members, Dr. Thomas Robertson, Dr. Yong Joe, Dr. Eric Hedin, and Dr. Muhammad Maqbool for their concern and for supporting me to continue to do my research.

Thanks also to Ball State University and the Department of Physics and Astronomy. I will always remember and appreciate the prayers and encouragement from my family and friends in Muncie, Fort Wayne, New Jersey, and Korea.
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Chapter 1: Introduction and Overview

In the nanotechnology era, people want to make electronic components smaller and faster and to put more information in a very high density. But, in fact it is hard to make things smaller without error, and it is time-consuming and difficult. Thus, organic materials which have self-organizing or self-assembly characteristics are considered as good candidates for nano-electronic devices. DNA is one of the more suitable solutions for nano-fabrication technology. Generally, as we know, DNA (deoxyribonucleic acid) is the molecule which stores genetic information in cells. The structure of DNA consists of two polymer chains of nucleotide units, which are called bases. There are four kinds of bases, guanine (G), adenine (A), cytosine (C), and thymine (T). Along each backbone, the sugar links together with the phosphates and bases. The DNA helix is about 2 nm in diameter with a vertical distance of about 0.34 nm between layers of the base-pairs and about 3.4 nm for each complete turn of the helix, as shown in Fig. 1.1 The two chains twist around each other through base pairings by hydrogen bonds. The pairing occurs only between G and C or between A and T; i.e. there are only two kinds of base-pairs, (G/C) and (A/T). One strand of DNA binds to another complementary strand with a high probability, giving the property of self-assembly.

Self-assembly is why DNA could be useful in nanotechnology for electric circuits, for instance, as a DNA chip. In addition, we can also synthesize DNA to contain whatever
sequence we want it to have. DNA can provide pathways for charge transfer processes because of the formation of \( \pi \)-stacked base-pairs in its double-helix structure. The process of charge transport, like oxidative hole transfer and reductive electron transfer through DNA, is an important process for detecting mismatches and for DNA repair [1]. Based on this natural charge transfer process in DNA, some applications have been developed in biochemistry and nanotechnology.

![Fig. 1.1. Schematic of DNA structure. The structure of DNA consists of two polymer chains which is called a duplex. There are four kinds of bases, guanine (G), adenine (A), cytosine (C), and thymine (T). They form pairs with each other, G with C, and A with T, by hydrogen bonds. The DNA helix is about 2 nm in diameter with a vertical distance of about 0.34 nm between layers of the base-pairs and about 10 base-pairs for each complete turn of the helix (www.britannica.com)](image)
Motivated by these potential properties, many recent experimental and theoretical studies of charge transport in DNA have been carried out. The question of whether DNA is intrinsically conducting is an unsolved problem. Because the experimental outcomes are amazingly different, DNA might serve as insulator [2-5], semiconductor [6-7], conductor [8-11], or even superconductor [12]. There are numerous variables which affect experiments in nanoscale dimensions. In particular, Porath et al. directly measured the electrical transport through 10 nm long (30-basepairs), double stranded poly (G)-poly (C) DNA molecules (Fig. 1.2(a)) [7]. The current-voltage curves that they measured between two metal nanoelectrodes show an asymmetric sharp rise of the current at a threshold voltage. Therefore, DNA molecules can transport high currents at low temperature. Mahapatro et al. observed electronic conduction through 15 base DNA oligonucleotide pairs which were in a dry state (Fig. 1.2 (b)) [13]. The single ds-DNA is immobilized in a definite nanogap which is the separation between the electrodes. A conductance of \( \sim 10^{-9} \) S was estimated for 15-base-pair G-C rich ds-DNA.

Xu’s group directly measured the conductance of single DNA molecules in aqueous solution [14]. Figure 1.3 (a) is the experimental layout by Xu et al. in which the current is measured between two gold electrodes through a DNA duplex. They observed that the measured conductance of a single DNA molecule depends on the base-pairs sequence and the DNA length. Roy’s group measured electrical transport in single and double-stranded DNA molecules [15]. They performed an experiment with two arbitrary samples which represent a single-stranded DNA molecule (upper), and a double-stranded one (lower) which is connected to a pair of functionalized single-walled carbon nanotubes (black rectangular) in Fig. 1.3(a). About 25-40 pA of current was measured for the ds-DNA, and \( \sim 1 \)
pA or less for the ss-DNA without base-pairs. Hence, the conductance of DNA is seen to be diverse, depending on experimental conditions and different samples.

Fig. 1.2. (a) Double-stranded poly (G)-poly (C) DNA molecules which are placed between two metal nanoelectrodes, with semiconductor behavior shown on I-V curves. (b) 15 base-pair DNA in a dry state is deposited and trapped between gold electrodes and observed to have electronic conduction.
Fig. 1.3. (a) Experimental layout of a single DNA conductance measurement by Xu et al. [4]. (b) Schematic drawings. The upper (lower) figure is for a single (double)-stranded DNA molecule [5]. The upper (lower) figure represents an arbitrarily shaped ss-DNA (ds-DNA) molecule, which is stretched and attached to the nanoelectrodes which are separated by a gap of 27±2 nm (80 bp DNA molecule, ~27 nm).

Theoretical effects on DNA transport also have been studied by many groups. For example, Roche et al. have reported energy and temperature-dependent transmission coefficients for two different cases, which are poly (dG)-poly (dC) and an aperiodic $\lambda$-phase DNA sequence [16]. By using tight-binding (TB) calculations, two bands were found, separated by a specific energy gap, with the number of resonant energy values dependent
on the length of the DNA molecules. Furthermore, they observed that temperature effects induce thermal fluctuations of consecutive bases and reduce coherent transmission. Cuniberti et al. also observed semiconducting behavior in DNA transport by studying low temperature current-voltage ($I-V$) curves through 30-poly (G)-poly (C) DNA oligomers [17]. Charges can propagate along the $\pi$-orbital stack via the nearest-neighbor bases or the backbone. They found that the backbone coupling determined the opening of a bandgap in the transmission. In addition, the calculation of the current shows good agreement with the experimental results, shown as closed circles and crosses on the $I$-$V$ curves in Fig. 1.4.

![Fig. 1.4. Current-voltage characteristics at low temperature (18 K: circles and 3.6 K: crosses). Theoretical results are plotted as solid lines. Both experimental and theoretical results match well. The upper inset shows the transmission as a function of energy for a 30-poly G-C DNA molecule. The normalized differential conductance is shown in the lower inset [17].](image)

Inspired by these interesting results, we model one-dimensional, quasi-one-dimensional, and two-dimensional DNA structures in order to better understand electron transport through DNA for future applications in nano-technology. The transport properties of the electronic transmission coefficient are computed as a function of electron incoming energy. Furthermore, we plot current-voltage ($I$-$V$ curves) characteristics and
contour plots of the transmission. In Chapter 2, we describe one-dimensional DNA model with 20 bases. We investigate the transmission coefficient and localization length for different sequences of DNA bases. In Chapter 3, we deal with the quasi-one-dimensional DNA model, which contains an energy-dependent onsite energy, including the structure of the base-pairs and backbone effects. We show impurity and temperature effects on the transmission. In addition, energy-dependent hopping integrals are included in the TB quasi-one-dimensional model. Chapter 4 contains a two-dimensional, four-channel DNA model, where we considered all possible pathways that an electron can transport, and show the results of the effects of the variation of several parameters, including an external magnetic flux. Finally, in Chapter 5 we conclude and summarize our projects.
Chapter 2: Sequence dependent electron transport through a one-dimensional one-channel DNA model

2.1. Introduction

DNA consists of four nucleotides, known by their abbreviations A, T, G, and C. With just four letters, they are used to determine the sequence of DNA, which is called the genetic code. The order of the sequence of DNA provides the genetic information for the living cell. The idea of studying sequence specific electronic conduction came from an observation made in several references. Transport experiments with 15-base-pair double-stranded DNA molecules between two gold electrodes by Mahapatro et al. are shown in Fig. 2.1 [13]. Electron transport through the $\pi$-orbital occurs by molecule-to-molecule hopping. The ionization potentials, which are onsite energies, correspond to quasibound states, which manifest as resonances in the transmission as a function of energy. The stronger the hydrogen bonding between base-pairs, the more charge transport occurs. The hydrogen bonds between A-T base-pairs are relatively weaker than those between G-C base-pairs. Mahapatro et al. systematically changed the central five base pairs from G-C to A-T base-pairs. As a result, the conductance is decreased exponentially by substituting A-T base-pairs at the center of the DNA molecule. Measured $I$-$V$ characteristics are presented with four kinds of DNA sequences in Fig. 2.2. The conductance ($G_{DNA}$) of the A-A’ configuration, which is homogeneous G-C base-pairs, is measured around $10^{-9}$ S. This conductivity decreases with the addition of more A-T base-pairs.
Fig. 2.1. Au/ds-DNA/Au structure. A-A’ (no A-T base-pairs), B-B’ (one A-T), C-C’ (three A-T), and D-D’ (five A-T at the center of the double-strand DNA) [13].

Fig. 2.2. The current-voltage characteristics are measured through immobilization of A-A’, B-B’, C-C’, and D-D’ DNA sequences. The conductance decreases as the number of A-T base-pairs increases [13].

Dong et al. also investigated the effects of the sequence on transmission with a double helix DNA model (N = 30 base-pairs) [18]. Using the transfer matrix method,
they obtained transmission coefficients and current-voltage curves for four different sequences of DNA models, such as a homogeneous poly(G)-poly(C) sequence, a periodic poly(G)-poly(C) sequence, a Fibonacci poly(G)-poly(C), and a quasi-periodic Rudin-Shapiro sequence. As the potential barriers change (i.e., the order of the sequence becomes more randomized), coherent charge tunneling is decreased which results in a lower conductivity.

In this chapter, we consider a one-dimensional (1-D) one-channel DNA of 20 bases between electrodes using TB models. Here, we do not consider a double-helix (base-pairs and backbone) on our one strand DNA model. We investigate the transmission coefficient, Lyapunov coefficient, and localization length in order to study the influence of DNA sequences. Furthermore, we observe the variation of the resonant peaks on the transmission by changing the position of base C on a homogeneous poly(G) DNA strand.

2.2 1-D one-channel TB model

Our model consists of 20 bases which are attached to two electrodes. In Fig. 2.3, the circles represent DNA bases and the discrete sites of the electrodes, and the lines between sites indicate hopping amplitudes. $e_i (e_o)$ is the onsite potential energy of the DNA (lead), $t_D (t_0)$ is the hopping probability between nearest-neighbor bases (lead sites), and $t_R (t_L)$ is the hopping amplitude between the right (left) lead and the end DNA bases. We assume that the electron transport occurs along the long axis of the DNA molecule because of $\pi$-orbital overlap between consecutive bases. Hence, electrons pass from the left lead and through 20 DNA bases and to the right lead.
There are several methods to calculate the transmission coefficient of a 1-D structure. The TB method is the most useful for describing the periodic potential in which the wave functions are overlapped between the lattices. In a periodic lattice, the interaction between nearest neighbors is the same over the system. Using the TB approximation, we can write the Schrödinger equation:

\[ -\sum_{n,m} t_{n,m} \psi_m + e_n \psi_n = E \psi_n, \]  

(2.1)

where the matrix elements \( t_{n,m} \) are couplings between sites \( m \) and \( n \) with the single-site potential of site \( n \), the sum runs over the nearest neighbors of \( n \), \( E \) is the electron energy, and \( e_n \) is the site energy. The total Hamiltonian of the system can be written as

\[ H_{\text{Tot}} = H_{\text{Lead}} + H_{\text{DNA}} + H_{\text{Lead-DNA}}. \]

(2.2)

It is classified as three parts that describe the Hamiltonian for the DNA molecule, for the leads themselves, and for the hopping amplitudes between the end DNA bases and right (left) lead:

\[
H_{\text{DNA}} = e_i \sum_i d_i^+ d_i - t_D \sum_i (d_i^+ d_{i+1} + \text{h.c.})
\]

\[
H_{\text{Leads}} = e_0 \sum_i l_i^+ l_i - t_0 \sum_i (l_i^+ l_{i+1} + \text{h.c.})
\]

\[
H_{\text{Lead-DNA}} = -t_L l_1^+ d_1 - t_R l_N^+ d_N + \text{h.c.}
\]

(2.3)
where $d_i^\dagger$ ($d_i$) and $l_i^\dagger$ ($l_i$) are the creation (annihilation) operators at the $i$-th base site and $i$-th of the leads.

According to the Bloch theorem, we propose a periodic solution in $k$-space from Eq. (2.1)

$$
\psi_n = A e^{i n \theta} \left( \theta = ka \right),
$$

(2.4)

where $a$ is a lattice constant, which is the distance between nearest-neighbors and $k$ is the wave vector that is connected with the energy by the dispersion relation for the Bloch states, $E = -2t_0 \cos ka + e_0$. For a 1-D system, the general incoming and outgoing wave function in the leads may be written as

$$
\psi_n = e^{in\theta} + r e^{-in\theta} \quad (n \leq 0),
$$

$$
\psi_n = t e^{i n \theta} \quad (n \geq 1),
$$

(2.5)

where $r$ is the reflection amplitude and $t$ is the transmission amplitude [19, 20]. Applying the wave functions into the TB Schrödinger equation, we form a 22 by 22 matrix (Eq. 2.6) in order to obtain the transmission amplitude as a function of the incoming electron energy, $E$, with other variables as parameters. Therefore, we can obtain the desired transmission coefficient by taking square of the transmission amplitude, $T = |t(E)|^2$. 
2. 3. Sequence dependent electron transport

2. 3. 1. Poly sequence

We investigate the transmission coefficient as a function of incoming energy with four different DNA sequences, which are homogeneous poly bases, periodic, Fibonacci, and random sequences using the 1-D single-stranded DNA molecule [16, 21]. Not only the transmission coefficient is plotted, but also the Lyapunov coefficient and localization length are generated as a function of incident energy based on the Anderson localization theory [22]. Furthermore, we investigate the transmission coefficient according to the different locations of two C bases in a strand with 18 G bases.

DNA bases G, A, C, and T are given by the ionization potentials, taken as 7.75, 8.24, 8.87, and 9.14 eV, respectively. Figure 2.4 shows the transmission coefficient of four kinds of DNA bases (N = 20 bases). Curves are shifted vertically by one unit for clarity. Notice that the pattern of transmission probability is shifted to higher energy as the base onsite energy is increased. We can also see that the number of peaks is the same

\[
\begin{pmatrix}
0 & -t_0 e^{i\theta} & t_L & 0 & \ldots & 0 & 0 & 0 \\
0 & -t_D & e+i_1 & -t_D & \ldots & \ldots & \ldots & 0 \\
0 & \ldots & -t_D & e+i_2 & -t_D & \ldots & \ldots & \ldots & 0 \\
0 & \ldots & \ldots & -t_D & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & \ldots & \ldots & \ldots & -t_D & e+i_{18} & -t_D & \ldots & \ldots \\
-\lambda e^{i\theta} & \ldots & \ldots & \ldots & \ldots & -t_D & e+i_{19} & -t_D & \ldots \\
t_0 & 0 & \ldots & \ldots & \ldots & 0 & 0 & \ldots & -t_R \\
\end{pmatrix}
= 
\begin{pmatrix}
t \\
0 \\
\psi_1 \\
\psi_2 \\
\psi_3 \\
\psi_4 \\
\psi_5 \\
\end{pmatrix}
\begin{pmatrix}
l_0 e^{i\theta} \\
L_e \\
\psi_1 \\
\psi_2 \\
\psi_3 \\
\psi_4 \\
\psi_5 \\
\end{pmatrix}
\]

(2.6)
as the number of DNA bases (20 bases) and the energy of the middle of resonance peaks in each mini-band is approximately the same as the ionization potential of each base.

Fig. 2.4. The transmission coefficients of poly 20 bases. Base G, A, C, and T have ionization potentials, 7.75, 8.24, 8.87, and 9.14 eV, respectively. \( e_0 = 7.75, t_0 = 1, t_{L(R)} = 0.5, \) and \( t_D = 0.4 \text{ eV} \)

2.3.2. Periodic sequence

We apply four periodic sequences to the 1-D DNA model: poly G-C (G-C-G-C-G-C-...), poly A-T (A-T-A-T-A-T-A-T-...), periodic G-C-A-T (G-C-A-T-G-C-A-T-...), and periodic A-T-G-C (A-T-G-C-A-T-G-C-...). Figure 2.5 shows the transmissions of these four periodic sequences with specific parameters \( e_0 = 7.75, t_0 = 1, t_{L(R)} = 0.5, \) and \( t_D = 0.4 \text{ eV} \) which are obtained from *ab initio* calculation [23]. The number of mini-bands is the same as the number of different bases, and each only reaches a maximum value of less than one. If we choose specific values of the hopping amplitudes, such as \( t_{L(R)} = t_D = 0.9 \text{ eV} \), it may reach to one. We found that the number of transmission peaks is \( N-2 \) [24]. Comparing G-C- with G-C-A-T- sequences (Fig. 2.5 (a) and Fig. 2.5 (c)), the width of the mini-bands for the latter are narrower, because as the energy levels at which
the electrons can hop (resonant tunneling) are not the same all along the strand, electron propagation is hindered and the transmission is decreased, even in a periodic sequence.

**Fig. 2.5.** Energy-dependent transmission coefficient for (a) periodic poly G-C, (b) periodic poly A-T, (c) periodic G-C-A-T, and (d) periodic A-T-G-C with \( N = 20 \) bases.

### 2. 3. 3. Fibonacci sequence

The Fibonacci poly G-C sequence is formed by starting from a G or C base and following the inflation rule \( G \rightarrow GC \), \( C \rightarrow CG \) and ending with \( C \rightarrow G \), \( G \rightarrow C \). Each subsequent number is the sum of the previous two. Figure 2.6 presents the transmission coefficient for two different configurations of Fibonacci sequences, which are \( G-GC-GCG-GCGGC-GCGGCGCG-G \) (\( N = 20 \)) and \( C-CG-CGC-CGCCG-CGC CGCGC-C \). The height and width of the Fibonacci transmission mini-bands are smaller than for the periodic G-C sequences, shown in Fig. 2.5(a). The transmission shows quasi-periodic features which are neither completely periodic nor random sequences.
2.3.4. Random sequence

Experimentally, the conductivity is measured with artificial or genomic DNA sequences, such as human chromosome 22 and bacteriophage λ-DNA, which is extracted from *E. coli* [11]. These sequences are close to random sequences. For example, the $\lambda_1$-chain is the first 60-base-pair of the phase sequence;

$$\text{GGGCGGCGACCTCGCGGGTTTTCGCTATTAT-}$$

and the $\lambda_2$-chain is the next 60-base-pair;

$$\text{TTCTTCTCGTACAACTTTAGTTTTATTTTTAATACCCCTCTGAAA-}$$

$\text{GAAAGGAAACG} [16]$. Although these sequences appear random, they are part of the specific coding in DNA which contains the instruction set for building proteins. In Fig. 2.7, we randomly chose 20 bases, each with 50% G and C bases (the upper (a) and (b)) and plotted $T(E)$. The bottom frames ((c) and (d)) are the random G-C-A-T sequences. When the system is disordered by randomly shifting the energies of the various trapping sites, the wave function exponentially decays. Therefore, the transmission mini-bands...
become more localized [25]. We note that in Fig. 2.7 the disorder effects, or Anderson localization, on the transmission coefficient of random sequences occur. Anderson localization is the quantum interference effect between many scattered wavelets. In other words, an electron hops from one site to another through quantum tunneling. If each lattice site has the same potential with all wells the same, the electron would be completely mobile. Whereas, if the lattice sites change randomly, the electron can become trapped, or localized, and the transmission is decreased. This means that the wave function of the electron exponentially decays in space due to the increased backscattering [26].

Figure 2.8 shows the energy-dependent transmission coefficient as well as the Lyapunov coefficient and the Localization length. The three figures in each row in Fig. 2.8 indicate transmission coefficient, Lyapunov coefficient, and Localization length for (a) the homogeneous poly (G) bases sequence, (b) the periodic G-C sequence, (c) the Fibonacci sequence, (d) the random G-C-A-T sequence.
nacci G-C sequence, and (d) the random G-C sequence, respectively. The Lyapunov coefficient and the localization length are calculated using the transmission coefficients in order to compare the transmission properties depending on the different sequences. The middle column depicts the Lyapunov coefficient, $\gamma_N = -\ln[T(E)]/(2N)$, and shows specific patterns according to the different sequences [27, 28]. Especially, the self-similarity feature (the series of elliptic bumps) is shown on the Fibonacci sequence compared to the random sequence. In addition, the Lyapunov coefficient is inversely related to the localization length, $\xi(E) = [\gamma_N]^{-1}$ [23, 26-36]. Let us take a look at the third column in Fig. 2.8(a, b, c, and d). If the system becomes randomized, the localization length becomes smaller because the transmission has poor behavior according to the relationship, $T \propto \exp[-L/\xi]$, where $L$ is total length of the system. In our case, it is fixed at 20 bases.
Fig. 2.8. Transmission coefficient (left frames), Lyapunov coefficient (middle frames), and localization length (right frames) for (a) the poly 20 G bases, (b) periodic GC sequence, (c) Fibonacci GC sequence, and (d) random GC sequence.

2.4. Position variables

We investigate the transmission coefficient by changing the position of C bases. In Fig. 2.9, by changing the position of two C bases in a certain DNA sequence (18 G bases and 2 C bases), we obtain some interesting results. Whether two C bases are on the front or the last position, the transmission of these two sequences of DNA is the same.
When two C bases are on the third and forth positions (Fig. 2.9 (c)) or on the 17th and 18th positions out of 20 bases total (Fig. 2.9(d)), the curves of the transmission coefficient are the same. Therefore, we can conclude that the transmissions are the same if two DNA sequences have mirror symmetry patterns. The transmission figures are different between (a, b) and (c, d) because of different sequences. Figure 2.9 (c) and (d) are more randomized than (a) and (b) so that the resonant peaks are lower than in the upper frames (a) and (b).

Fig. 2.9. Transmission coefficient for
(a) CCGGGGGGGGGGGGGGGGG, (b) GGGGGGGGGGGGGGGGGC, (c) GGGGGGGGGGGGGGGGG, and (d) GGGGGGGGGGGGGGGCGG.
Chapter 3: Backbone-induced effects on charge transport through a quasi-one-dimensional DNA molecule

3.1. Introduction

We have studied charge transfer through single-stranded DNA in Chapter 2, but real DNA has double-strands (ds) which include base-pairs formed by complementary bases (A with T or C with G) and sugar-phosphate backbones to hold in the double-helix structure. Many theoretical models have been formulated to explain the experimental results, such as 1-D TB model and ds-TB model. The electric conductance of DNA is dominated by the structure and the base sequence. Further, overlapping $\pi$-orbitals located on the stacked base-pairs are considered by many theoretical calculations as the way in which charge transport can occur. However, Cuniberti et al. have reported charge transport through a short poly(G)-poly(C) double-stranded DNA molecule ($N = 30$ base-pairs long) by considering the backbone effect [17]. They showed that the backbone coupling, the hybridization of the overlapping $\pi$-orbitals in the base-pair to the backbone, controls the opening of a gap in the transmission. They also found semiconducting behavior in the $I$-$V$ characteristics which shows good agreement with the experimental results by Porath et al [7]. Macia et al. have suggested a major role of the backbone-induced effects in the charge transfer with poly(G)-poly(C) and poly(A)-poly(T) chains. They introduced a two-step renormalization process in order to describe the realistic double-stranded DNA
molecule in terms of an effective 1-D TB model. They described significant changes with subsequent strong impact in the transmission and $I$-$V$ characteristics, such as the voltage threshold and the turn-on current capability [37].

Motivated by this idea, we introduce a quasi-1-D TB model for charge transport. In part 1, we use a single step renormalized onsite energy and show the variation of the transmission, depending on the sequence and temperature effect. In the second part, we apply a renormalized onsite energy and hopping integral and show the effects of inhomogeneous backbone onsite energies, asymmetric energy-dependent hopping amplitude between DNA base-pairs and the backbone, and the asymmetric contact coupling between the leads and DNA base-pairs, illustrating the diverse circumstances which may affect experiment results. We show the overall contour plot of the transmission, the current-voltage characteristics, and the differential conductance.

3. 2. The quasi-1-D one-channel TB model

We consider a single-channel model for charge carrier propagation through the DNA duplex, shown schematically in Fig. 3.1 The electron transport in the DNA molecule, connected between two semi-infinite electrodes, arises through the central conduction channel which consists of base-pairs and is connected to the upper and the lower backbone sites. This model is called fishbone model.

Using a quasi-1-D TB model, a single and effective Hamiltonian for charge transport through the ds-DNA between two metallic leads can be written as [16, 17, 25, 37],

$$H_{\text{Tot}} = H_{\text{Lead}} + H_{\text{DNA}} + H_{\text{Lead-DNA}}. \quad (3.1)$$
Fig. 3.1. Schematic illustration of the fishbone model. The left and right ends of the DNA are connected to the electrode, lines denote hopping amplitudes, circles denote base-pairs, and pentagons are backbone structure.

Here, the Hamiltonian for a short DNA molecule is described by

$$H_{DNA} = \varepsilon_D \sum_i d_i^\dagger d_i - t_D \sum_i (d_i^\dagger d_{i+1} + h.c.) + \sum_{i,\alpha = G,C,A,T} \sigma_\alpha b_{i\alpha}^\dagger b_{i\alpha} - \sum_{i,\alpha = G,C,A,T} t_\alpha (b_{i\alpha}^\dagger d_{i\alpha} + h.c.),$$

where $d_i^\dagger (d_i)$ and $b_{i\alpha}^\dagger (b_{i\alpha})$ are the creation (annihilation) operators at the $i$-th base-pairs and the $i$-th upper and lower backbone site, $\varepsilon_D$ is the average of DNA base-pairs, and $t_D$ is the hopping integral between nearest-neighbor base-pairs. The influence of the backbone is considered in the third and fourth terms in Eq. (3.2), where $\sigma_\alpha (\alpha = A, T, G, \text{and} C)$ is the backbone onsite energy (8.5 eV) and $t_\alpha$ is the hopping integral from each base (G, C, A, or T) to the upper and lower backbone site. In order to map the original double-chain into the equivalent single-channel, we introduce an effectively renormalized and energy-dependent onsite potential $\varepsilon(E)$:

$$\varepsilon (E) = \varepsilon_D + \frac{t_\alpha^2}{E - \sigma_\alpha} + \frac{t_\alpha^2}{E - \sigma_\alpha},$$

(3.3)
where $\epsilon_D$ is the average of two complementary bases which are paired each other, such as $\epsilon_D = (\epsilon_C + \epsilon_G)/2$. Our DNA molecule is linked to two semi-infinite metallic leads by the tunneling Hamiltonian

$$H_{\text{Leads-DNA}} = -t_L l_L^\dagger d_1 - t_R l_R^\dagger d_N + h.c., \quad (3.4)$$

where $t_L (t_R)$ is the coupling strength between the left (right) lead and the end DNA base-pairs, 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

$$H_{\text{Lead}} = \epsilon_0 \sum_i l_i^\dagger l_i - t_0 \sum_i (l_i^\dagger l_{i+1} + h.c.), \quad (3.5)$$

where the lead onsite energy is $\epsilon_0 = 7.75 \text{ eV}$ and the hopping amplitude is taken as $t_0 = 1 \text{ eV}$.

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

$$-\sum t_{n,m} \psi_m + \epsilon_n \psi_n = E \psi_n, \quad (3.6)$$

where the matrix elements $t_{n,m}$ are hopping integrals between sites $m$ and $n$ with the single-site potential of site $n$, the sum runs over the nearest neighbors of $n$, $E$ is the electron energy, and $\epsilon_n$ is the site energy. Hence, the general incoming and outgoing wave functions in the leads from the solution of Eq. (3.6) may be written as

$$\psi_n = e^{in\theta} + re^{-in\theta}, \quad n \leq 0,$$

$$\psi_n = te^{in\theta}, \quad n \geq 1,$$  

(3.7)
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 amplitudes in the leads and DNA molecules can be obtained as

\begin{align}
-t_0 e^{i\theta} - t_0 r e^{-i\theta} + t_L \psi_1 &= 0, \\
t_k \psi_5 + t_0 t e^{2i\theta} + (E - \varepsilon_0) t e^{i\theta} &= 0, \\
t_L (1 + r) + t_D \psi_2 + (E - \varepsilon) \psi_1 &= 0, \\
t_D \psi_1 + t_D \psi_3 + (E - \varepsilon) \psi_2 &= 0, \\
t_D \psi_2 + t_D \psi_4 + (E - \varepsilon) \psi_3 &= 0, \\
t_D \psi_3 + t_D \psi_5 + (E - \varepsilon) \psi_4 &= 0, \\
t_D \psi_4 + t_K t e^{i\theta} + (E - \varepsilon) \psi_5 &= 0,
\end{align}

where the energy-dependent onsite potential $\varepsilon$ is defined by Eq. (3.3). Rearranging Eq. (3.8) in a matrix form and inverting this matrix, we obtain the transmission amplitude $t(E)$ of the system and the transmission coefficient by taking the square of the amplitude, $T = |t(E)|^2$. In the following, we demonstrate the opening of a transmission band gap, the variation of the transmission with base-pair sequence, $I-V$ characteristics, and the temperature effects.

For the second model, we use a two-step renormalization process for a short poly(G)-poly(C) DNA molecule. The first step of the renormalization is the energy-dependent transfer integral ($\tau_{\alpha}$) from a G or C base to the backbone site:

$$
\tau_{\alpha} = t_{\alpha} + \frac{\varepsilon_{\alpha}(E - \varepsilon_{\alpha})}{t_{\alpha}}.
$$

The second step is the energy-dependent onsite potential $\varepsilon(E)$ which incorporates the existence of the backbone and renormalized hopping integrals:
\[ \varepsilon(E) = \varepsilon_{GC} + \frac{\tau_G^2}{E - \sigma_G} + \frac{\tau_C^2}{E - \sigma_C}, \]  

(3.10)

where \( \varepsilon_{GC} = t_{GC} + (\varepsilon_G + \varepsilon_C)/2 \) with the onsite energy of G or C bases, \( \varepsilon_C = 8.87 \text{ eV} \) and \( \varepsilon_G = 7.75 \text{ eV} \), given by the ionization potentials of the respective bases, and the hopping integral \( t_{GC} = 0.04 \text{ eV} \), which describes the hydrogen bonds connecting G-C base-pairs.

We obtain the transmission amplitude \( t(E) \) of the system:

\[ t(E) = \frac{t_0 t_L t_R t_D^2 (1 - e^{2i\theta})}{t_D^2 P(E) - t_L^2 t_R^2 e^{2i\theta} Q(E) - t_0^2 (t_L^2 + t_R^2) e^{i\theta} R(E)}, \]

(3.11)

where

\[
\begin{align*}
P(E) &= \{(E - \varepsilon)^4 - 4(E - \varepsilon)^2 t_D^2 - 3t_D^4\}, \\
Q(E) &= \{(E - \varepsilon)^2 - 2t_D^2\}, \\
R(E) &= \{(E - \varepsilon)^4 - 3(E - \varepsilon)^2 t_D^2 + t_D^4\}.
\end{align*}
\)

(3.12)

Eq. (3.11) allows us to find the conductance through the DNA molecules by the Landauer-Buttiker approach [38, 39]: \( G = (2e^2 / h)T \), where \( T = |t(E)|^2 \). We show the result of the second model for the backbone contribution and contact effects with a fixed hopping probability between nearest-neighboring poly(G)-poly(C) base-pairs (\( t_D = 0.4 \text{ eV} \)). More specifically, to simulate the complicated experimental situations, we modulate parameters of the system such as the onsite energies of the backbone (\( \sigma \)), the hybridized hopping amplitude (\( t_a \)) between a G (or C) base and the backbone, and the contact coupling strength (\( t_L \) and \( t_R \)) both symmetrically and asymmetrically. In our numerical calculations, we use the re-scaled parameters, \( t_G(t_C), \sigma_G(\sigma_C), t_L(t_R) \), and the electron energy \( E \), all of which are normalized with respect to the hopping integral of the leads \( t_0 = 1 \text{ eV} \).
### 3.3. One-step renormalized onsite energy

#### 3.3.1. Sequence dependent charge transport

The electrical transport properties of DNA have been widely studied with different sequences of DNA using direct measurements [10], *ab-initio* calculations [40], and the transfer matrix method [18, 37], where the strong sequence dependence of results is indicated. Based on this idea, we consider four sequences of a DNA system: a poly(G)-poly(C) sequence, a poly(A)-poly(T) sequence, an alternate G/C-A/T sequence, and an A/T-G/C sequence. In Fig. 3.2, four all transmission coefficients have two mini-bands and a band gap. However, the width of each mini-band, the width of the band-gap, and the shape of the resonant peaks are different. In Eq. (3.3), we fixed the following parameters; \( \sigma_\alpha = 8.5, \varepsilon_0 = 7.75, t_b = 1, t_d = 1, t_L(t_K) = 0.5, t_a = 0.7; \) but \( \varepsilon_\sigma \) is different for a G/C base-pair, \( (\varepsilon_G + \varepsilon_A)/2 = 8.31 \), or for an A/T base-pair, \( (\varepsilon_A + \varepsilon_T)/2 = 8.69 \). As the onsite energy changes from G/C base-pairs \( (\varepsilon_\sigma = 8.31) \) to A/T base-pairs \( (\varepsilon_\sigma = 8.69) \), two mini-bands are shifted toward higher energy.

![Fig. 3.2. Transmission coefficient as a function of a renormalized energy-dependent onsite potential determined from Eq. (3.3). There is a gap between two the mini-bands and five peaks total arise in the first mini-band. However, the shapes of the transmission, the distance of the band-gap, and the width of each mini-band vary depending on the sequence of the base pairs; (a) G/C-G/C-G/C-G/C-G/C, (b) A/T-A/T-A/T-A/T-A/T, (c) G/C-A/T-G/C-A/T-G/C, and (d) A/T-G/C-A/T-G/C-A/T.](image-url)
The current is defined as the rate of charge transport, and it is of direct interest since it corresponds to an experimentally observable quantity. The transmission function, which has different resonant shapes due to the variable sequences of the base-pairs, is directly related to the current [6] (see Eq. (3.13)). The $I$-$V$ characteristics are obtained from the Landauer-Buttiker (scattering) formula at room temperature and expressed as

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E)[f_L(E) - f_R(E)].$$  \hfill (3.13)

Here, \( f(E) \) is the Fermi-Dirac distribution given by \( f_{L(R)}(E) = 1/(e^{\beta(E - \mu_{L(R)})} + 1) \), where \( \beta = 1/k_B T \) and \( \mu_{L(R)} \) stands for the electrochemical potential of the left (right) leads whose values depend 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 \( \eta \) is a parameter describing the possible asymmetry of contact to leads, chosen here as \( E_f = 5.4 \) eV and \( \eta = 1/2 \), respectively [38, 41]. The shape of the $I$-$V$ curves are changed very sensitively depending on the relative values of the Fermi energy, because the Fermi energy window mainly contributes to the conduction. Therefore, we adjust the Fermi energy as 5.4 eV in order to compare our result with the experimental one. Figure 3.3 shows the current-voltage curves of a poly(G)-poly(C) sequence (blue dotted line), according to Eq. (3.13). The existence of the gap in the $I$-$V$ curves indicates a semiconductor-like behavior. Several experimental measurements, directly probing the electric current as a function of the potential applied across synthetic DNA molecules, have evidenced the presence of conduction in the current-voltage features at room temperature. The upper inset in Fig. 3.3 is a schematic diagram of the test device to
measure current through a 10.4-nm-long DNA molecule which is trapped between two electrodes [7]. The blue curve is the result which is measured after trapping a DNA molecule as shown in the upper inset. Our numerical $I$-$V$ calculations in Fig. 3.3 fit well with the experimental result.

![Graph of $I$ vs $V_{sd}$](image)

Fig. 3.3. Current as a function of the source-drain applied voltage for different sequences, where the Fermi level energy is 5.4 eV and the temperature is 300 K: Poly(G/C) sequence (blue, dotted line), Poly(A/T) sequence (black, dot-dashed line), alternate (G/C-A/T) sequence (green, dashed line), and alternate (A/T-G/C) sequence (red, solid line). The inset shows the experimental result for a 10.4-nm-long DNA molecule [30 base-pairs, double-stranded poly(dG)-poly(dC)]. The upper inset is a schematic diagram of the test device to measure conduction at room temperature [7, 37].

Since the influence of a mismatched (or impurity) DNA sequence is important in biology or medical research, we investigate the transmission and $I$-$V$ characteristics for the poly(G)-poly(C) base-pairs with one mismatched base-pair (G with G). Transmission vs. electron incoming energy is presented in Fig. 3.4(a) with (orange, solid line) and without (blue, dotted line) an impurity base-pair. The existence of the impurity in a short DNA sequence leads to a distortion of the transmission bands and a reduced peak height in the transmission. We also calculate the $I$-$V$ curve from Eq. (3.13) in the presence of a
mismatched base-pair. It is clearly seen from the \( I-V \) curve in Fig. 3.4(b) that the current gap with an impurity (orange, solid line) is reduced in comparison with normal poly(G)-poly(C) base-pairs (blue, dotted line). It is interesting to note that when we change the location of the mismatched base-pair, there is no significant change in the \( I-V \) characteristics.

![Image](image)

Fig. 3.4. (a) The transmission \( T(E) \) for a one-chain TB model with a poly G/C sequence (blue, dotted line) and a G/G mismatched sequence, G/C-G/G-C-G/C-G/C-G/C (orange, solid line). (b) The corresponding \( I-V \) characteristics with Fermi Energy (\( E_f = 5.4 \) eV).

3.3.2 Variation of the band-gap

The nucleobase in DNA can interact with the sugar-phosphate backbone by means of the hopping integral between the base and the backbone. Therefore, the onsite energy of the base-pairs with a finite backbone coupling is renormalized as expressed in Eq. (3.3). Since the backbone coupling controls an opening of the gap in the transmission, the gap width between the two mini-bands can be written as

\[
\Delta_{\text{gap}} = 2 \sqrt{t_D^2 + 2 t_a^2} - 2 t_D ,
\]  

(3.14)
where $t_D$ is the hopping amplitude between neighboring base-pairs and $t_\alpha$ is the coupling between the base-pairs and the sugar-phosphate backbone [17, 37]. In Fig. 3.5(a), the transmission for poly(G)-poly(C) versus electron energy is plotted with fixed $\sigma_\alpha = 8.5$, $\epsilon_0 = 7.75$, $t_0 = 1$, $t_L(t_R) = 0.5$, and $t_\alpha = 0.7$ for different hopping strengths $t_D = 0.1, 0.3, 0.6, \text{ and } 0.9$ (bottom to top) between nearest-neighboring DNA base-pairs. Figure 3.5(b) presents the gap, which is the distance between two mini-bands in the transmission, as a function of the value of $t_D$ (from 0.01 to 0.9). The blue dots are measurements of the distance between the two mini-bands and the line plot (red, solid line) is obtained from the Eq. (3.14), where $t_\alpha$ is fixed at 0.7. As you can see, the data fit the equation well. The width of the first mini-band as a function of the hopping strength ($t_D$) is shown in Fig. 3.5(c). The width of the mini-band is broadened as the coupling increases. When $t_D = 0.9$, for example, the width of the first mini-band is extended by around 10 times in comparison with the case of $t_D = 0.1$. 
3.3 Temperature effects on the transmission

The variation of the temperature induces thermal vibrations and twisting of DNA molecules. Thus, electron transport can be changed significantly due to the structural disorder. Here, we investigate finite temperature effects on the transmission through a short poly(G)-poly(C) DNA molecule. In principle, inelastic electron-phonon scattering can occur because of the thermal vibrations in the system. However, we ignore inelastic scattering effects because they play a minor role on the conductance [40]. Neglecting inelastic scattering effects, the transmission \( T_{\text{temp}} \) at temperature \( T \) can be calculated by thermally averaging the zero-temperature results with the appropriate Fermi-factor, and can be written as:
\[
T_{\text{temp}}(\tilde{E}) = \int T(E, \text{temp} = 0) \cdot (-\frac{df}{dE})dE,
\]

where \( (-\frac{df}{dE}) = \frac{\beta}{4 \cdot \cosh^2(\frac{\beta}{2} (E - \tilde{E}))} \) with \( \beta = \frac{1}{k_B T} \) and \( f(E) = \frac{1}{e^{(E-E_0)/k_B T} + 1} \).

In Fig. 3.6, we show the total temperature-dependent transmission coefficient as a function of electron energy for the various temperatures, \( T = 0, 25, 100, 300 \) K. It is clearly seen that as the temperature is increased from zero to room temperature, the sharp transmission oscillations are smeared out and the resonant peak heights are suppressed \( (T(E) < 1) \).

![Fig. 3.6. Temperature dependence of the transmission as a function of electron energy with fixed \( \sigma_o = 8.5, \epsilon_0 = 7.75, t_o = 1, t_L(t_R) = 0.5, t_D = 0.5, \) and \( t_u = 0.7, \) for different temperature \( T = 0, 25, 100, \) and 300 K.](image)

**3.4. Two-step renormalized onsite energy**

**3.4.1. Variation of the hopping strength**

First, we examine the transmission characteristics along the long axis of the five poly(G)-poly(C) DNA base-pairs which have a two-step renormalized onsite energy...
(energy-dependent transfer integral from a G (or C) base to the backbone, and energy-dependent nucleotide onsite potential). We vary the hopping integral between the DNA base-pairs and the upper and lower backbone both symmetrically and asymmetrically. Figure 3.7(a) shows a contour plot of the transmission as a function of both electron energy \( E \) and hopping strength \( t_G \) and \( t_C \) for fixed \( G = 8.5 \) and \( t_L = t_R = 0.4 \).

When \( t_G = t_C \approx 3 \), it is seen that there are two mini-bands with a gap in the transmission, which is a typical semiconducting feature. As both \( t_G \) and \( t_C \) are decreased, however, an overlapping of the two mini-bands occurs and a single merged mini-band appears. The single mini-band without a gap in the transmission becomes localized in a small window of energy at higher electron energy, \( E \approx 8.4 \).

We also show a contour plot of transmission for fixed \( t_G = 3.5 \) in Fig. 3.7(b) by modulating the hopping strength \( t_C \) between base C and the lower backbone. In this symmetry-breaking DNA structure, two transmission mini-bands with a gap progressively approach each other and eventually merge into a single mini-band as the difference of the hopping amplitudes \( |t_G - t_C| \) becomes larger. It is interesting to note, however, that the transmission in this asymmetric system disappears completely when \( t_C \approx 5.8 \) or \( t_C \approx 2.7 \). Therefore, the backbone coupling to DNA base-pairs controls the opening of a gap and the merging and a collapsing of a mini-band in the transmission.
3. 4. 2. Variation of backbone onsite energy

We also modulate the onsite energies of the backbone ($\sigma_\sigma$) both symmetrically and asymmetrically. We first examine the transmission of DNA molecules with a symmetric variation of the backbone onsite energies $\sigma_G$ and $\sigma_C$. In Fig. 3.8(a), we show a contour plot of the transmission as a function of electron energy ($E$) and backbone onsite energies ($\sigma_G$ and $\sigma_C$) for fixed $t_G = t_C = 1.5$ and $t_L = t_R = 0.4$. When $6.0 \leq \sigma_G(= \sigma_C) \leq 7.8$, two transmission mini-bands with a gap arise in the lower electron energy window.
As the backbone onsite energy increases, the transmission bands are shifted towards higher energies and the two mini-bands in the transmission merge into a single mini-band, since the onsite potential energy of the DNA is affected by the backbone onsite energies. The inset of Fig. 3.8(a) shows that each mini-band has five distinctive resonant peaks, where each peak reaches full transmission.

Access to transmission properties can be provided by measuring $I$-$V$ curves. In order to compare our results with experimentally measured data [7], we evaluate the $I$-$V$ characteristics of the system with the transmission function $T(E)$ using Eq. (3.13) with $E_f = 6.2$ eV and $\eta = 1/2$. In Fig. 3.8(b), the current ($I$) as a function of the applied voltage ($V_{sd}$) at room temperature is shown for different values of $\sigma_g = \sigma_c = 7.0$ (black, dotted line), 7.5 (green, dashed line), 8.0 (yellow, solid line), 8.5 (red, dot-dashed line), and 9.0 (blue, thick-dashed line). The $I$-$V$ curves show negligible current up to a threshold voltage followed by a sharp rise of the current, which is a typical feature of a semiconductor. We note that the current gap in the $I$-$V$ curve widens on increasing the backbone onsite energy.
Fig. 3.8. (a) Contour plot of the transmission as a function of electron energy and symmetric backbone onsite energies ($\sigma_G$ and $\sigma_C$). Five distinctive resonant peaks with full transmission in each mini-band are shown in the inset. (b) Current ($I$) as a function of the source-drain applied voltage $V_{sd}$ with $k_B T \approx 26$ meV and $E_f = 6.2$ eV for different values of $\sigma_G = \sigma_C = 7.0$ (black, dotted line), 7.5 (green, dashed line), 8.0 (yellow, solid line), 8.5 (red, dot-dashed line), and 9.0 (blue, thick-dashed line), where typical semiconducting characteristics are shown.

Next, we examine the asymmetrical effects of the backbone onsite energy on the transmission. A contour plot of the transmission with variation of the lower backbone onsite energy $\sigma_c$, for fixed $\sigma_g = 7.5$, $t_G = t_C = 1.5$, and $t_L = t_R = 0.4$ is shown in Fig. 3.9. When $\sigma_c$ is equal to $\sigma_G = 7.5$, we see two mini-bands with a gap in the transmission as shown before. As the difference $|\sigma_G - \sigma_c|$ between the two values of the backbone onsite energies is increased, however, an overlapping of the two mini-bands occurs and the
single-merged mini-band eventually disappears. Most importantly, it is clearly seen that an additional sharp resonance peak appears at higher energy ($E \approx 7.5$) as soon as the symmetry of the DNA backbone onsite energy is broken. This extra resonance peak, which in turn is a mini-band with five distinctive resonance peaks [see Fig. 3.10(i)], remains even when the single-merged mini-band disappears at $\sigma_c \approx 7.64$ and $\sigma_c \ll 7.25$. Notice here that we have generated each contour plot of the transmission with a different energy scale and combined these together because this extra resonance peak is so narrow and sharp.

Fig. 3.9. Contour plots of the transmission of the DNA with asymmetric backbone onsite energy. When the symmetry of DNA backbone onsite energy is broken, two transmission mini-bands overlap in the lower energy and an additional sharp resonance peak appears in the range of $7.45 < E < 7.6$.

In order to understand these resonance phenomena of DNA transport more clearly, we plot the transmission as a function of electron energy in Fig. 3.10 for a variation of the backbone onsite energy. For a fixed $\sigma_g = 7.5$, the resonance characteristics of the transmission are shown in Fig. 3.10 as (a) $\sigma_c = 7.5$, (b) $\sigma_c = 7.4$, (c) $\sigma_c = 7.3$, and (d) $\sigma_c =$
7.24. When $\sigma_G = \sigma_c = 7.5$, the transmission $T$ of the structure exhibits weakly split groups of transmission resonances in each mini-band due to the inter-base-pair tunneling. As the system moves away from the symmetry point about the transport direction (namely, when $\sigma_G \neq \sigma_c = 7.4$), the two mini-bands are shifted with a reduced gap to lower energy, and a pronounced resonance peak appears at $E \approx 7.47$ in Fig. 3.10(b). From the enlarged plot of this resonance peak, depicted in Fig. 3.10(i), it is seen to be a single mini-band with five well-defined resonance peaks. This extra mini-band shifts gradually to lower energy, and its width increases slightly as $\sigma_c$ decreases. This extra mini-band remains as long as $|\sigma_G - \sigma_c| \neq 0$, unlike the two primary mini-bands which eventually disappear.

The two primary mini-bands with a gap become overlapped and their gap disappears at $\sigma_c = 7.3$ [Fig. 3.10(c)]. This combined mini-band completely disappears at $\sigma_c = 7.24$ [Fig. 3.10(d)]. In order to make sure that this single-merged mini-band indeed disappears (and is not just shifted to a lower energy window), we change the backbone on-site energy over a small scale in Fig. 3.10(e)-(h). When $\sigma_c = 7.255$, the merged mini-band acquires the form of two pronounced Breit-Wigner (BW) resonances at $E \approx 7.034$ and $E \approx 7.054$. When $\sigma_c$ reaches the critical value $\sigma_c = \sigma_{crit} = 7.253$, total overlapping of the BW resonances results in a single BW resonance. This can be qualitatively interpreted by saying that the variation of $\sigma_c$ effectively makes the energy levels in the DNA base-pairs degenerate, and induces a strong interaction between them. When $\sigma_c < \sigma_{crit}$, the amplitude of the BW resonance in the transmission is less than unity, as seen in Fig.
3.10(g). The appearance of an under-unity resonance (less than full transmission, called a “quasi-resonance” with nonzero reflection), is also observed in asymmetrical quantum-dot systems [42, 43]. It is considered here that this under-unity resonance may occur when the effective coupling between the dot and the nearby left and right wells becomes weaker. Hence, the variation of the lower backbone onsite energy for a fixed $\sigma_\sigma$ determines the degree of asymmetry of the DNA molecule and therefore, the modulation of $|\sigma_\sigma - \sigma_c|$ has the equivalent effect of controlling the coupling between the leads and DNA base-pairs. It is also found in Fig. 3.10(h) that the peak value of the transmission coefficient decreases and eventually becomes zero with decreasing $\sigma_c$, which is equivalent to the absence of transmitting states.
Fig. 3.10. The resonance characteristics of the transmission as a function of electron energy are plotted for various backbone onsite energy values. The merging and collapse of the two mini-bands as well as the appearance of an extra resonance peak are shown in (a)-(d). The enlarged plot of the extra resonance peak, depicted in (i), shows it to be a single mini-band with five well-defined resonance peaks. The sequence of overlapping of the two BW resonances into a single BW resonance, forming an under-unity resonance which eventually collapses as the backbone asymmetry increases, is shown in (e)-(h).

Using Eq. (3.13) and the transmission $T(E)$ of Fig. 3.10(a)-(d), we investigate the characteristics of $I$-$V$ curves at room temperature ($k_B T \approx 26$ meV) for an asymmetric DNA structure. Figure 3.11 demonstrates nonlinear $I$-$V$ curves, which exhibit a variable current gap at low applied bias, with a variation of $\sigma_c = 7.3$ (red, dashed-dot line), $\sigma_c = 7.4$ (green, dotted line), $\sigma_c = 7.5$ (blue, solid line), and $\sigma_c = 7.24$ (black, dashed line)
for fixed $\sigma_c = 7.5$. It is clearly seen that the voltage threshold is modulated as the backbone onsite energy changes. In other words, the current gap gets wider as $\sigma_c$ increases. This can be qualitatively explained as follows: as the backbone onsite energy, $\sigma_\sigma$, increases, the main DNA onsite energy $\varepsilon(E)$ also increases. When $\varepsilon(E)$ becomes larger, the mini-bands in the transmission are shifted to higher electron energy and therefore, the onset of current arises at a higher source-drain voltage $V_{sd}$. This requires a higher voltage threshold to observe a current and a wider current gap in the $I-V$ curves. When $\sigma_c = 7.24$ (black, dashed line), on the other hand, the voltage threshold increases to $V_{sd} \approx 1.4$ volts (V) and the current remains constant after a voltage of $V_{sd} \approx 1.8$ V, because the main contribution to the transmission from the merged mini-band has disappeared, as shown in Fig. 3.10(d). In all cases, the system behaves as a semiconductor with a current gap that varies with the modulation of $|\sigma_G - \sigma_c|$ (or the effective couplings). In addition, we calculate the differential $I-V$ curve ($dI/dV$) as a function of $V_{sd}$ for $\sigma_c = 7.24$ (black, dashed line) and $\sigma_c = 7.5$ (blue, solid line) in the inset of Fig. 3.11. The differential conductance for $\sigma_c = 7.24$ exhibits a double-peak structure with an amplitude of 30 $nA/V$ and a peak width of $\sim 0.2$ V.
Fig. 3.11. The current-voltage characteristics calculated from the transmission $T(E)$ of Fig. 3.10(a)-(d) at 300 K where the Fermi energy is 6.2 eV. The nonlinear I-V curves exhibit a current gap at low applied bias, which is an indication of semiconductor behavior. The inset shows the differential conductance $dI/dV$ versus applied voltage $V_{sd}$, corresponding to I-V curves for $\sigma_c = 7.24$ (black, dashed line) and $\sigma_c = 7.5$ (blue, solid line).

### 3. 4. 3. Variation of coupling between leads and DNA

The role of contacts deserves particular attention because the precise details of DNA-lead contacts in most experiments are not uniformly known or reported. In many experimental measurements, it is difficult to prove that the DNA molecule is in direct contact with the electrodes because the contact with the metal electrodes is achieved by laying down the molecules directly onto the electrodes. Such an uncertain experimental situation with regards to DNA-electrode contacts makes it difficult to set the basis for a meaningful theoretical approach to study intrinsic DNA electrical transport properties. In order to specifically address DNA-lead contact effects on charge transport, we examine the transmission effects of DNA-lead coupling by varying the coupling strengths between the molecule and the leads, both symmetrically and asymmetrically. In Fig. 3.12(a), we present a contour plot of the transmission as a function of the electron energy and the in-
coming (outgoing) coupling strength $t_L(t_R)$ for a fixed hopping integral $t_D$ between DNA base-pairs. In the weak coupling regime, electron tunneling between the leads and the DNA decreases and the transmission shows sharp and narrow unit resonances in each mini-band due to the localization of states, depicted in Fig. 3.12(b) for $t_L = t_R = 0.2$. For the strong coupling regime, on the other hand, overlapping of the wave functions increases due to mixing of energy states between the molecule and the electrodes, and well-separated resonant peaks in each mini-band become overlapped in the transmission as $t_L$ ($= t_R$) increases.

Finally, we consider an asymmetric DNA structure with variation of the incoming coupling strength $t_L$ for fixed outgoing coupling, $t_R = 0.5$. The results are presented in a contour plot of the transmission as a function of energy and $t_L$ in Fig. 3.12(c). In the strong contact coupling regime, the general trend of the transmission, which is an increased overlapping of the wave functions due to the mixing of energy states, is the same as in the symmetric DNA system. When $t_L$ becomes smaller ($t_L \ll 0.2$), however, a distinct and under-unity resonance in each band appears in Fig. 3.12(d). This under-unity transmission, which is a direct consequence of asymmetric contact effects, can be interpreted as resulting from interference between the DNA molecular bands and the electronic structure of the leads at the DNA-lead interface.
Fig. 3.12. Contour plots of the transmission vs. electron energy and (a) symmetric coupling strength $t_L = t_R$ and (c) asymmetric coupling strength $t_L$ with a fixed $t_R = 0.5$. Specific features of the transmission in the weak coupling regime: (b) well-separated resonant peaks in each miniband for $t_L=t_R = 0.2$ and (d) under-unity resonance in the transmission due to interference effects for $t_L = 0.2$ and $t_R = 0.5$. 
4.1. Introduction

DNA structure was discovered by Watson and Crick in 1953 and the inter-base hybridization of $\pi$-orbitals perpendicular to the planes of the stacked base-pairs in double-stranded (ds) DNA was found by Eley and Spivey in 1962. Both positive charges (holes) and electrons can propagate through $\pi$-stacks of DNA bases. Thus, the idea of using DNA as a component of future molecular electronic devices has been reported and is still being explored in nanotechnology and nanoelectronics [44-47]. Various experimental results [3, 7, 9] have been observed and have motivated a number of theoretical studies of the electronic properties of DNA, for instance, one-dimensional (1-D) and two-dimensional (2-D) tight-binding (TB) models [17, 48, 49], and density-functional methods [50, 51, 52, 53]. Most previous research has used a 1-D two-channel TB model which ignored the possibility of electron transport along the backbone. Klotsa et al. [25] performed two TB models of DNA, which are a one-channel fishbone model and a two-channel ladder model, and obtained the electronic properties in terms of localization lengths. There is a sugar-phosphate backbone of DNA, but electron transport is not allowed along the backbone in their model. They showed that as backbone disorder increased, the localization lengths increased and thus, larger currents flow. They also sug-
gested that the more appropriate model for their study was the ladder model, which is a more realistic model than the fishbone model. Iguchi investigated the semiconductivity of DNA by using a ladder system which has two main chains with hopping between nearest-neighbor sites, and interchains between the ds-DNA [54]. Iguchi also suggested the backbone chains and hydrogen bonds lead to electronic properties of DNA. In this chapter, we present charge transmission properties of a 2-D four-channel DNA model, which is more representative of the actual DNA molecule. We particularly consider the inhomogeneous hopping strength between base and backbone sites, the hydrogen bonds between base-pairs, and the intra-coupling along the backbone in our new model.

Yi et al. demonstrated the electronic properties of DNA molecules with twisted hairpinlike shapes in the presence of a magnetic field [55]. They showed that the current was oscillated by the applied field. Roche reported electronic conduction through poly(dG)-poly(dC) and $\lambda$-phase sequences as a function of temperature-dependent base-base couplings [16]. A higher number of transmitting states have been shown in the transmission spectrum at low temperature. Motivated by these interesting results, we employ TB model and calculate the overall contour plot of the transmission, temperature effects, and magnetic field effects in order to understand the possible conditions for using DNA as an electronic component. We show that the behavior of the transmission coefficient varies depending on the changing parameters. Furthermore, suppression and oscillations can be seen in the transmission due to the Aharonov-Bohm (AB) magnetic flux effect and due to the fluctuations in the twisting angle from thermal effects.
4.2. 2-D four-channel TB model

We consider four possible conduction channels for charge carrier propagation by incorporating inter-backbone couplings [9-11] and hydrogen bonds, shown schematically in Fig. 4.1 which is called the “chess” model. Electron transport through the DNA molecule, connected between two semi-infinite electrodes, arises through four different channels which consist of π-orbital overlapping through the nearest neighboring-bases from two main conduction chains and along the upper and lower backbones. Each nucleotide is represented by a site which has an energy given by the ionization potentials of respective bases, taken as $G = 7.75$, $C = 8.87$, $A = 8.24$, and $T = 9.14$ eV. These are interconnected and linked to the backbone, leads, and nearest-neighbor nucleotides by π-π stacking interaction, and hydrogen bonds. Every line between sites denotes a hopping amplitude.

![Fig. 4.1. The “chess” model for electronic transport through 4-channel DNA model: Circles denote sites; $E_{0}= 7.75$ (lead sites), $E_{a}= 8.5$ (backbone sites), $E_{i} = 7.75$ ($i = 1-5$, G base), $E_{i} = 8.87$ ($i = 6-10$, C base) which have different onsite energies, Lines; $t_{0} = 1$ (inter-lead coupling), $t_{1,2}, t_{R,1,2} = 0.3$ (hopping amplitude between the lead onsite and the end bases), $t_{i,i+1}, T_{i,i+1} = 0.2$ (intra-chain of the nearest neighboring bases), and $h_{i}(i = 1-5$, hydrogen bonds) denote various hopping amplitudes.](image-url)
In Fig. 4.1, we show a short poly(G)-poly(C) chess model. The individual upper purple circles (lower pink circles) represent DNA G (C) bases, the green hexagons are sugar-phosphate backbone sites, and the yellow circles are the lead sites. These are interconnected by the couplings, \( t_{i,i+1} (T_{i,i+1}) \), between bases along the long axis and linked to the backbone (\( \sigma \)) by the hopping amplitudes, \( t_\sigma \), and couplings, \( t_{L1(2)} (t_{R1(2)}) \) to the leads from the end bases. The backbone and leads are also inter-linked by the hopping amplitudes, \( B_\sigma \) and \( t_0 \). Each base-pair (\( \varepsilon_i - \varepsilon_{i+1} \)) is coupled by the hydrogen bonds, \( h_i \).

Using a 2-D four-channel TB model, the Hamiltonian for the chess model can be written as

\[
H_{\text{Tot}} = H_{\text{Lead}} + H_{\text{DNA}} + H_{\text{Lead-DNA}}. \tag{4.1}
\]

Here, the Hamiltonian for a short poly(G)-poly(C) DNA molecule is described by

\[
H_{\text{DNA}} = \sum_{i,j} (\varepsilon_i c_i^+ c_j + \varepsilon_j d_j^+ d_j + \sigma a_i^+ a_i + \sigma b_j^+ b_j) - \sum_i (t_\sigma a_i^+ a_i + t_\sigma d_j^+ b_j + h_i c_i^+ d_i + h.c.)
- \sum_i (t_{i,i+1} c_{i+1}^+ c_i + t_{i,i+1} d_{i+1}^+ d_i + B_\sigma a_i^+ a_{i+1} + B_\sigma b_j^+ b_{j+1} + h.c.). \tag{4.2}
\]

where \( c_i^+ (c_i) \), \( d_j^+ (d_j) \), \( a_i^+ (a_i) \), and \( b_j^+ (b_j) \) are the creation (annihilation) operators at the \( i\)-th G/C base and the \( i\)-th upper and lower backbone, and \( \varepsilon_{i(j)} \) is the onsite potential energy of DNA G(C) base.

The DNA molecule is coupled to two semi-infinite metallic leads by the tunneling Hamiltonian

\[
H_{\text{Lead-DNA}} = -t_{L1} l_0^+ c_1 - t_{L2} l_0^+ d_1 - t_{R1} l_1^+ c_N - t_{R2} l_1^+ d_N + h.c. \tag{4.3}
\]
where \( t_{\text{L}i(2)}(t_{\text{R}i(2)}) \) are the hopping strengths between the left (right) lead and the end DNA bases, and \( l^\dagger_i(l_i) \) is the creation (annihilation) operator at the \( i\text{-th} \) site of the leads. The leads themselves are modeled by another TB Hamiltonian as

\[
H_{\text{leads}} = \varepsilon_0 \sum_i t^\dagger_i l_i - t_0 \sum_i (l^\dagger_i l_{i+1} + \text{h.c.}) ,
\]

where the lead onsite energy is \( \varepsilon_0 = 7.75 \text{ eV} \) and the hopping amplitude is taken as \( t_0 = 1 \text{ eV} \), taken from Ref. [23]. In our numerical calculations, we use re-scaled parameters and the electron energy \( E \), all of which are normalized with respect to the hopping integral of the leads \( t_0 = 1 \text{ eV} \). We apply the wave functions into the TB Schrödinger equations for 22 sites (5 G bases, 5 C bases, 10 sugar-phosphate backbone sites, and 2 lead discrete sites) and combine them into the following the 22×22 matrix form. Therefore, by solving the matrix equation for the linearized TB Hamiltonian we obtain the transmission amplitude as a function of the incoming electron energy, \( E \). The desired transmission coefficient is obtained by taking the square of the transmission amplitude, \( T = |t(E)|^2 \).

\[
\begin{bmatrix}
0 & -t_0 e^{-i\theta} & t_{i1} & t_{i2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & t_{i1} & E - \varepsilon_i & h_i & t_{\alpha} & 0 & t_{i2} & 0 & 0 & 0 & 0 & 0 \\
0 & t_{i2} & h_i & E - \varepsilon_i & 0 & t_{\alpha} & 0 & T_{i2} & 0 & 0 & 0 & 0 \\
0 & 0 & t_{\alpha} & 0 & E - \sigma_{\alpha} & 0 & 0 & 0 & B_{\alpha} & 0 & 0 & 0 \\
0 & 0 & 0 & t_{\alpha} & 0 & E - \sigma_{\alpha} & 0 & 0 & 0 & B_{\alpha} & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
-t_0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\]
4. 3. The effects of various parameters on the DNA transmission and I-V characteristics

4. 3.1. Coupling between the DNA bases and the backbone

First, we investigate the transmission characteristics along the long axis of the DNA molecule with five poly(G)-poly(C) base-pairs by changing the hopping amplitude \( t_α \) between DNA bases and the upper and lower backbone, symmetrically. Figure 4.2(a) shows the transmission coefficient as a function of the incoming energy for different hopping strengths, \( t_α = 0.001, 0.1, 0.5, \) and \( 0.8 \) (bottom to top). For clarity, each curve is vertically offset by one unit. In addition, we show a contour plot of the transmission as a function of both electron energy \( (E) \) and hopping strength \( (t_α) \) with fixed \( t_0 = 1, t_L(R) = 0.3, t(T)_{l+1} = 0.2, ε_0 = 7.75, \) and \( σ_α = 8.5 \) for different hopping strength from 0.001 to 0.9 in Fig. 4.2(b). Electron transport through the sugar-phosphate backbone and hydrogen bonds are neglected in order to focus on the effects of varying \( t_α \) \( (B_e = h_i = 0.001). \)

Even in the absence of the coupling between the backbone and the bases \( (t_α = 0.001), \) two mini-bands arise with a gap in the transmission. These mini-bands are due to the different site energies of the G and C bases in the upper and lower strands, where each provide a pathway for electron transport and lead to conducting behavior. When \( t_α \approx 0.1, \) extra peaks appear at \( E = 8.5, \) which is the same as the backbone onsite energy. As the coupling gets stronger, the gap between the two extra mini-bands increases and the width of extra mini-bands broadens. When the incoming energy matches with the onsite energies of ds-DNA bases, in other words, when the incoming wave function is close to the
value of the energy level of the bases, resonant tunneling occurs with full unit transmission consisting of 5-peak, semi-overlapped band structure. Once the backbone onsite energy is coupled into the system through $t_a$ (i.e., the role of the bridge to the backbone), the incoming wave function overlaps at the energy level of the backbone and another mini-band is developed in the transmission probability [53, 56].

Fig. 4.2. (a) Transmission as a function of electron energy for $t_a = 0.001, 0.1, 0.5, \text{ and } 0.8$ (from bottom to top), and (b) contour plot of the transmission with fixed $t_0 = 1, t_{L(R)} = 0.3, t(T)_{i,i+1} = 0.2, B_a = h_i = 0.001, \epsilon_0 = 7.75, \text{ and } \sigma_a = 8.5$ for different hopping amplitudes $t_a$ from 0.001 to 0.9. The backbone effect causes extra mini-bands in the transmission.
4.3.2. Hydrogen bonds

The complementary bases (A with T or G with C) are held together by hydrogen bonds and form a unique DNA double-helix structure. Iguchi found that the transmission band-gap was reduced by the hopping amplitude between adjacent chains, which means that electrons travel through the transverse axis of two main chains of the DNA [54, 57, 58]. Jauregui et al. studied the transverse electron transport through ds-DNA nucleotides (A/T nucleotide molecule and G/C nucleotide molecule) [59]. They showed asymmetrical current (pA) in the I-V characteristics for direct and reverse biases. Motivated by these results, we examine how the hydrogen bonds affect electron transport through DNA by modulating the coupling ($h_i$) in the absence of backbone effects. In addition, hydrogen bonds cause small loops inside double-chains of DNA, for example six small loops are made by hydrogen bonds in five poly(G)-poly(C) base-pairs. Figure 4.3(a) shows a contour plot of the transmission as a function of both electron energy ($E$) and hydrogen bonds ($h_i, \ i = 1-5$) with fixed $t_0 = 1, \ t_{i(R)} = 0.3, \ t(T)_{i,s+1} = 0.2, \ B_u = t_a = 0.001, \ e_0 = 7.75,$ and $\sigma_u = 8.5$ for different $h_i$ from 0.001 to 0.9. In Fig. 4.3(b), we show plots of the transmission versus $E$ for various hydrogen bonds $h_i = 0.001, 0.3, 0.6, \text{ and } 0.9 \ (\text{from bottom to top}).$ For clarity, each curve is vertically offset by one unit. It is clearly seen that as hydrogen bonds are increased from almost zero (0.001), the five peaks in the left mini-band merge and shift toward lower energies, while the other peaks in the right mini-band become more pronounced. For weak inter-coupling between base-pairs, meaning a high barrier, the electrons separately tunnel through the G bases in the upper and C bases in the lower strand. By increasing $h_i$, the isolated quasi-bound states in each base-pair grad-
ually mix together. The distinct resonant peaks in the left mini-band overlap and merge, while the peaks in the right mini-band become sharper, indicating increased localization of the higher energy states.

Fig. 4.3. (a) Contour plot of the transmission as a function of electron energy and the hydrogen bonding \( h_i \) between the bases. The left resonant peaks merge and reach to unit transmission, whereas, the five resonant peaks in the right mini-band are more pronounced and shifted toward higher energies as \( h_i \) is increased from 0.001 to 0.9. (b) The resonant characteristics of the transmission as a function of electron energy are plotted for various inter-couplings between base-pairs: \( h_i = 0.001, 0.3, 0.6, \) and 0.9 (from bottom to top).

4.3.3. Intra-strand couplings along the backbone

Next, we consider all the couplings between nearest-neighboring onsites with variation of the intra-strand coupling along the backbone \( B_a \). Electron transport through a one or two-stranded DNA molecule using the TB model has been studied by many groups without considering the sugar-phosphate channel [7, 9, 25, 60]. We show a contour plot of the transmission as a function of electron energy \( E \) and coupling \( B_a \) from 0.001 to 0.9 for fixed \( t_0 = 1, t_{L,K} = 0.3, t(T),_{l,r} = 0.2, t_a = 0.3, h_i = 0.5, \varepsilon_0 = 7.75, \) and \( \sigma_a = 8.5 \) in Fig 4.4(a). As \( B_a \) is increased, the resonant peaks of the extra mini-bands
spread out and collapse into the main two mini-bands. It is clearly seen that the intra-strand couplings along the backbone system affect the four mini-bands on the transmission very sensitively. We also plot the transmission within a small electron energy window \((E = 7 \text{ to } E = 8)\) for a variation of \(B_a = 0.3, 0.4, \text{ and } 0.5\) (bottom to top). The behavior of the transmission zero and pole, called a Fano resonance, is shown in Fig. 4.4(b) [61]. The Fano resonance is a manifestation of interference between the localized quasi-bound states of the quantum dot in one arm and the continuum states in the other arm, characterized by a zero-pole pair in the complex-energy plane [61-63]. As intra-coupling along the backbone is increased, the sharp zero-pole pair peak is shifted toward lower energy. It is also found in Fig. 4.5 that the pattern of the zero-pole pair is changed from peak to dip at \(B_a = 0.3\), to peak to dip at \(B_a = 0.4\), to dip to peak at \(B_a = 0.5\) in the energy window \(E = 7.5 \text{ to } 7.9\) as the coupling \(B_a\) is increased. This is called the swing of Fano resonances.
Fig. 4.4. (a) Contour plot of the transmission as a function of electron energy and intra-coupling $B_a$ between backbone sites. As $B_a$ is increased, the peaks on the extra mini-bands extend out and become overlapped with the main mini-bands. (b) The transmission within a small electron energy range (7 to 8), plotted for various couplings, $B_a = 0.3, 0.4, \text{ and } 0.5$ for fixed $t_0 = 1, t_{L(R)} = 0.3$, $t(T)_{i,i+1} = 0.2, t_a = 0.3, h = 0.5$, $\epsilon_0 = 7.75$, and $\sigma_a = 8.5$.

Fig. 4.5. The resonance characteristics of the transmission as a function of electron energy are plotted for various $B_a = 0.3, 0.4, \text{ and } 0.5$ (bottom to top). Curves are shifted vertically by one unit for clarity. The swing of a Fano resonance in the transmission appears. $B_a = 0.3 \text{ eV}: \text{ dip } \rightarrow \text{ peak}$, $B_a = 0.4 \text{ eV}: \text{ peak } \rightarrow \text{ dip}$, and $B_a = 0.5 \text{ eV}: \text{ dip } \rightarrow \text{ peak}$. 
4. 4. Temperature effects

Charge transport in DNA is a complex phenomenon because the environment plays a significant role in determining the conductivity of DNA. Temperature is one of the important factors in experiments with bio-materials, since variation of the temperature induces structural disorder and fluctuations of the system. Figure 4.6 shows a schematic for a 2-D, four-channel DNA model with applied thermal fluctuations. Here, we investigate the transport behavior for electrons through a short poly(G)-poly(C) DNA molecule by applying temperature-dependent hopping strengths in order to observe the effects of temperature in our system. Hence, we apply the variation of the temperature into the hopping integrals in terms of twist-angle fluctuations. These are based on a Gaussian distribution with average twist angle $\langle \theta_{i,i+1} \rangle = 0$, where $\theta_{i,i+1}$ is a relative twist angle deviated from its equilibrium value between $i$ and $i+1$ with the help of the equipartition theorem, $\langle \theta_{i,i+1}^2 \rangle = k_B T / I \Omega^2$, where $I \Omega / k_B = 250K$, $T$ is temperature, $I$ is the reduced moment of inertia for relative rotation of the two adjacent bases, and $\Omega$ is the oscillator frequency of the mode [11, 16, 30, 64-66]. Using these formulas, the temperature-dependent hopping integrals can be obtained as $t(T)_{i,i+1} \rightarrow t(T)_{i,i+1} \cos \theta_{i,i+1}$, $t_a \rightarrow t_a \cos \theta_{i,i+1}$, and $h_i \rightarrow h_i \cos \theta_{i,i+1}$. Inserting $\cos \theta_{i,i+1} \equiv 1 - \theta^2 / 2 \equiv 1 - k_B T / 2I \Omega^2 \times \chi_i$, we can now form the final hopping integrals as

$$t(T)_{i,i+1} \rightarrow t(T)_{i,i+1} \{1 - (k_B T / 2I \Omega^2) \times \chi_i\}$$

$$t_a \rightarrow t_a \{1 - (k_B T / 2I \Omega^2) \times \chi_i\}$$

$$h_i \rightarrow h_i \{1 - (k_B T / 2I \Omega^2) \times \chi_i\},$$
where $\chi_i$ is a factor giving the random fluctuation such as $\chi_i = 0.5, -0.3, 0, 0.3, -0.5$.

Figure 4.6. 2-D four-channel TB model for electron transport along the long axis of the DNA in the presence of thermal fluctuations. Thermal effects induce structural disorder and twist-angle fluctuations on the hopping integrals.

Figure 4.7 shows a contour plot of the transmission as a function of both electron energy ($E$) and temperature ($Temp$) and two plots of the transmission coefficient as a function of electron energy at 0 K and 300 K with fixed $t_0 = 1, t_{L(L)} = 0.3, t(T)_{i,i+1} = 0.2, t_o = 0.3, h_i = 0.5, B_a = 0.001, \epsilon_0 = 7.75, \sigma_a = 8.5$, and a random factor $\chi_i = 0.5, -0.3, 0, 0.3, -0.5$. It is clearly seen that as temperature is increased from 0 K to 300 K, the resonant peaks on the four mini-bands, which initially had unit transmission, become suppressed and smear out below unity due to the random variation of the hopping integrals.

We also show the localization length as a function of electron energy for two different temperatures, 0 K and 300 K, in Fig. 4.8. Localization length is inversely related to the Lyapunov coefficient and calculated using transmission coefficients to compare the transmission properties. The localization length can be written as $\xi(E) = [\gamma_N]^{-1}$, where $\gamma_N = -\ln[T(E)]/(2N)$ and $N$ is the number of base-pairs [23, 26-36]. An asymptotic be-
behavior of the localization length indicates that the thermal fluctuations can destroy coherent charge transport and reduce the mean transmission coefficient. In other word, high temperature leads to the disorder of the system and a reduction of the localization length and consequently a reduction of the electron conductance according to the relationship, $T \propto \exp[-L/\xi]$, where $L$ is total length of the system.

Fig. 4.7. Contour plot of the transmission vs. electron energy and temperature, and two plots of the transmission coefficient for 0 K and 300 K. We apply temperature-dependent hopping integrals in order to see thermal fluctuation effects in our system.

Fig. 4.8. Localization lengths as a function of energy are plotted for different temperature, 0 K and 300 K.
4.5. Magnetic flux effects

Finally, we investigate the electronic properties of a short poly(G)-poly(C) DNA molecule in the presence of an external magnetic field. Our model becomes a single loop or a ring due to the ds-DNA structure, which is attached to the semi-infinite electrodes and linked by couplings between adjacent bases and inter-base hydrogen bonds in the absence of the backbone effect, as shown in Fig. 4.9. We color the backbone sites and couplings light gray in order to indicate lack of consideration of the backbone effect.

Aharonov and Bohm theorized that a beam of electrons approaching a long solenoid would split in two, and recombine out of phase by a factor proportional to the enclosed flux. A magnetic field of flux density penetrating at the center of the 2-D DNA structure induces AB phase difference between the electron wave functions of the upper and lower DNA strands and produces AB oscillations in the transmission $T(E)$. The hopping integrals are multiplied by a phase factor in order to observe the quantum interference through the double-helix DNA, defined as

$$t(T)_{i,i+1} \rightarrow t(T)_{i,i+1} e^{\pm i\phi}, \ h_i \rightarrow h_i e^{\pm i\phi}, \text{ and } t_{\alpha} \rightarrow t_{\alpha} e^{\pm i\phi},$$
where $\phi = 2\pi \Phi/(N\Phi_0)$ denotes the total phase shift. $\Phi$ measures the total flux through our system in units of the flux quantum, $\Phi_0 (h/e)$, and the plus or minus signs in the exponential phase factor are applied when the electron moves in the counter-clockwise or clockwise direction, respectively. $N$ is the number of sites; for example, a 2-D 5 base-pair DNA molecule which is attached to the left and right leads has 12 sites ($N = 12$; 5 G bases, 5 C bases, and 2 lead onsites). Figure 4.10 shows contour plots of the transmission as a function of magnetic flux ($\Phi/\Phi_0$) and electron energy (top) and the transmission vs. electron energy (bottom) with fixed $t_0 = 1$, $t_{L,R} = 0.3$, $t(T)_{i,i+1} = 0.2$, $t_a = 0$, $h_i = 0$, $B_a = 0$, $\epsilon_0 = 7.75$, and $\sigma_a = 8.5$ for different numbers of base-pairs: 1 base-pair, 2 base-pairs, and 5 base-pairs (top to bottom), in the absence of backbone effect and hydrogen bonds. As the number of base-pairs increases, the amplitude of the AB oscillations in the transmission probability decreases. The AB interference is small for the case of five base-pairs due to the transmission being restricted more to only one or the other strand, giving less interaction between the two strands. As a result, only small oscillations in the transmission can be seen in the inset of Fig. 4.10 for five base-pairs [64, 65].
Fig. 4.10. Transmission contour plots vs. electron energy and magnetic flux ($\Phi/\Phi_0$) with fixed $t_0 = 1$, $t_{L(R)} = 0.3$, $t(T)_{i=1} = 0.2$, $h_l = 0$, $B_o = 0$, $\varepsilon = 7.75$, and $\sigma_a = 8.5$ without considering backbone effect and hydrogen bonds for different number of base-pairs, from one, two, five base-pairs (top to bottom). Transmission coefficient plots vs. electron energy for fixed incoming energy ($E = 8$) are shown below the contour plots. As the number of base-pairs increases, the amplitude of the AB oscillations decreases. However, there are still small oscillations in the transmission, as shown in the inset for five base-pairs.

Next, we investigate the phase shift with hydrogen bonds through short poly(G)-poly(C) DNA molecules. As the number of base-pairs changes, the number of loops va-
ries. For instance, a single base-pair has 2 loops, and 5 base-pairs has 6 loops due to the hydrogen bonds ($h_i, i = 1...5$) connecting bases across the long axis of DNA. We show the transmission $T(E)$ vs. magnetic flux ($\Phi/\Phi_0$) with fixed $t_0 = 1$, $t_{i,i+1} = 0.3$, $t(T)_{i,i+1} = 0.2$, $h_i = 0.5$, $t_a = 0$, $B_a = 0$, $\varepsilon_0 = 7.75$, $\sigma_a = 8.5$ and incoming energy ($E = 7.5$) for different numbers of base-pairs, 1 base-pair (top) and 5 base-pair (bottom). It is interesting to note from Fig. 4.11 that the periodicity of the AB oscillations is directly proportional to the number of loops in the DNA molecules. One base-pair (2 loops, green) has a periodicity of $2\Phi_0$ and five base-pairs (6 loops, green) has a periodicity of $6\Phi_0$ in the transmission vs. flux.

Fig. 4.11. Flux dependence of the transmission for one base-pair (top) and five base-pairs (bottom), showing periodic AB oscillations. The periodicity in terms of $\Phi_0$ is the same as the number of loops through the DNA.
Chapter 5: Summary and Conclusions

In this thesis, we have numerically studied electron transport properties through a 1-D one-channel DNA model, a quasi-1-D one-channel DNA model, and a 2-D four-channel DNA model. We investigated the transmission, contour plots of transmission, localization length, and $I$-$V$ characteristics as a function of incoming electron energy and magnetic field by solving the TB Schrödinger equation.

In Chapter 2, we started with a single strand, 20 base DNA model. We analyzed the electron transmission with varying sequences, such as the homogeneous poly G bases sequence, the periodic G-C sequence, the Fibonacci G-C sequence, and the random G-C sequence. The Lyapunov coefficient and localization length, which can be determined from the transmission characteristics, were calculated as well in order to understand Anderson localization or disorder effects. We have shown that as the system becomes more randomized by arbitrarily choosing the 20 bases, the transmission resonances become narrower and the localization length is decreased.

Next, we examined the transmission properties of ds DNA by using a one-channel TB model in Chapter 3. We utilized the renormalized onsite potential energy in order to incorporate the effects of the backbone in our calculations. The backbone-induced effects produce a gap in the transmission, which indicates a semiconductor-like behavior of the DNA. Our numerical calculations of the $I$-$V$ characteristics are in agreement with the ex-
experimental result [7]. We have also investigated the characteristics of electron transport through both symmetric and asymmetric DNA molecules having energy-dependent renormalized onsite energies and hopping integrals from DNA base-pairs to the backbone. We have shown that as the asymmetric backbone onsite energies are increased, overlapping of the two transmission mini-bands occurs, and the merged single mini-band eventually disappears and an extra resonance band remains. In the $I-V$ curve, the voltage threshold increases and the current remains constant at a critical asymmetric backbone onsite energy. When the asymmetric contact coupling is decreased, electron tunneling is also decreased and a distinct and under-unity resonance is shown in each band.

Finally, in Chapter 4 we investigated charge transport through a 2-D four-channel poly(G)-poly(C) DNA model by varying parameters; the coupling between DNA bases and the backbone, hydrogen bonds between bases, and inter-backbone coupling. Extra transmission mini-bands appeared when the backbone couplings exist. The transmission resonant peaks merge and shift to lower energy as the hydrogen bonds are increased, since the isolated quasi-bound state in each base-pair mixes together. By considering the inter-backbone couplings we obtained the swing of Fano resonances in a specific small energy window. We applied a variation of the temperature and AB phase shifts into the hopping integrals in order to consider thermal fluctuations and magnetic field effects on the transmission. As temperature increases, the transmission oscillations are suppressed and the localization lengths are decreased. A magnetic flux penetrating at the center of the 2-D DNA induces AB oscillations which are directly proportional to the number of loops, and which have an oscillation amplitude inversely proportional to the number of base-pairs.
Our findings provide possible characteristics and applications for using DNA as a component in molecular electronics. For future study, we will apply a magnetic field through a 2-D four-channel DNA model with backbone effect. This might be more complicated because many loops can be formed by the backbone couplings. We will also investigate current-voltage characteristics which are the measurable quantity for conductivity of DNA in the presence of magnetic field. Furthermore, different sequences of DNA and longer DNA base-pair chains can be considered in our future work.
REFERENCES


APPENDIX A:

Sample Mathematica 7.0 Program for quasi 1D DNA model and 2-D four-channel DNA model

Clear["Global`*""]
n2 := 7;
m1 = Array[M, {n2, n2}];
Do[M[i, j] := 0, {i, 1, n2}, {j, 1, n2}];
Array[vid, n2];
Array[en, n2 - 2];
M[1, 1] := 0;
M[2, 2] := -vL;
M[1, 3] := vL;
M[n2, n2] := -vR;
en[1] := e1;
en[2] := e2;
Do[M[i, i + 1] := vid[i], {i, 1, n2 - 1}];
M[n2 - 1, 1] := -vR*Exp[I*θ];
M[n2, 1] := v0;
M[2, 3] := v0*Exp[-I*θ];
MatrixForm[m1]
c1 := Array[const, n2];
Do[const[i] := 0, {i, 1, n2}];
const[1] := v0*Exp[I*θ];
const[2] := vL, 0
MatrixForm[c1]
Mc := Inverse[m1];
rtp := Mc.c1;
Part[rtp, 1];
Part[rtp, 2];
T2[e_] := Module[{}, e := en; θ := ArcCos[(-e + ε0)/(v0 2.)]; t1 := t; Return[t1]];
R1[e_] := Module[{}, e := en; θ := ArcCos[(-e + ε0)/(v0 2.)]; r1 := r; Return[r1]];
v0 := 1.;
vL := 0.5;
vR := 0.5;
ε0 := 7.75;
tb := 0.7;
sb := 8.5;
\[ A:=8.24; \quad T:=9.14; \quad G:=7.75; \quad C:=8.87; \]
\[ e1:=\frac{A+T}{2}; \quad e2:=\frac{G+C}{2}; \quad e3:=\frac{G+G}{2}; \]
\[ v_a:=0.1; \quad v_d:=0.1; \quad v_b:=0.1; \quad v_c:=0.1; \]
\[ e1:=e2-tb^2/(eb-e)-tb^2/(eb-e); \quad e2:=e2-tb^2/(eb-e)-tb^2/(eb-e); \quad e3:=e2-tb^2/(eb-e)-tb^2/(eb-e); \quad e4:=e2-tb^2/(eb-e)-tb^2/(eb-e); \quad e5:=e2-tb^2/(eb-e)-tb^2/(eb-e); \]
\[ \text{Plot}[\text{Abs}[T2[e]]^2,\{e,5.75,9.75\},\text{Axes}→\text{False},\text{Frame}→\text{True},\text{FrameStyle}→\text{Thick},\text{PlotRange}→\{(5.75,9.75),(-0.1,1)\},\text{PlotStyle}→\{\text{AbsoluteThickness}[3]\},\text{FrameLabel}→\{"E","T(E)"\},\text{BaseStyle}→\{\text{"Helvetica"},22\}] \]
\[ M[n2-3,1] := vR2 \text{Exp}[I*\theta]; \]
MatrixForm[m1];

c1 := Array[const, n2];
Do[const[i] := 0, {i, 1, n2}];
const[1] := v0 \text{Exp}[I*\theta];
const[2] := -vL1;
const[3] := -vL2;
MatrixForm[c1];

JBF := LinearSolve[m1, c1, Method → "DivisionFreeRowReduction"];
t := Part[JBF, 1];
T[en_] := Module[{}, e := en; \theta := \text{ArcCos}[(-e+\varepsilon 0)/(v0*2)]; Return[t];]

Plot[Abs[T[e]]^2, {e, 5.75, 9.75}, Axes → False, Frame → True, FrameLabel → {"E", "T(E)"}, BaseStyle → "Helvetica", 20, PlotStyle → {AbsoluteThickness[2.3]}, PlotRange → {{5.75, 9.75}, {-0.1, 1.1}}]
Electron transport through asymmetric DNA molecules

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A R T I C L E   I N F O
Article history:
Received 8 February 2010
Received in revised form 5 March 2010
Accepted 23 March 2010
Available online 30 March 2010
Communicated by R. Wu

Keywords:
DNA molecule
Electron transport
Resonance

A B S T R A C T
We investigate quantum mechanical electron transport along the long axis of the DNA molecule using an effective tight-binding model. The overall contour plot of transmission, the current–voltage characteristics, and the differential conductance are examined for the variation of backbone onsite energy, the energy-dependent hopping strength, and the contact coupling between the leads and the DNA molecule. It is shown that as backbone asymmetry increases, the merging and collapse of the two mini-bands take place and an extra resonance peak in the transmission appears. In addition, we present the modulation of voltage threshold in the current–voltage curves and a double-peak structure in the differential conductance due to the disappearance of the merged mini-band. Finally, in the Coulomb blockade regime of asymmetric contact coupling, a distinct and under-unity resonance in the transmission appears due to the interference effects between the DNA molecular bands and the electronic structure of the leads at the DNA–lead interface.

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1. Introduction

Recently, much interest has arisen in the process of charge transport through DNA due to its fundamental roles in biological processes and in possible novel molecular electronics. Modern developments enable us to directly measure DNA transport phenomena. In particular, direct conductance measurements on DNA molecules under diverse conditions have been attempted by many groups [1–11]. The diversity comes from the methods of measurement and the preparation of the DNA samples, contact between DNA and electrodes, and the nucleotide sequences of the DNA. For example, Porath et al. directly measured the electrical transport through 10 nm long (30-base-pairs), double-stranded (ds) poly(G)-poly(C) DNA molecules which are placed between two metal nano-electrodes [1]. The measured current–voltage (I–V) characteristics at room temperature have evidenced typical semi-conducting features with a gap of the order of 1 V. The electronic conduction through 15 base-pair ds-DNA oligonucleotides in dry state, bonded between two gold electrodes separated by approximately 5 nm has also been studied by Mahapatro et al. [11].

In order to support these experimental results, numerous theoretical works of electrical transport through dry and wet DNA has been extensively studied [12–24]. A model Hamiltonian for describing charge transport through short homogeneous ds-DNA molecules were proposed by Cuniberti et al. in which they found the existence of a gap in the nonequilibrium I–V characteristics at low temperature [13]. In addition, backbone-induced electronic effects on the charge transport through synthetic DNA molecules have been emphasized by studying the energy spectrum and transmission coefficients [14]. Furthermore, the biological relevance of sequence-dependent charge transport in DNA was discussed by investigating the localization lengths for different real environments of DNA with various types of disorder [15]. Another device application of DNA has been proposed by studying the transistor effect, a possibility of driving the electric field through the DNA by the perpendicular electric field, in the poly[G]-poly[C] synthetic DNA [16].

Despite all these efforts, the theoretical interpretation of recent experiments and the elucidation of possible mechanisms for charge transport in DNA have not been unequivocally unified in their conclusions thus far, because bio-materials are heavily influenced by environmental parameters such as sequence or length of DNA, temperature, substrate surface properties, humidity and residual salt bridges. In most theoretical works, homogeneous charge distribution through the backbone and symmetric contact coupling between the leads and DNA base-pairs are assumed as a first approximation. Even if a uniform charge distribution along the backbone sites can induce an opening of the band gap in the homogeneous DNA chain, it seems to be oversimplified to simulate the environmental complications of experiments as mentioned above. Therefore, a more sophisticated depiction of the DNA, particularly regarding the inhomogeneous backbone onsite energies, asymmetric energy-dependent hopping amplitude between DNA base-pairs and the backbone, and the asymmetric contact coupling between the leads and DNA base-pairs, is proposed in this article to study electron transport through a short ds-DNA molecule. In this system, we employ an effective tight-binding (TB) model and calculate...
the overall contour plot of the transmission, the current-voltage characteristics, and the differential conductance. We show that as the asymmetric backbone onsite energies increase, the merging and collapse of the two transmission mini-bands as well as the appearance of an extra resonance peak occurs in the transmission. Furthermore, the variation of backbone asymmetry induces the modulation of voltage threshold in the I-V curve and a double-peak structure in the differential conductance due to the disappearance of the merged mini-band. Finally, we present a distinct, under-resonance in the transmission which arises from interference effects in the weak coupling regime of asymmetric contact coupling strength.

2. Theoretical model and calculations

DNA is a macro-molecule consisting of repeated stacks of bases formed by either AT (TA) or GC (CG) pairs [made from four different nucleotides: Adenine (A), Thymine (T), Cytosine (C), and Guanine (G)] coupled via hydrogen bonds and held in the double-helix structure by a sugar-phosphate backbone. In order to describe the charge transport in DNA quantitatively, we consider a single channel model for charge carrier propagation through the DNA duplex, shown schematically in Fig. 1. The electron transport in the DNA molecule, connected between two semi-infinite electrodes, arises through the central conduction channel which consists of poly(G)-poly(C) base-pairs and is connected to upper and lower backbone sites.

Using a quasi-one-dimensional TB model, a simplest and effective Hamiltonian for charge transport through the ds-DNA between two metallic leads can be written as [13-15,18],

$$H_{\text{total}} = H_{\text{DNA}} + H_{\text{Lead}} + H_{\text{Lead-DNA}}.$$

(1)

Here, the Hamiltonian for a short poly(G)-poly(C) DNA molecule is described by

$$H_{\text{DNA}} = \varepsilon_D \sum_i d_i^\dagger d_i - t_D \sum_i (d_i^\dagger d_{i+1} + \text{h.c.})$$

$$+ \sum_{i,a,G,C} \sigma_a \beta_{i,a} ^\dagger \beta_{i,a} + \sum_{i,a,G,C} \tau_a (\beta_{i,a} ^\dagger d_{i,a} + \text{h.c.}),$$

(2)

where $d_i$ ($d_i^\dagger$) and $\beta_{i,a}$ ($\beta_{i,a}^\dagger$) are the creation (annihilation) operators at the i-th G/C base site and the i-th upper and lower backbone site, $\varepsilon_D$ is the onsite potential energy of DNA, and $t_D$ is the hopping probability between nearest-neighbor G/C pairs. The influence of the backbone is considered in the third and fourth terms in Eq. (2), where $\sigma_a$ ($a = G$ or C) is the backbone onsite energy and $\tau_a$ is an energy-dependent transfer integral from base G or C to backbone site:

$$\tau_a(E) = \tau_a + \frac{\varepsilon_a(E - \sigma_a)}{\tau_a}.$$

We note here that $\tau_a$ is the hopping strength from each site G or C on the main DNA sites to the upper and lower backbone. In order to map the original poly(dG)-poly(dC) chain into the equivalent single-channel, we introduce an effectively renormalized and energy-dependent onsite potential $\varepsilon_D(E)$ which incorporates the existence of the backbone:

$$\varepsilon_D(E) = \varepsilon_D + \frac{(\tau_G(E))^2}{E - \sigma_G} + \frac{(\tau_C(E))^2}{E - \sigma_C},$$

(3)

where $\varepsilon_D = \varepsilon_D + (\varepsilon_G + \varepsilon_C)/2$ with the onsite energy of G or C bases, $\varepsilon_G = 7.75$ eV and $\varepsilon_C = 8.87$ eV, given by the ionization potentials of the respective bases, and the hopping integral $\tau_{GC}$ which describes the hydrogen bonds connecting the G-C pairs.

Our DNA molecule is coupled to two semi-infinite metallic leads by the tunneling Hamiltonian

$$H_{\text{Lead}} = -t_L \sum_i d_i^\dagger d_i - t_R \sum_i d_i^\dagger d_i + \text{h.c.},$$

(5)

where $t_L$ ($t_R$) is the coupling strength between the left (right) lead and the end DNA base pair, and $d_i^\dagger$ ($d_i$) is the creation (annihilation) operator at the i-th site of the leads. The leads themselves are modeled by another TB Hamiltonian such as

$$H_{\text{Lead}} = \varepsilon_L \sum_i d_i^\dagger d_i - \sum_i (d_i^\dagger d_{i+1} + \text{h.c.}),$$

(6)

where the lead onsite energy is $\varepsilon_L = 7.75$ eV and the hopping amplitude is taken as $t_L = 1$ eV. We note here that a different hopping amplitude $t_D$ in the semi-infinite leads does not alter the main characteristics of electron transport through DNA molecules, which will be shown in the results section.

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

$$-\sum_{m} t_{n,m} \psi_m + \varepsilon_n \psi_n = E \psi_n,$$

(7)

where the matrix elements $t_{n,m}$ are hopping integrals (or coupling parameters) between sites $n$ and $m$ with the single-site potential of site $n$, the sum runs over the nearest neighbors of $n$, $E$ is the electron energy, and $\varepsilon_n$ is the site energy. Hence, the general incoming and outgoing wave functions in the leads from the solution of Eq. (7) may be written as [25,26]

$$\psi_n = e^{i \kappa n} + r e^{-i \kappa n}, \quad n \leq 0,$$

$$\psi_n = e^{i \kappa n}, \quad n > 1,$$

(8)

with $\kappa = ka$. Here, $k$ is the wave vector that is connected with the energy by the dispersion relation for the Bloch states $E = -2 t_0 \cos ka + \varepsilon_n$, and $t$ and $r$ are the transmission and reflection amplitudes, respectively. The Schrödinger equation for amplitudes in the leads and DNA molecules can be written as
\(-t_0 e^{i\theta} - t_0 e^{-i\theta} + t_1 \psi_1 = 0,
(\bar{\gamma}_l \psi_5 + \bar{\gamma}_l e^{i\theta} + (E - \varepsilon_D) \psi_5 = 0,
(\tau_1(1 + r) + t_0 \psi_2 + (E - \varepsilon_D) \psi_2 = 0,
(\tau_2 \psi_3 + t_0 \psi_4 + (E - \varepsilon_D) \psi_3 = 0,
(\tau_3 \psi_3 + t_0 \psi_4 + (E - \varepsilon_D) \psi_4 = 0,
(\tau_4 \psi_4 + t_0 e^{i\theta} + (E - \varepsilon_D) \psi_4 = 0,\)
(9)
where the energy-dependent onsite potential \(\varepsilon_D\) is defined by Eq. (4). Rearranging Eq. (9) in a matrix form and inverting this matrix, we obtain the transmission amplitude \(t(E)\) of the system:
\[t(E) = \frac{t_0 e^{i\theta} (t_1 e^{-i\theta} - t_0 e^{i\theta})}{t_0^2 P(E) - t_1^2 + t_1^2 Q(E) + t_0^2 R(E)},\]
(10)
where
\[P(E) = (E - \varepsilon_D)^4 - 4(E - \varepsilon_D)^2 t_1^2 - 3t_1^4,\]
\[Q(E) = (E - \varepsilon_D)^4 - 2t_0^2 (E - \varepsilon_D)^2 - 4t_0^4,\]
\[R(E) = (E - \varepsilon_D)^4 - 3(E - \varepsilon_D)^2 t_1^2 + t_1^4.\]
Eq. (10) allows us to find the conductance through DNA molecules by the Landauer–Büttiker approach \([27,28]\): \(G = \frac{e^2}{h} T\), where \(T = (t(E))^2\).

In the following, we present results for the backbone contribution and contact effects with a fixed hopping probability between nearest-neighbor GC pairs \((t_0 = 0.4 \text{ eV})\). More specifically, to simulate the complicated experimental situations, we modulate parameters of the system such as the onsite energies of the backbone \((\sigma_G)\), the hybridized hopping amplitude \((t_0)\) between a GC pair and the backbone, and the contact coupling strengths \((t_1\) and \(t_2)\) both asymmetrically and symmetrically. In our numerical calculations, we use the re-scaled parameters \(t_0\) \((t_0)\), \(\sigma_G\) \((\sigma_G)\), \(t_1\) \((t_1)\), and \(t_2\) \((t_2)\), and the electron energy \(E\), all of which are normalized with respect to the hopping integral of the leads \(t_0 = 1 \text{ eV}\).

3. Results

3.1. Variation of the hopping strength

First, we examine the transmission characteristics along the long axis of the DNA molecule with five poly(G)-poly(C) base-pairs by varying the hopping strength between the DNA base-pairs and the upper and lower backbone, both symmetrically and asymmetrically. Fig. 2(a) shows a contour plot of the transmission as a function of both electron energy \(E\) and hopping strength \((t_1\) and \(t_2)\) for fixed \(t_0 = \sigma_G = 8.5\) and \(t_1 = t_2 = 0.4\). When \(t_0 > t_2 > 3\), it is seen that there are two mini-bands with a gap in the transmission, which is a typical semiconducting feature. As both \(t_1\) and \(t_2\) are decreased, however, an overlapping of the two mini-bands occurs and a single mini-band appears. A single mini-band without a gap in the transmission is localized in a small window of energy at higher electron energy \(E \approx 8.4\).

We also show a contour plot of transmission for fixed \(t_0 = 3.5\) in Fig. 2(b) by modulating the hopping strength \(t_1\) between base C and the lower backbone. In this symmetry-breaking DNA structure, two transmission mini-bands with a gap progressively approach each other and eventually merge into a single mini-band as the difference of the hopping amplitudes \(t_0\) and \(t_1\) \((t_0 - t_1)\) becomes larger. It is interesting to note, however, that the transmission in this asymmetric system disappears completely when \(t_1 \geq 5.8\) or \(t_2 \leq 2.7\) (see more details below in Fig. 5). Therefore, the backbone coupling to DNA base-pairs controls the opening of a gap and the merging and a collapsing of a mini-band in the transmission.

3.2. Variation of backbone onsite energy

In order to consider the environmental complications of experiments, we also modulate parameters of the system such as the onsite energies of the backbone \((\sigma_G)\) both symmetrically and asymmetrically. We first examine the transmission of DNA molecules with symmetric variation of the backbone onsite energies \(\sigma_G\) and \(\sigma_C\). In Fig. 3(a), we show a contour plot of the transmission as a function of electron energy \(E\) and backbone onsite energies \((\sigma_G\) and \(\sigma_C)\) for a fixed \(t_0 = \sigma_G = 3.5\) and \(t_1 = t_2 = 0.4\). When \(6.0 \leq \sigma_C = \sigma_G < 7.8\), two transmission mini-bands with a gap arise in the lower electron energy window. As the backbone onsite energy increases, the transmission bands are shifted towards higher energies and the two mini-bands in the transmission merge into a single mini-band because the onsite potential energy of the DNA is affected by the backbone onsite energies. The inset of Fig. 3(a) shows that each mini-band has five distinctive resonant peaks, where each peak reaches full transmission.

Access to transmission properties can be performed by measuring \(I - V\) characteristics. In order to compare our results with experimentally measured data \([1]\), we evaluate the \(I - V\) characteristics of the system with the transmission function \(T(E)\) using a standard Landauer–Büttiker formula \([27–30]\) as
\[I = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E) [f_1(E) - f_0(E)],\]
(11)
Here, $f(E)$ is the Fermi function given by

$$f_{L/R}(E) = \frac{1}{\exp(-\frac{E - \mu_{L/R}}{k_b T}) + 1},$$

where $\beta = 1/k_b T$ and $\mu_{L/R}$ stands for the electrochemical potential of the left (right) leads whose values depend 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 $\eta$ is a parameter describing the possible asymmetry of contact to leads, chosen here as $E_f = 6.2$ eV and $\eta = \frac{1}{3}$, respectively. In Fig. 3(b), the current $I$ as a function of the applied voltage $V_{sd}$ at room temperature is shown for different values of $\sigma_C = \sigma_C = 7.0$ (black, dotted line), 7.5 (green, dashed line), 8.0 (yellow, solid line), 8.5 (red, dot-dashed line), and 9.0 (blue, thick-dashed line). The $I$--$V$ curves show negligible current up to a threshold voltage followed by a sharp rise of the current, which is a typical feature of a semiconductor. We note that the current gap in the $I$--$V$ curve widens on increasing the backbone on-site energy (see more detailed explanation below).

Next, we examine the asymmetrical effects of the backbone on-site energy on the transmission. A contour plot of the transmission with variation of the lowest backbone on-site energy $\sigma_C$ for fixed $\sigma_C = 7.5$, $\tau_C = \tau_C = 1.5$, and $\tau_L = \tau_R = 0.4$ is shown in Fig. 4. When $\sigma_C$ is equal to $\sigma_C = 7.5$, we see two mini-bands with a gap in the transmission as shown before. As the difference $|\sigma_C - \sigma_C|$ between the two values of the backbone on-site energies is increased, however, an overlapping of the two mini-bands occurs and the single-merged mini-band eventually disappears. Most importantly, it is clearly seen that an extra sharp resonance peak appears at higher energy ($E \approx 7.5$) as soon as the symmetry of DNA backbone on-site energy is broken. This extra resonance peak, which in turn is a mini-band with five distinctive resonance peaks [see Fig. 5(d)], remains even when the single-merged mini-band disappears at $\sigma_C \geq 7.64$ and $\sigma_C \leq 7.25$. Notice here that we have generated each contour plot of the transmission with a different energy scale and combined these together because this extra resonance peak is so narrow and sharp.

In order to understand these resonance phenomena of DNA transport more clearly, we plot the transmission as a function of electron energy in Fig. 5 for a variation of the backbone on-site energy. For a fixed $\sigma_C = 7.5$, the resonance characteristics of the transmission are shown in Fig. 5 as (a) $\sigma_C = 7.5$, (b) $\sigma_C = 7.4$, (c) $\sigma_C = 7.3$, and (d) $\sigma_C = 7.24$. When $\sigma_C = \sigma_C = 7.5$, the transmission $T$ of the structure exhibits weakly split groups of transmission resonances in each mini-band due to the inter-base-pair tunneling. As the system moves away from the symmetry point about the transport direction (namely, when $\sigma_C \neq \sigma_C = 7.4$), the two mini-bands are shifted with a reduced gap to lower energy, and a pronounced resonance peak appears at $E \approx 7.47$ in Fig. 5(b). From the enlarged plot of this resonance peak, depicted in Fig. 5(c), it is seen to be a single mini-band with five well-defined resonance peaks. This extra mini-band is shifted to lower energy, and its width increases slightly as $\sigma_C$ decreases. This extra mini-band remains as long as $|\sigma_C - \sigma_C| \neq 0$, unlike the two primary mini-bands which eventually disappear (see below).

The two primary mini-bands with a gap become overlapped and their gap disappears at $\sigma_C = 7.3$ [Fig. 5(c)]. This combined mini-band completely disappears at $\sigma_C = 7.24$ [Fig. 5(d)]. In order to make sure that this single-merged mini-band indeed disappears (and is not just shifted to a lower energy window), we change the backbone on-site energy over a small scale in Fig. 5(e)–(h).
When $\sigma_C = 7.255$, the merged mini-band acquires the form of two pronounced Breit–Wigner (BW) resonances at $E \approx 7.034$ and $E \approx 7.054$. When $\sigma_C$ reaches the critical value $\sigma_C = \sigma_{\text{crit}} = 7.253$, total overlapping of the BW resonances results in a single BW resonance. This can be qualitatively interpreted to say that the variation of $\sigma_C$ effectively makes the energy levels in the DNA base-pairs degenerate, and induces a strong interaction between them. When $\sigma_C < \sigma_{\text{crit}}$, the amplitude of the BW resonance in the transmission is less than unity, as seen in Fig. 5[g]. The appearance of an under-unity resonance (less than full transmission, called a "quasi-resonance" with nonzero reflection), is also observed in asymmetrical quantum-dot systems [31,32]. It is considered here that this under-unity resonance may occur when the effective coupling between the dot and the nearby left and right wells becomes weaker. Hence, the variation of the lower backbone onsite energy for a fixed $\sigma_C$ determines the degree of asymmetry of the DNA molecule and therefore, the modulation of $|\sigma_C - \sigma|_n$ has the equivalent effect of controlling the coupling between the leads and DNA base-pairs. It is also found in Fig. 5[h] that the peak value of the transmission coefficient decreases and eventually becomes zero with decreasing $\sigma_C$, which is equivalent to the absence of transmitting states.

Using Eq. (11) and the transmission $T(E)$ of Fig. 5[a]–(d), we investigate the characteristics of $I$–$V$ curves at room temperature ($k_B T = 26$ meV) for an asymmetric DNA structure. Fig. 6 demonstrates nonlinear $I$–$V$ curves, which exhibit a variable current gap at low applied bias, with a variation of $\sigma_C = 7.3$ [red, dashed-dot line], $\sigma_C = 7.4$ [green, dotted line], $\sigma_C = 7.5$ [blue, solid line], and $\sigma_C = 7.24$ [black, dashed line] for a fixed $\sigma_D = 7.5$. It is clearly seen that the voltage threshold is modulated as the backbone onsite energy changes. In other words, the current gap gets wider as $\sigma_C$ increases. This can be qualitatively explained as follows: as the backbone onsite energies $\sigma_D$ increase, the main DNA onsite energy $\sigma_D$ also increases. When $\sigma_D$ becomes larger, the mini-bands in the transmission are shifted to higher electron energy and therefore, the onset of current arises at a higher source-drain voltage $V_{sd}$. This requires a higher voltage threshold to observe a current and a wider current gap in the $I$–$V$ curves. When $\sigma_C = 7.24$ [black dashed line], on the other hand, the voltage threshold increases to $V_{sd} \approx 1.4$ and the current remains constant after a voltage of $V_{sd} \approx 1.8$, because the main contribution to the transmission from the merged mini-band has disappeared, as shown in Fig. 5(d). In all cases, the system behaves as a semiconductor with a current gap that varies with the modulation of $|\sigma_C - \sigma|_n$ or the effec-
tive couplings). In addition, we calculate the differential $I-V$ curve ($dI/dV$) as a function of $V_{sd}$ for $\alpha_C = 7.24$ (black, dashed line) and $\alpha_C = 7.5$ (blue, solid line) in the inset of Fig. 6. The differential conductance $dI/dV$ for $\alpha_C = 7.24$ exhibits a double-peak structure with an amplitude of 30 nA/V and a peak width of $\sim 0.2$ volts.

3.3. Variation of contact coupling between leads and DNA

The role of contacts deserves particular attention because the precise details of DNA-lead contacts are not uniformly known or reported. In many experimental measurements, it is difficult to prove that the DNA molecule is in direct contact with the electrodes because the contact with metal electrodes is achieved by laying down the molecules directly onto the electrodes. Such an uncertain experimental situation with regards to DNA-electrode contacts makes it difficult to set the basis for a meaningful theoretical approach to study intrinsic DNA electrical transport properties. In order to specifically address DNA-lead contact effects on charge transport, we examine the transmission effects of DNA-lead coupling by varying coupling strengths between the molecule and the leads, both symmetrically and asymmetrically. In Fig. 7(a), we present a contour plot of the transmission as a function of the electron energy and the incoming (outgoing) coupling strength $t_L$ ($t_R$) for a fixed hopping integral $t_D$ between DNA base-pairs. In the weak coupling (Coulomb blockade) regime, electron tunneling between the leads and the DNA decreases and the transmission shows sharp and narrow unit resonances in each mini-band due to the localization of states, depicted in Fig. 7(b) for $t_L = t_R = 0.2$. For the strong coupling regime, on the other hand, overlapping of the wave functions increases due to mixing of energy states between the molecule and the electrodes, and well-arranged resonant peaks in each mini-band become overlapped in the transmission as $t_L$ ($= t_R$) increases.

Finally, we consider an asymmetric DNA structure with variation of the incoming coupling strength $t_L$ for fixed outgoing coupling, $t_R = 0.5$, with a contour plot of the transmission result presented in Fig. 7(c). In the strong contact coupling regime, the general trend of transmission, which is an increased overlapping of the wave functions due to the mixing of energy states, is the same as a symmetric DNA system. When $t_L$ becomes smaller (say, $t_L = 0.2$), however, a distinct and under-unity resonance in each band appear in Fig. 7(d). This under-unity transmission, which is a direct consequence of asymmetric contact effects, can be interpreted as resulting from interference between the DNA molecular bands and the electronic structure of the leads at the DNA-lead interface.

4. Conclusions

In summary, we have investigated the characteristics of electron transport through both symmetric and asymmetric DNA molecules using a quasi-one-dimensional TB model. In this system, the main conduction arises along the long axis of the DNA, and the sugar-phosphate backbone and the energy-dependent hopping amplitude between each site of the base and the backbone are incorporated.
into an energy-dependent on-site potential in the main DNA site. We have calculated overall contour plots of the transmission, the current–voltage characteristics, and the differential conductance for the variation of backbone on-site energy, the energy-dependent hopping strength, and the contact coupling between the leads and the DNA molecule. We have found that as the backbone coupling to the DNA changes, two transmission mini-bands with a gap progressively approach each other and eventually merge into a single mini-band. As backbone asymmetry is increased, on the other hand, merging and collapse of the two mini-bands occurs, with the additional appearance of an extra resonance peak in the transmission. We have also presented a sequence of the overlapping of two DW resonances into a single DW resonance and the formation of an under-unity resonance near a critical value of the lower backbone on-site energy. Finally, variation of the contact coupling in an asymmetric DNA structure has been discussed by illustrating a distinct under-unity resonance in the transmission.

Acknowledgement

This work is partially supported by the ASPIRE Grant at Ball State University.

References