ELECTRONIC PROPERTIES OF DNA MOLECULES UNDER DIFFERENT ELECTRIC FIELD EXPOSURE CONFIGURATIONS

A THESIS
SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE
MASTER OF SCIENCE

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MUNCIE, INDIANA
May 2014
To my love, Nastaran
ABSTRACT

In recent years, the electronic behavior of DNA molecules has received much interest ranging from interpreting experimental results to electronic based applications, including DNA sequencing and DNA-based nanotransistors. Here we study the electronic properties of poly(G)-poly(C) double stranded DNA molecules by means of the tight binding approximation to understand how the molecules act under different physical conditions. For instance, the effects of DNA tilting, stretching and compressing on the electronic properties are elucidated. Very interesting features such as a tunable energy band gap and a metal-semiconductor transition are disclosed for DNA under different conditions.
ACKNOWLEDGEMENTS

I have been privileged in my life for having many dedicated and devoted teachers who have taken interest in me and from whom I have learned a lot about life. Foremost, I would like to thank my advisors and mentors, Dr. Yong Joe and Dr. Eric Hedin for the continuous support of my study and research, for their patience, motivation, enthusiasm, and immense knowledge.

I would like to thank Dr. Thomas Robertson, our former department chair, for all his supports. Then, my appreciation goes to my thesis committee members, Dr. Thomas Jordan and Dr. Ranjith Wijesinghe for all their time and efforts. Third, special thanks go to Dr. Antonio Cancio for his valuable discussions and suggestions in the area of Condensed Matter Physics of DNA molecules.

Finally, I would like to thank the Department of Physics and Astronomy at large; I learned and understood far more than I expected I could with their help, and I was made to feel very welcome.
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Chapter 1: Introduction and Overview

This chapter gives a general overview on the emerging field of DNA electronics. First, we address the silicon-based electronic limitations which lead us to look for alternative materials to overcome these problems, and then we express why the DNA molecule can be a good candidate. Subsequently, some experimental attempts at characterizing DNA conduction behaviors are cited. These controversial results motivate us to seek a better understanding of charge transport mechanisms along DNA molecules. Consequently, the main transport mechanisms for charge transport along any general conductive channel are presented. Lastly a preview for this thesis is given.
1.1 Introduction

During the past decades, DNA molecules have found a central place on the biological research stage as a result of the significant biological role of protein functioning and as the expressed form of hereditary, genetic information. However, after the discovery of DNA electrical conductivity in the past few years, physicists and engineers have attempted to discover other roles for DNA that nature did not suggest. In particular, due to the classical silicon-based electronics limitations, DNA may be a candidate to overcome these problems.

Recently, the importance of nanoelectronics is revealed for everyone. Further miniaturization leads us to have a faster and more energy efficient electrical device. But the miniaturization is heading towards physical, technical and economic limits [1]. As an example, there is a certain limit for the number of silicon atoms in transistor insulating layers to prevent the electron leakage which causes short-circuit [2]. Furthermore, production costs drastically increase with size reduction. These problems are forcing researchers to look for other materials that may allow them to go further in miniaturizations. Such efforts included new alternative technologies by the use of new materials such as polyphenylene-based diode switches and carbon nanotubes [3]. But these techniques are still having many challenges. For instance, electrical properties of carbon nanotubes are highly related to their geometrical properties such as their diameter and chirality. Lack of control over nanotube fabrication and their production costs are still annoying. The techniques available yield only tubes of variable proportions.
Therefore the desire to have smaller electronic devices may lead us into a new field of DNA electronics. Basically, DNA offers solutions to many of these difficulties for the design of electric circuits as small as possible. Its unique properties, such as self-assembly and self-recognition make DNA the best (and also inexpensive) nanowire in existence.

The immediate goal is to improve the old technology with new concepts. This domain is highly interdisciplinary, from physics, chemistry to biology, engineering and so on. It aims to have a new range of electronic devices that are much smaller, faster and more energy efficient than the present semiconductor-based electronic devices.

1.2 DNA Conductivity

When we talk about DNA conductivity measurements, it is important to know that it is not as easy as a two wire connection. It needs sophisticated instruments such as atomic force microscopy and optical tweezers to align a single DNA molecule and a highly sensitive system for measuring current vs. voltage responses, since the currents are in the femto ($10^{-15}$) ampere range. The toughest part is to bind the DNA molecule to the electrodes especially to validate an available experimental result (see Fig. 1.1).
By the way, all these efforts are rewarded by DNA electrical behaviors. The molecule acts as an insulator, a semiconductor, a conductor or a proximity induced superconductor depending on its sequence, length and orientation.

The first experimental attempt to measure DNA conductivity was reported by Fink & Schonenberger [5] using a modified low-energy electron point-source microscope. They used a gold-coated carbon grid as the sample holder, for a 600-nm-long λ-DNA connected to a tungsten manipulation tip. A metallic conduction behavior for the DNA molecule was obtained (Fig. 1.2). Several other efforts also confirm the metallic behavior for the DNA.

Figure 1.1: Experimental scheme for DNA electrical measurements [4].

Figure 1.2: Current voltage behavior of a 600-nm-long λ-DNA [5].
Interestingly, Porath et al. [6] have shown that a 10.4-nm-long (30-base-pair) poly(G)–poly(C) sequence has a semiconducting characteristic. They measured the current voltage curve and found a certain threshold where below the threshold the DNA is an insulator and above the threshold it is a conductor (Fig. 1.3).

![Figure 1.3: Current voltage behavior of a 30-base-pair poly(G)–poly(C) DNA [6].](image)

Very interestingly, there are also some reports of a 16 μm λ-DNA which is behaving like a proximity-induced superconductor [7]. Any other physical properties, such as DNA sequence, diameter and stiffness could change its electrical properties. Bharadwaj et al. [8] showed that guanine is the base with the lowest oxidation potential, which then easily becomes positive. Therefore, for a G-rich DNA a positive charge can move from a single guanine towards a multiple guanine sequence that attracts such electron holes [9]. In general, it has been shown that GC DNA has p-type properties while AT DNA has n-type ones [10].
Among all these attempts, the main point which seems crucial is that the DNA conductivity is strongly influenced by the DNA sequence, the length of the DNA molecule, the environment of DNA (influence of water and counter-ions) and the microstructure of DNA (dependent upon humidity, stretching, or combing preparation conditions), etc. Accordingly there is a need to develop reliable theoretical models to describe the quantum transport mechanisms along the molecule.

1.3 Quantum transport

1.3.1 Transport mechanisms

The process of electron transfer is one of the fundamental topics of materials science. In general there are two accepted electron transport mechanisms through molecules. The first consists of single step electron tunneling from source to drain. The electron does not exchange any energy with the molecule and so the electron is never localized. The transport rate is exponentially decreased with the source-drain distance. A schematic for this kind of transport is shown in Fig. 1.4. This mechanism is called Coherent Transport [11].

![Coherent Transport Scheme](image)

Figure 1.4: Coherent transport scheme along a DNA molecule [12].
The second kind of electron transport mechanism is for long distance transport, which is referred to as thermal hopping transport. In contrast to coherent transport, for this mechanism, the electron is localized on the molecule and the motion can be thought as a diffusive transport pattern. Hence this transport is called Incoherent Transport. Figure 1.5 shows a schematic for this transport process.

![Figure 1.5: Incoherent transport scheme along a DNA molecule [12].](image)

1.3.2 DNA transport mechanism

DNA structure consists of two helically-wound strands which are coupled together by the hydrogen bonds in between. The strands are made by a polymeric backbone built from repeating sugar and phosphate molecules. Each sugar group is attached to one of four bases of guanine, cytosine, adenine and thymine. Naturally, guanine can just bond with cytosine, and adenine bonds just with thymine. Fig. 1.6 is the planar picture of a double stranded DNA molecule.
The well-accepted electron transport process for DNA is as follows. The mechanism is related to the $\pi$ orbital overlapping of the bases, which is called **Stacking Interactions**. Figure 1.7 shows this process schematically. The experimental and theoretical efforts also clarified both the coherent tunneling and thermal hopping mechanisms for the DNA electron transport.

Figure 1.6: Planar picture of a double stranded DNA molecule [13].

Figure 1.7: $\pi$-$\pi$ stacking along DNA molecule [14].
1.4 The thesis work

This report aims to interpret the controversial experimental results on DNA conductivity in which the molecule acts under different circumstances as an insulator, conductor and even semiconductor. Based on the tight binding approximation, an updated model which considers the next nearest neighbor effects is proposed to study charge transport along the DNA molecule under different electric field exposure conditions such as tilting, stretching and compressing. For each case, charge transmission probabilities, current voltage characteristics, conductance as well as electronic structure (e.g. band structure and local and total density of states) are studied.

1.5 Preview

Here, a brief preview of the chapters is given to explain how proceeding chapters address the research topic. The next chapter, Chapter 2, will describe the updated, two-dimensional tight binding model including the next nearest neighbor effects. The model is applied to a 30 base pair poly(G)-poly(C) ds-DNA molecule, and the results are compared with those obtained without considering the next nearest neighbor (NNN) effects. Chapter 3 presents the transport properties of a 10 base-pair poly(G)-poly(C) ds-DNA molecule, tilted with respect to the intercontact electric field direction by the use of the model introduced in Chapter 1, extended to consider the helical geometry of the DNA molecule. In Chapter 4, the effects of mechanical strains on the electronic properties of the DNA molecule are studied. To this goal, the theories of Slater-Koster and linear elasticity are also implemented.
Finally in Chapter 5, a conclusion for the final results of this collective work and possible further works are presented.
Chapter 2:

Second Order Tight Binding Model

The second order two-dimensional tight-binding model, including the next nearest-neighbor effects for quantum mechanical electron transport through double-stranded DNA molecules is proposed in this chapter. Considering the next nearest-neighbor hopping strengths between sites gives a more rational and realistic model for the electron path-way through DNA molecules. We show higher overall transmission and enhanced current for a 30 base-pair poly(G)–poly(C) DNA molecule with the inclusion of diagonal electron hopping between the sites. In addition, an optimum condition of the contact hopping strength and Fermi energy to obtain the maximum current for the system is demonstrated. Finally, we present the current-voltage characteristics, showing a transition from a semiconductor-like to a metal-like DNA molecule with the variation of the Fermi energy.
2.1 Introduction

DNA, as one of the most important biopolymers, plays an outstanding role in molecular electronics due to its unique self-assembly and self-recognition characteristics [15]. As a result, it has attracted much attention by researchers studying its charge transfer behavior [16]. Direct charge transport experiments have disclosed that, under different conditions, DNA molecules can act as insulators [17-20], semiconductors [21-24], and also conductors [25-28], which again confirms the immense importance of DNA-based electronic systems and devices. As an example, Qian et al. measured direct charge transport through single DNA molecules, via gold nanoparticle DNA complexes bound to a gold substrate, using scanning tunneling microscopy or current-sensing atomic force microscopy [29]. They presented semiconductor-like charge transport characteristics for different strands of DNA, 13 poly(A)-poly(T) base-pairs, and observed several different current-voltage (I–V) characteristics which are associated with different complex configurations.

Among the theoretical efforts towards interpreting these fascinating experimental results, model-based Hamiltonian methods are of particular interest due to their ease of application and generality [30-41]. Wei and Chan [42] proposed a tight-binding (TB) model to interpret the experimental I–V curves of the poly(G)-poly(C) DNA molecules reported in Ref. [6]. The model fit well with the experimental data, providing a satisfactory theoretical interpretation of experimental I–V features. Furthermore, several characteristics and effects such as
gap behavior in I–V curves [31], the influence of backbone on transmission spectra [32], and the sequence-dependence of DNA charge transport under different physical environments with various types of base-pair ordering [33] have been investigated. Recently, using a quasi-one-dimensional effective TB model, the electron transport through asymmetric DNA molecules was examined, including the effects of 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 [43].

It is noteworthy that in most of the efforts using TB modeling for DNA charge migration analysis so far, the hopping strengths between side-by-side sites have been taken into account to capture the pathways of electrons through the DNA structure. The correlation between DNA charge transport properties and the locations of cancerous mutations was studied by taking a simple TB model included with a simple set of diagonal hopping terms only between the base pairs [44]. In this system, however, only purine-purine transfer has a noticeable hopping magnitude and other hopping amplitudes between all sites are not equally emphasized. For example, the hydrogen bond between the base pairs has a negligible effect, and intra-backbone couplings and diagonal electron hopping between the backbone and the base pairs are neglected. In order to produce a more realistic elucidation of possible mechanisms for charge transport in DNA, hopping amplitudes between all the next nearest-neighbor (NNN) sites should also be addressed in the modeling. Accordingly in this paper, an advanced TB model including the NNN effects between
all sites is proposed, and the characteristics of quantum mechanical electron transport through a 30 base-pair poly(G)-poly(C) double stranded DNA molecule are investigated as a case study. It is shown that the NNN effects enhance higher overall transmission and current in this system. We also find that under different contact conditions, these effects play significant roles on electron transmission, which lead to changes in the patterns of average transmission spectra and increases the current flow in the DNA. Hence, an optimum condition of the contact hopping strength and Fermi energy to obtain the maximum current for the system is discussed.

2.2 Theoretical Modeling

The planar projection of a DNA duplex connected to two electrode leads is shown schematically in Fig. 2.1. There are four central conduction branches, linked to one another with interconnected nearest-neighbor sites.

![Figure 2.1: The schematic model of electronic transport through a 30 base pair, four-channel, poly(G)-poly(C) DNA molecule.](image)
Using a two-dimensional TB model, a simple and effective Hamiltonian for charge transport through the ds-DNA between two metallic leads can be written as

\[ H_{\text{Total}} = H_{\text{DNA}} + H_{\text{Lead}} + H_{\text{Lead-DNA}} \]  \hspace{1cm} (2.1)

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

\[ H_{\text{DNA}} = \sum_i \left( \epsilon_G G_i^\dagger G_i + \epsilon_C C_i^\dagger C_i + \epsilon_B B_{i,G}^\dagger B_{i,G} + \epsilon_B B_{i,C}^\dagger B_{i,C} \right) 
- \sum_i \left( t_G G_i^\dagger B_{i,G} + t_H G_i^\dagger C_i + t_A C_i^\dagger B_{i,C} + \text{h.c.} \right) 
- \sum_i \left( t_B B_{i,G}^\dagger B_{i+1,G} + t_G G_i^\dagger G_{i+1} + t_C C_i^\dagger C_{i+1} + t_B B_{i,C}^\dagger B_{i+1,C} + \text{h.c.} \right) - H_{\text{NNN}}, \]  \hspace{1cm} (2.2)

where \( G_i \) / \( C_i \) (\( G_i \) / \( C_i \)) and \( B_{i,G/C}^\dagger \) (\( B_{i,G/C} \)) are the creation (annihilation) operators at the i-th G/C base sites and the i-th upper and lower backbone sites, respectively. \( \epsilon_{G/C} \) and \( \epsilon_B \) are the onsite potential energies of the DNA base pair and backbone sites, respectively. \( t_A \), \( t_B \), \( t_G \), \( t_C \) and \( t_H \) are the hopping amplitudes between backbone and DNA base pairs, between backbone sites, between guanine sites, between cytosine sites, and for guanine-cytosine inter-site hopping, respectively.

The last term in Eq. (2.2), \( H_{\text{NNN}} \), is the part of the Hamiltonian related to the NNN sites, which can be written as

\[ H_{\text{NNN}} = \sum_i \left( t_{BG} [B_{i,G}^\dagger G_{i+1}^\dagger + B_{i,G}^\dagger G_{i-1}^\dagger + B_{i,C}^\dagger C_{i+1}^\dagger + B_{i,C}^\dagger C_{i-1}^\dagger] + t_{AG} [G_{i,G}^\dagger B_{i+1,G}^\dagger + G_{i,G}^\dagger B_{i-1,G}^\dagger] + t_{GH} [G_{i,G}^\dagger G_{i+1}^\dagger + G_{i,G}^\dagger G_{i-1}^\dagger] + t_{AC} [C_{i,C}^\dagger B_{i+1,C}^\dagger + C_{i,C}^\dagger B_{i-1,C}^\dagger] \right), \]  \hspace{1cm} (2.3)
where the coefficients \( t_{kl} \) are the NNN hopping strengths which are determined in the form of a relation as follows:

\[
t_{kl} = \frac{\sqrt{t_k^2 + t_l^2}}{z}; \quad k(l) = A, C, G(B, C, G, H) \text{ and } z = \text{integer.} \tag{2.4}
\]

We note here that the NNN coefficients \( t_{kl} \) in Eqs. (2.3) and (2.4) have direction-dependent hopping strengths due to the spatially anisotropic quantum confinement and possible internal structural reorganization of the nucleobases in response to charge transfer [45-47]. The DNA molecule is coupled to two semi-infinite metallic leads by the tunneling Hamiltonian

\[
H_{\text{Leads-DNA}} = -t_L l_0^+(C_1 + G_1) - t_R l_0^+(C_N + G_N) + h.c., \tag{2.5}
\]

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

\[
H_{\text{Leads}} = \varepsilon_0 \sum_i l_i^+ l_i^- - t_0 \sum_i (l_i^+ l_{i+1}^- + h.c.), \tag{2.6}
\]

where \( \varepsilon_0 \) is the lead onsite energy, and \( t_0 \) is the hopping amplitude between sites in the leads.

By discretizing the system spatially, with lattice constant \( a \) and denoting the wave function on site \( n \) by \( \psi_n \), the Schrödinger equation in the TB approximation can be written as
\[- \sum t_{n,m} \psi_m + \varepsilon_n \psi_n = E \psi_n, \]  \hspace{1cm} (2.7)

where the matrix elements $t_{n,m}$ are hopping integrals (or coupling parameters) between sites $m$ and $n$ with the single-site potential of site $n$, the sum runs over the nearest (or next-nearest) neighbors of $n$, $E$ is the electron energy, and $\varepsilon_n$ is the site energy. The general incoming and outgoing wavefunctions in the leads from the solution of Eq. (2.7) may be written as [48, 49]

$$
\psi_n = e^{in\theta} + r e^{-in\theta}, \quad n \leq 0,
\psi_n = t e^{in\theta}, \quad n \geq 1,
$$  \hspace{1cm} (2.8)

with $\theta = k a$. Here, $k$ is the wave vector that is connected with the energy by the dispersion relation for the Bloch states $E = -2t_0 \cos ka + \varepsilon_0$, and $t$ and $r$ are the transmission and reflection amplitudes, respectively. The Schrödinger equation for the amplitudes in the two lead sites and the 120 DNA sites (30 G sites, 30 C sites, 60 sugar-phosphate backbone sites) can be written and combined into a matrix form as follows:

$$
[\text{M}]_{122\times122} [\Psi]_{122\times1} = [\text{Z}]_{122\times1},
$$  \hspace{1cm} (2.9)

in which

$$
\overline{\Psi} = [r \ \psi_1 \ \psi_2 \ \ldots \ \psi_{119} \ \psi_{120} \ \ t],
\overline{Z} = [t_0 e^{i\theta} \ 0 \ -t_L \ -t_L \ 0 \ 0 \ \ldots \ \ 0],
$$  \hspace{1cm} (2.10)
where $\overline{\Psi}$ and $\overline{Z}$ are the transpose of $\Psi$ and $Z$, respectively, and the matrix $M$ is a banded diagonal matrix formed by hopping amplitudes and site energy terms. Therefore, by solving the matrix equation for the linearized TB Hamiltonian, Eq. (2.9), we obtain the transmission amplitude ($t$) as a function of the incoming electron energy, $E$. The desired transmission coefficient, $T(E)$ is obtained by taking the square of the transmission amplitude, $|t(E)|^2$. This completes the necessary background required for the analysis of the problem. In the next section, we present results for some numerical examples.

**2.3 Results and Discussion**

In order to demonstrate the nature and general behavior of the enhanced TB model, we consider a four-channel 30 base-pair poly(G)-poly(C) DNA molecule which has energies given by the ionization potentials of the respective base, taken as $\epsilon_G = 7.75 \text{ eV}$ and $\epsilon_C = 8.87 \text{ eV}$, and of the backbone sites, taken as $\epsilon_B = 8.85 \text{ eV}$. The DNA is assumed to be connected between two semi-infinite electrodes with an onsite energy of $\epsilon_o = 7.75 \text{ eV}$ and a hopping amplitude of $t_0 = 1 \text{ eV}$ between sites. Notice that a different hopping amplitude $t_0$ in the semi-infinite leads does not alter the main characteristics of electron transport through DNA molecules. According to values suggested in the literature [50-52], all numerical parameters used in the computations, such as DNA hopping probabilities (every line between sites in Fig. 2.1), are listed in Table 2.1.
Table 2.1: Tight-binding model parameters used in the present study.

<table>
<thead>
<tr>
<th>Onsite energies (eV)</th>
<th>Hopping amplitudes (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_o = 7.75$</td>
<td>$t_o = 1$</td>
</tr>
<tr>
<td>$\varepsilon_G = 7.75$</td>
<td>$t_G = 0.3$</td>
</tr>
<tr>
<td>$\varepsilon_C = 8.87$</td>
<td>$t_C = 0.3$</td>
</tr>
<tr>
<td>$\varepsilon_B = 8.85$</td>
<td>$t_H = 0.3$</td>
</tr>
<tr>
<td>$\varepsilon_H = 0.2$</td>
<td>$t_B = 0.1$</td>
</tr>
</tbody>
</table>

First, we compute the transmission coefficient, $T(E)$, for selected contact hopping amplitudes ($t_L = t_R = 0.1, 0.5, 0.9$) with and without considering the NNN effects. Furthermore, the average transmission coefficient, $T_a(E)$, is shown, which can be calculated by integrating the transmission coefficient as follows:

$$T_a(E) = (E - E_{\text{min}})^{-1} \int_{E_{\text{min}}}^{E} T(\varepsilon) d\varepsilon,$$

where $E_{\text{min}} = 5.75$ eV. Figures 2.2a-f display the transmission spectra of the DNA as a function of electron energy, and Fig. 2.2g-i show the average transmission spectra as a function of electron energy for selected values of $t_L$ and $t_R$. Plots (a, d and g) are with $t_L = t_R = 0.1$ eV, plots (b, e and h) are with $t_L = t_R = 0.5$ eV, and plots (c, f and i) are with $t_L = t_R = 0.9$ eV. [Here, we take the largest possible value of $t_{ld}$ by taking $z = 1$ in Eq. (2.4) in order to see the maximum effects of the NNN hopping]. By comparing Figs. 2.2d-f ($H_{\text{NNN}} \neq 0$) with Figs. 2.2a-c ($H_{\text{NNN}} = 0$), it is clearly seen that the electrons with the lower energies can be transmitted with the inclusion of NNN effects, which broadens the transmission spectra. Therefore, we attribute this enhancement of electron transport through DNA molecules to the inclusion of
diagonal electron hopping between the sites. Furthermore, this result can be shown more clearly in the average transmission spectra from Figs. 2.2g-i [gray line ($H_{NNN} = 0$) and black line ($H_{NNN} \neq 0$)].

![Graphs showing transmission spectra](image)

Figure 2.2: Transmission spectra as a function of electron energy without (a–c) and with (d–f) the NNN effects. (g–i) average transmission spectra as a function of electron energy: gray line ($H_{NNN} = 0$) and black line ($H_{NNN} \neq 0$). Plots (a, d and g) have $t_L = t_R = 0.1$ eV, plots (b, e and h) have $t_L = t_R = 0.5$ eV, and plots (c, f and i) have $t_L = t_R = 0.9$ eV.

When the contact hopping strength is small ($t_L = t_R = 0.1$ eV), the effect on the NNN hopping between the sites is minimal (the two curves are almost indistinguishable in Fig. 2g). As the contact hopping parameter increases ($t_L = t_R = 0.5$ eV and 0.9 eV), however, an enhancement in the average transmission spectra of DNA molecules appears due to the NNN effects, as seen in Fig. 2.2h and 2.2i. In addition, from the calculation of $T_a$ for decreasing NNN hopping strengths, obtained by increasing the integer $z$ in Eq. (2.4) [not shown here], we observe that the average transmission decreases as NNN hopping strengths become smaller (with increasing $z$ value). For example, the onset of $T_a$ for $t_L = t_R = 0.5$ eV arises at $E=6.1$
for $z=1$, $E=6.6$ for $z=2$, and $E=6.8$ for $z=3$, for the cases with $H_{NNN} \neq 0$, and $E=7.0$ for $H_{NNN} = 0$. $T_a$ almost linearly increases until it saturates in each case. We also note that at the higher energy edge of the window, the average transmission for all NNN hopping strengths with $H_{NNN} \neq 0$ converges to $T_a = 0.52$. The magnitude of $T_a$ at the high-energy edge for $H_{NNN} \neq 0$ is approximately 18% greater than for $H_{NNN} = 0$.

Next, we focus on the evaluation of the current-voltage characteristics of the DNA in the system. Accordingly, we assess here the I-V characteristics of the system with the transmission coefficient, $T(E)$, using a standard Landauer-Buttiker formula [53-56] as

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E)[f_L(E) - f_R(E)]dE. \quad (2.12)$$

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

Figure 3.3a (3.3b) shows a contour plot of the room temperature current for a fixed Fermi energy, $E_F = 5.5$ eV, by modulating the applied voltage ($V_{sd}$) and the
symmetrical contact coupling ($t_L = t_R$) between the leads and the DNA molecule without (with) NNN effects. In agreement with transmission spectra, the current is enhanced in magnitude when the NNN effects are taken into account. In other words, the current gap (shown as a green color), which is a typical characteristic of a semiconductor, is decreased by the diagonal electron hopping between the sites.

Figure 2.3: Contour plots of the current as a function of source-drain voltage and contact hopping strengths: (a) $H_{NNN} = 0$ and (b) $H_{NNN} \neq 0$; (c) Current as a function of source-drain voltage when $H_{NNN} = 0$ and $t_L = t_R = 0.42$ eV (gray solid line), and when $H_{NNN} \neq 0$ for two values of $t_L = t_R = 0.42$ eV (black dashed line) and $0.62$ eV (black solid line). The Fermi energy is 5.5 eV.

In Fig. 3c, the current as a function of the source-drain voltage is shown for three special cases: $H_{NNN} = 0$ and $t_L = t_R = 0.42$ eV (gray solid line), and $H_{NNN} \neq 0$ for two values of $t_L = t_R = 0.42$ eV (black dashed line) and 0.62 eV (black solid line). It is clearly seen that when $H_{NNN} \neq 0$, the voltage threshold decreases from $V_{sd} \approx 3.3$ to $V_{sd} \approx 1.6$. For $H_{NNN} = 0$, the highest current is obtained at $t_L = t_R = 0.42$ eV, but for $H_{NNN} \neq 0$, it is obtained at $t_L = t_R = 0.62$ eV. (Notice that the onset of current for both $t_L = t_R = 0.42$ eV and 0.62 eV arises at the same $V_{sd}$). Therefore, in order to achieve maximum current for a given $V_{sd}$ in the system, we should take into account the NNN
hopping between the sites and choose a symmetrical contact coupling \( t_L = t_R = 0.62 \) eV. We also note that the current is enhanced by increasing the interconnecting coupling between the backbones, because the onset of average transmission arises in the lower energy regime.

The contact hopping strengths have been kept symmetrical (i.e., \( t_L = t_R \)) so far. Next, the current behavior is investigated as a function of source-drain voltage when the asymmetry of the contact couplings (i.e., \( |t_L - t_R| \)) is increased. Figure 2.4a shows a contour plot of the room temperature current with NNN effects and a fixed Fermi energy, \( E_F = 5.5 \) eV, by modulating the applied voltage \( V_{sd} \) and the coupling contact, \( t_R \), between the right lead and the DNA molecule, for fixed \( t_L = 0.42 \) eV. Figure 2.4b displays current-voltage curves and the corresponding differential conductance for the system when \( t_L = t_R = 0.42 \) eV (dashed line), and \( t_L = 0.42 \) eV and \( t_R = 0.62 \) eV (solid line). Compared to the symmetric case (\( t_L = t_R = 0.42 \) eV), increasing the asymmetry of the contacts by increasing \( t_R \) leads to higher current values (and a higher differential conductance—see inset in Fig. 2.4b) until \( t_R > 0.62 \) eV. Further increasing \( t_R \) beyond \( t_R = 0.62 \) eV reverses the trend, resulting in lower current values. It is also seen that increasing the asymmetry of the contact hopping configuration does not lead to any significant difference in the voltage gap size (\( \approx 4 \) V).
Figure 2.4: (a) Contour plot of the current as a function of source-drain voltage, $V_{sd}$, and DNA-lead coupling, $t_R$, for $H_{NNN} \neq 0$ when $t_L = 0.42$. (b) Currents as a function of source-drain voltage for $H_{NNN} \neq 0$ when $t_L = t_R = 0.42$ eV (dashed line), and for $t_L = 0.42$ eV and $t_R = 0.62$ eV (solid line); the inset shows the differential conductance, $dI/dV$, versus applied voltage corresponding to the I-V curves. The Fermi energy is 5.5 eV.

Finally, we examine a desirable condition to obtain the maximum current with variation of the Fermi energy for an asymmetric DNA structure. For asymmetric contact couplings, where the right contact hopping amplitude is tuned to $t_R = 0.5$ eV, the contour plots of current as a function of source-drain voltage and Fermi energy are shown in Fig. 2.5 for $t_L = 0.42$ eV and $H_{NNN} = 0$ [Fig. 2.5a], and $t_L = 0.62$ eV and $H_{NNN} \neq 0$ [Fig. 2.5b]. By comparison of Fig. 2.5b with Fig. 2.5a, it may be concluded that the NNN effects induce current at lower Fermi energies ($E_F = 4.0$ eV for $H_{NNN} \neq 0$, whereas $E_F = 4.8$ eV for $H_{NNN} = 0$). By the same token, the maximum current for $H_{NNN} \neq 0$ is obtained at the lower $E_F = 8.0$ eV in comparison with $E_F = 8.2$ eV for $H_{NNN} = 0$, as indicated by the dashed lines in Fig. 2.5a and 2.5b.
These two maximum currents are plotted in the same frame at Fig. 2.5c \([H_{NNN} = 0\) (gray line) and \(H_{NNN} \neq 0\) (black line)].

It is interesting to note that these I-V curves show a nearly linear behavior in the range of low applied voltage. This Ohmic behavior, with no current gap, is clear evidence that the DNA molecule now has a metallic characteristic with a significant difference in the saturated currents. The inset of Fig. 2.5c shows an enlargement for the I-V curves in a small voltage region near the origin in order to see the negligible current gap. The variation of the Fermi energy in the system causes a transition from a semiconductor-like to a metal-like DNA molecule.

Figure 2.5: Contour plots of current as a function of source-drain voltage and Fermi energy when \(t_R = 0.5\) eV: (a) \(H_{NNN}=0\) and \(t_L = 0.42\) eV, (b) \(H_{NNN} \neq 0\) and \(t_L = 0.62\) eV; (c) Currents as a function of source-drain voltage: \(H_{NNN} = 0\), \(t_L = 0.42\) eV and \(E_F = 8.2\) eV (gray line), \(H_{NNN} \neq 0\), \(t_L = 0.62\) eV, and \(E_F = 8\) eV (black line); the inset shows an enlargement of the I-V curves in a small voltage window near the origin.
Chapter 3:

Tilted DNA Molecule

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

The diverse functionality of DNA molecules, ranging from insulators to semiconductors and conductors, expresses the immense importance of DNA-based electronic systems and devices. Among the theoretical efforts towards interpreting these fascinating experimental results, model-based Hamiltonian methods are of particular interest due to their ease of application and generality.

Here the molecule is subjected to a perpendicular gating electric field and so the helix conformation of the strands becomes important [34]. This situation takes place when the trapped molecule is not aligned with the intercontact electric field so that there exists a component of the field perpendicular to the molecular axis (see Fig. 3.1).

![Figure 3.1: Problem geometry](image)
3.2 Theoretical Modeling

Here, we include the helix geometry of the strands in the traditional ladder model. We consider a 10 base-pair full twisted DNA molecule. The on-site energies ($\varepsilon_i$) become (neglecting the difference between major and minor grooves) [34]:

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

(3.1)

where $\varepsilon_i^0$ is on-site energy of the $i$-th base molecule at zero field, $V_{sd}$ is the source-drain voltage, $\alpha$ is the tilted DNA angle, $d$ is the DNA diameter, $L$ is the DNA length, $\phi_0$ determines the initial orientation of the DNA molecule, and the positive sign is for the two top DNA strands and the negative sign for the two bottom strands. Therefore the onsite energies of the TB model introduced in Chapter 2 are updated with Eq. (3.1). The Schrödinger equation for the amplitudes in the two lead sites and the 40 DNA sites (10 G sites, 10 C sites, 20 sugar-phosphate backbone sites) can be written and combined into a matrix form as follows:

$$
[M]_{42\times42} [\Psi]_{42\times1} = [Z]_{42\times1},
$$

(3.2)

in which

$$
\bar{\Psi} = [r \ \psi_1 \ \psi_2 \ \ldots \ \psi_{39} \ \psi_{40} \ \psi_t],

\bar{Z} = [t_0 e^{i\phi} \ 0 \ -t_L \ -t_L \ 0 \ 0 \ \ldots \ 0],
$$

(3.3)

where $\bar{\Psi}$ and $\bar{Z}$ are the transpose of $\Psi$ and $Z$, respectively, and the matrix $M$ is a banded diagonal matrix formed by hopping amplitudes.
3.3 Results and Discussion

The DNA is assumed to be connected between two semi-infinite electrodes with an on-site energy of $\varepsilon_0 = 7.75$ eV and a hopping amplitude of $t_o = 1$ eV between sites. Notice that choosing different hopping amplitude $t_o$ in the semi-infinite leads does not alter the main characteristics of electron transport through DNA molecules. All numerical parameters are the same as Table 2.1 for $t_{ul} \approx 0.08$ eV.

Here we study the effects of contact and tilt angle on the quantum transport behavior of the DNA molecule. The parameters describing the possible asymmetry of contact to leads and Fermi energy are chosen here as $E_F = 5.5$ eV and $\eta = 0.5$.

We display the transmission spectra of the DNA as a function of electron energy for selected values of $t_L = t_R = 0.1, 0.5$ and $0.9$ eV in Fig. 3.2. It is clearly seen that the electrons with the lower energies can be transmitted with the inclusion of NNN effects, which broadens the transmission spectra.
Figure 3.2: Transmission spectra as a function of electron energy with and without NNN effects for selected contact couplings.

**Figure 3.3** shows the resonant tunneling (RT) current by modulating the voltage ($V_{sd}$) for three special cases: $t_L = t_R = 0.1$, 0.5 and 0.9 eV, without and with NNN effects. The highest current is obtained at $t_L = t_R = 0.5$ eV, with the inclusion of NNN effects. Therefore, in order to achieve maximum current for a given $V_{sd}$ in the system, we should take into account the NNN hopping between the sites.
Figure 3.3: Current as a function of source-drain voltage with (solid) and without (dashed) NNN effects for selected contact couplings.

In Fig. 3.4, we show the transmission spectra of the tilted DNA as a function of electron energy for selected tilt angles ($\alpha = 0^\circ, 30^\circ$ and $60^\circ$) and source-drain voltages ($V_{sd} = 0, 2$ and $4$ Volts) with fixed contact hopping strengths ($t_L = t_R = 0.5$ eV). Spectra become slightly broader in the case with NNN effects which means more electron energies contribute to the transmission. It is clear from Eq. (3.1) that
by increasing the tilt angle or the source-drain voltage, the normal electric field component is enhanced. This leads to changes in the surface charge distribution over the DNA strands which regulate the conductivity of the charge carrier in the DNA molecule. This behavior can easily be seen in Fig. 3.4, which shows that the transmissions are washed out by increasing tilt angle as well as by higher source-drain voltages.

Figure 3.4: Transmission spectra as a function of electron energy with and without NNN effects for selected tilt angles and source-drain voltages.
Figure 3.5: Current as a function of source-drain voltage with (solid) and without (dashed) NNN effects for selected tilt angles.

Figure 3.5 shows the room temperature current as a function of voltage ($V_{sd}$) for selected tilt angles ($\alpha = 0^\circ, 30^\circ$ and $60^\circ$) under the symmetrical contact couplings ($t_L = t_R = 0.5$ eV). In agreement with transmission spectra, the current is enhanced in magnitude when the NNN effects are taken into account. In other words, the current
gap, which is a typical characteristic of a semiconductor, is decreased by the diagonal electron hopping between the sites. As we discussed before, current is diminished by increasing the tilt angle. It is noticeable that there is a critical voltage which is attributed to the highest current for a tilted DNA molecule.
Chapter 4:

Strain-dependent DNA electronics

Small mechanical strain perturbations are considered in calculations of the poly(G)-poly(C) DNA molecular electronic structure, using a tight-binding framework in conjunction with the theories of Slater-Koster and linear elasticity. Results reveal a strain-induced band gap for DNA which is linearly dependent on the induced strain. Local density of states calculations expose that the contribution of the guanine-cytosine base pairs in the charge transport mechanism is significantly enhanced relative to the backbones when DNA is compressed. Transport investigations also disclose a strain-induced metal-semiconductor transition for the DNA molecule, which suggests possible potential uses for sensing applications.
4.1 Introduction

It is now well established that DNA’s electronic and self-assembly properties are important for understanding its functionalities and applications in living cells and in nanoscience. With regards to its conductance behavior, however, DNA still remains highly controversial. Several experimental studies have shown DNA conductance behavior ranging from a wide-gap insulator to a semiconductor, to a proximity-induced superconductor.

One reason for this variety of conductance behavior, which is hardly interpretable by solid state physics, is the highly dynamic nature of DNA molecules. Based on molecular dynamics (MD) simulations, a DNA base pair can easily stretch or compress about a tenth of the Watson-Crick spacing (i.e. 0.3 to 0.4 Å), which is an order of magnitude higher than in crystals at room temperature [57]. As a result, several attempts have been made to explore the mechanics of DNA molecules under stretching [58, and following comments in the same issue]. Interestingly, by the use of MD simulations, Konrad and Bolonick showed that in the case of 3’ ends stretching, the DNA molecule can maintain its interstrand base pairing even up to 70% mechanical strain which shows the hyperelastic nature of DNA molecules [59].

Therefore, it is reasonable and very crucial to consider the structural consequences of mechanical strain on DNA quantum transport studies. Experimentally, Xu et al. studied electrode spacing effects on DNA electron transport [28]. They found a stepwise decrease in DNA conductance during the stretching process. Theoretically, Maragakis et al. investigated the electronic eigenstates of a
periodic homopolymer of poly(G)-poly(C) with 10 base-pairs under overstretching of up to 90% relative to its natural length by means of a self-consistent-charge density-functional tight-binding method [60]. They predicted a dramatic decrease in hole conductivity due to the subsequent drastic drop in hopping matrix elements during the stretching process. Using a similar technique, considering DNA under twisting and stretching processes simultaneously, Song et al. has arrived at very interesting results [61]. For a pure twisting, when the base pair spacing is kept fixed, decreasing the twist angle causes a reduction in the hopping matrix elements, while for a pure stretching process, couplings are exponentially suppressed. Hence, there are local minima and maxima for the coupling integral between two nearest neighbor sites which facilitates control of the conductivity. Recently, the efficiency of hole transport in ds-DNA molecules was theoretically studied in terms of molecular stretching by considering mechanical stress [62]. A slight disturbance in the transport efficiency for small strains was found, while as the molecule is stretched further, such strain dependency was revealed. A minor effect due to a small strain might originate from the slight sensitivity of their macroscopic point of interest. The so-called transport sensitivity to small internal disturbances prevents the study in theory about what happens with transport mechanisms during mechanical stretching or compressing processes.

Therefore, there is a need to have a microscopic understanding of DNA charge transport under conditions of strain in order to construct a more detailed model of DNA electronic structure. Furthermore, small mechanical strains are very
probable for the molecule under many circumstances, such as substrate lattice mismatch, details of the chemical synthesis, and experimental perturbations. Most importantly, in much of the Hamiltonian-based current research, the effects of possible transport mechanisms along the sugar-phosphate backbones are neglected, even though they are very sensitive to strain due to their greater onsite energies.

Accordingly, we first elucidate the electronic structure of an infinite length ds-DNA molecule under small strains in a tight-binding framework, in conjunction with Slater-Koster theory. The electronic band structure, eigenstates, local and total density of states under stretching and compressing are studied. Next, the conduction behavior of a molecule with finite length, coupled between two lead electrodes, is investigated. Transmission spectra, current-voltage characteristics, and conductance behavior are shown for selected mechanical strains.

### 4.2 Infinite length DNA

For the first step, we consider an infinite repeating chain of ds-DNA which is schematically shown in Fig.1. To calculate the electronic structure of the system, it is necessary to identify the repeating unit-cell from which the entire system can be constructed. In this case, it is easily seen that the repeating cell consists of eight molecules with a lattice constant $a$. The repeating unit-cell is bounded by a dashed line (see Fig. 4.1). Here we only consider the $p_z$ electrons forming π-bonds. They are presumably orthogonal to the plane of DNA molecule when we model it in an extended ladder model.
Upon considering both nearest-neighbor terms and the next nearest-neighbor (diagonal) hopping effects [63], the Hamiltonian of the infinite DNA chain in real space can be written as:

\[
H = \sum_{m=-\infty}^{i=+\infty} \epsilon_{m} |i,m\rangle \langle i,m| + \sum_{i,m\neq n} (t_{mn} |i,m\rangle \langle i,n| + \tilde{t}_{mn} |i,m\rangle \langle i+1,n| + h.c.),
\]

in which \( \epsilon_{m} \) is the on-site energy of the \( m-th \) site, \( t_{mn} \) are the hopping integrals between inner unit-cell sites and \( \tilde{t}_{mn} \) are ones between two adjacent cells. By taking the Fourier transform of Eq. (4.1), the quasi-one-dimensional \( k \)-space Hamiltonian can be obtained as follows:

\[
H_{k} = \sum_{k,m=1}^{m=8} \epsilon_{m} |k,m\rangle \langle k,m| + \sum_{k,m \neq n} (t_{mn} |k,m\rangle \langle k,n| + \tilde{t}_{mn} e^{-i\kappa a} |k,m\rangle \langle k,n| + h.c.),
\]

Figure 4.1: Schematic picture of an infinite DNA chain with a repeating unit-cell (bounded by the dashed line).
where \( \mathbf{k} \) is the wavevector. Eq. (4.2) can be written in a matrix form where the Hamiltonian \( H_k \) is given by

\[
H_k = \begin{bmatrix}
\varepsilon_1 & t_{12} & 0 & 0 & H_{1,5} & H_{1,6} & 0 & 0 \\
t_{12} & \varepsilon_2 & t_{23} & 0 & H_{2,5} & H_{2,6} & H_{2,7} & 0 \\
0 & t_{23} & \varepsilon_3 & t_{34} & 0 & H_{3,6} & H_{3,7} & H_{3,8} \\
0 & 0 & t_{34} & \varepsilon_4 & 0 & 0 & H_{4,7} & H_{4,8} \\
H_{1,5}^* & H_{2,5}^* & 0 & 0 & \varepsilon_5 & t_{56} & 0 & 0 \\
H_{1,6}^* & H_{2,6}^* & H_{3,6}^* & 0 & t_{56} & \varepsilon_6 & t_{67} & 0 \\
0 & H_{2,7} & H_{3,7} & H_{4,7}^* & 0 & t_{67} & \varepsilon_7 & t_{78} \\
0 & 0 & H_{3,8} & H_{4,8}^* & 0 & 0 & t_{78} & \varepsilon_8
\end{bmatrix}
\]  

(4.3)

where \( H_{i,j} = t_{ij} + \tilde{t}_{ij} e^{i\mathbf{k} \cdot \mathbf{a}_{ij}} \) and \( H_{i,j}^* = t_{ij}^* + \tilde{t}_{ij} e^{-i\mathbf{k} \cdot \mathbf{a}_{ij}} \). Diagonalizing the Hamiltonian of Eq. (4.3) yields the band structure for the infinite DNA in the first Brillouin zone.

For our numerical calculation, we are studying a poly(dG)-poly(dC) ds-DNA molecule with the on-site energies \( \varepsilon_1 = \varepsilon_4 = \varepsilon_5 = \varepsilon_8 = 8.85 \text{eV} \) for sugar-phosphate, \( \varepsilon_2 = \varepsilon_6 = 7.75 \text{eV} \) for guanine, and \( \varepsilon_3 = \varepsilon_7 = 8.87 \text{eV} \) for cytosine sites [52]. By taking the advantage of semi-empirical Slater-Koster theory [64] which relates the hoppings to the inter-orbital distance, the hopping integrals for the system are determined as follows:

\[
t = -\eta_{pp\pi} \frac{\hbar^2}{m_e d_0^2} e^{-d/R_c},
\]

(4.4)

where \( d \) is the inter-orbital distance, \( m_e \) is the mass of electron, \( \hbar^2 / m_e d_0^2 = 7.62 \text{ eV} \) for \( d_0 = 1 \text{ Å} \), and \( \eta_{pp\pi} \) and \( R_c \) are determined by matching to the ab initio results.
These parameters for two parallel GC base-pairs of a B-DNA molecule were determined as $\eta_{pp,\pi} = 2.26$ and $R_c = 0.87\,\text{Å}$ [65]. We use these results to calculate the hopping between guanine and cytosine sites. For an unstrained DNA, the distances between two adjacent base-pairs is about 3.4 Å and the outer diameter would be around 20 Å by considering DNA as a rod. Hence, we can pick the value of 6.7 Å for the distance between each conduction line. Using these values and Eq. (4.4), the hopping integral between GC sites is -0.35 eV.

In order to calculate these values for the backbone sites, however, we have to modify the parameters. As $R_c$ is mostly attributed to the wavefunction decay, it is reasonable to keep its value the same as for GC, and here we just modify the value of $\eta_{pp,\pi}$ for the backbone hopping integrals. By taking the hoppings between backbone sites and the guanine and cytosine sites to be about -0.1 eV, the appropriate $\eta_{pp,\pi}$ would be 0.65. As a result, we have developed appropriate hopping integrals as a function of inter-orbital distance between two different sites.

In the condition of small strain, for the DNA rod model, Poisson’s ratio ($\sigma$) for the DNA (which relates the transverse strain to the applied longitudinal strain) can be developed. Manning has reported an unusual behavior for the DNA molecule when it is stretched [66]. When DNA is considered as a macroscopic, homogenous, isotropic elastic rod with circular cross section, it expands transversely when stretched, unlike common bulk materials. This behavior is related to a negative
Poisson’s ratio, which he has estimated for DNA to be about -0.5. According to the theory of linear elasticity [67], transverse strain ($s_t$) is given by:

$$s_t = -\sigma s_z,$$  \hspace{1cm} (4.5)

in which $s_z$ is the applied longitudinal strain. This completes the necessary background for the problem parameterization.

Subsequently as we described earlier in relation to the eigenvalues of the Hamiltonian matrix, Eq. (4.3), the band structure of the infinite DNA in the first Brillouin zone for selected strain percentages is shown in Fig. 4.2. There are eight energy bands, while two pairs are degenerate to each other because of symmetrical backbone sites at the top and bottom of the unit cell. The overall band structure is symmetric due to vertical bilateral symmetry in the DNA. For positive strains (stretching), the bands shrink, and ultimately an energy band gap is produced. For a specific 10% strain, the energy gap is 0.18 eV. The situation is reversed when DNA is compressed (i.e. negative strains). In this case, the bands intermingle and simultaneously expand along the energy axis.
Figure 4.2: The infinite DNA band structure in the first Brillouin zone for selected percentage strains ($s_i = -10, -5, 0, 5, 10$).

The magnitude of the wavefunction coefficients are also depicted in Fig. 4.3 for the eight eigenstates, illustrating the bonding and anti-bonding occurring for particular energy configurations at $k = 0$ for unstrained single-cell DNA. Positive coefficients are shown in blue and negative coefficients are in red. The states are in order of increasing energy beginning with the ground state where the system is in a state of total bonding. Anti-bonding is then introduced in each successive state, increasing the energy, ending with the most energetic state where each atom forms anti-bonds with its neighbors. It is also revealed that as a consequence of the top and bottom backbones shown in Fig. 4.1, some states (and bands) are degenerate ($E_4 = E_5$ and $E_6 = E_7$).
Figure 4.3: Coefficients of eigenstates for unstrained single-cell DNA at the $\Gamma$ point.

The total density of state (DOS) is another important electronic property of the system which can be calculated using the final relation,

$$
\text{DOS} = \sum_i \frac{1}{2\pi} \int \delta(E_{i,k} - E) dk \approx \frac{1}{N} \sum_{i,k} (\pi k_B T)^{1/2} e^{-(E_{i,k} - E)^2 / (2 k_B T)},
$$

(4.5)

where $\delta(x)$ is the Dirac delta function, $E$ is some energy in the first Brillouin zone, $E_{i,k}$ is the energy of the $i$-th band and the wavevector $\vec{k}$, $N$ is the number of points in $k$-space, and $k_B T$ has been set at $2 \times 10^{-4}$ eV. The DOS describes the number of states per lattice length per unit energy. Here the minimal activation of temperature is necessary because the calculation is done computationally and an analytic form of $E(k)$ is not found. Therefore, the approximation on the right-hand side of Eq. (4.5) is
used which includes an adjustable parameter in the form of $k_B T$, while an effort is made to avoid unnecessary thermal-broadening.

By localization of the DOS at some site in real space, the local density of states (LDOS) can also be determined. Here, the coefficients of the wavefunctions ($C_{i,k}$) are obtained rather than the wavefunction itself. Therefore, the LDOS can be introduced as follows:

$$\text{LDOS} \sim \sum_i \int C_{i,k}^* C_{i,k} \delta(E_{i,k} - E)dk \approx \frac{1}{N} \sum_{i,k} (\pi k_B T)^{-1/2} C_{i,k}^* C_{i,k} e^{-(E_{i,k} - E)^2/k_B T}, \quad (4.6)$$

in which the indices $i$ and $k$ indicate the band and wavevector magnitude, respectively. The LDOS is computationally determined using Eq. (4.6) for only the unit cell sites with the same thermal activation as for DOS. Figure 4.4 shows DOS’s and LDOS’s of the infinite DNA model as a function of energy for selected strain percentages. In comparison with relaxed DNA DOS (Fig. 4h), the other DOS’s show similar states localizing and delocalizing behaviors under stretching (Fig. 4.4a and b) and compressing (Fig. 4.4c and d) of the DNA, in agreement with the associated band structure. The same energy gap seen in the band structure for 10 percent stretching is also observable here, marked by an arrow (Fig. 4.4a). To study the origin of the peaks in the DOS’s, we show LDOS’s for guanine, cytosine, and backbone sites in Fig. 4.4e-g. Symmetrical LDOS’s around local onsite energies are noticeable, which shows the potential of LDOS measurements using scanning tunneling microscopy of DNA molecule for sequencing purposes. As expected, the
main available states over the entire energy band correspond to guanine and cytosine sites. It seems that the backbones’ contribution to the conduction is dramatically decreased, which ultimately leads to the guanine-cytosine conduction mechanism through DNA during compression.

By looking at these results, higher conduction during compression (states delocalizing) is more expected (e.g. there is a small peak between backbone peaks due to guanine LDOS broadening for 10 percent compression (see Fig. 4.4d).

![Graphs showing DOS and LDOS for different strain percentages](image)

Figure 4.4: Total DOS for selected strain percentages: (a) $s_I = 10$, (b) $s_I = 5$, (c) $s_I = -5$, (d) $s_I = -10$. Local DOS of (e) Guanine sites, (f) Cytosine sites, and (g) Backbone sites for selected strain percentages: -10 (dashed red), -5 (solid red), 0 (black), +5 (solid blue), and +10 (dashed blue). (h) Total DOS of the relaxed DNA with $s_I = 0$. 
4.3 Coupled finite length DNA

Another interesting property of DNA, especially according to the experimental point of view, is its current-voltage behavior. In order to investigate this property, we deal with a finite ds-DNA molecule (30 base-pairs) coupled between two semi-infinite metallic leads (see Fig. 4.5). The effective Hamiltonian for charge transport through this system can be written as

$$H_{Total} = H_{DNA} + H_{Lead} + H_{Lead-DNA}.$$  \hfill (4.7)

Here, the Hamiltonian for a ds-DNA molecule is described by a summation over all base-pair sites as follows:

$$H_{DNA} = \sum_{i=1}^{15} \varepsilon_i |i,m\rangle \langle i,m| + \sum_{i,m \neq n} (t_{mn} |i,m\rangle \langle i,n| + t_{nm} |i,m\rangle \langle i+1,n| + h.c.).$$  \hfill (4.8)

Figure 4.5: Schematic picture of a 30 base-pair DNA chain coupled between two semi-infinite lead electrodes.

The DNA molecule is coupled to two semi-infinite metallic leads by the tunneling Hamiltonian...
where \( t_L(t_R) \) are the hopping strengths between the left (right) lead and the end DNA bases, and \( l_0 \) and \( l_1 \) denote the sites in the left and right leads, respectively, which connect to the end DNA bases. The leads themselves are modeled by another TB Hamiltonian as

\[
H_{\text{Leads}} = \sum_i \varepsilon_0 |l_i\rangle\langle l_i| + \sum_i (t_0 |l_i\rangle\langle l_{i+1}| + h.c.),
\]

where \( \varepsilon_0 \) is the lead onsite energy, and \( t_0 \) is the hopping amplitude between sites in the leads. By discretizing the system spatially with lattice constant \( a \) and denoting the wave function on site \( n \) by \( \psi_n \), the Schrödinger equation in the TB framework can be written as

\[
\sum_{m} t_{mn} \psi_m + \varepsilon_n \psi_n = E \psi_n,
\]

where the matrix elements \( t_{mn} \) 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 \( \varepsilon_n \) is the site energy.

The general incoming and outgoing wavefunctions in the leads, which are solutions of Eq. (4.11) may be written as [48, 49]
\[ \psi_n = e^{in\theta} + re^{-in\theta} (n \leq 0), \]
\[ \psi_n = te^{in\theta} (n \geq 1), \] (4.12)

with \( \theta = k'a \). Here, the wave vector \( (k') \) is connected with the energy by the dispersion relation for the Bloch states \( E = 2t_0 \cos k'a + \varepsilon_0 \), and \( t \) and \( r \) are the transmission and reflection amplitudes, respectively. By solving the matrix form of the Schrödinger equation for the amplitudes in the two lead sites, we obtain the transmission amplitude \( (t) \) as a function of the incoming electron energy, \( E \). The desired transmission coefficient, \( T(E) \), is obtained by taking the square of the transmission amplitude, \( |t(E)|^2 \). For the following calculations, the contact hopping strengths are kept fixed at -1 eV.
Figure 4.6: Transmission spectra of the 30 base pair DNA as a function of electron energy for selected percentage strains.

Figure 4.6 demonstrates transmission spectra of the coupled DNA for selected percentage strains. When compared with the infinite DNA band structure, finite DNA transmission spectra show strong similarity. Similar localizing and delocalizing behaviors and specifically, the same energy gap matched with the energy band gap of the infinite DNA at 10% stretching are revealed. It is worthwhile to examine how the gap width behaves for different number of base pairs. After 10
base pairs, it is seen that not only the width of the gap remains constant but also the width of the transmission bands remains constant, although the number of resonance peaks in each miniband increases (not shown here).

It is also meaningful to see how the DNA energy gap behaves with strain. Figure 7 shows the energy gap variation under stretching. The gap is opened right after +5% strain and grows linearly with increasing strain. This gap modulation with strain suggests possible applications, such as DNA-based pressure sensors.

![Graph showing DNA energy band gap variation under stretching](image)

**Figure 4.7:** DNA energy band gap variation under stretching.

With the knowledge of the transmission, $T(E)$, we can evaluate the current-voltage ($I-V$) characteristics of the DNA in the system by applying the standard Landauer-Buttiker formula [53-56] as
\[ I = \left(\frac{2e}{h}\right) \int_{-\infty}^{+\infty} T(E)[f_L(E) - f_R(E)]dE. \] (4.13)

Here, \( f_{L/R}(E) = \frac{1}{e^{(E-\mu_{L/R})/k_B T} + 1} \) is the Fermi distribution function with \( \beta = 1/k_B T \), where \( k_B \) is a Boltzmann constant and \( \mu_{L/R} \) stands for the electrochemical potential of the left (right) lead, whose value depends on the applied bias voltage. We choose \( \mu_L = E_F + (1-\eta)V_{sd} \) and \( \mu_R = E_F - \eta V_{sd} \), 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 which is here set to \( \eta = 0.5 \) for symmetric contacts.

Next, we study the current-voltage characteristics and conductance behaviors of the DNA molecule with a small mechanical strain perturbation at different Fermi energies. First, we show the current-voltage and conductance behaviors of the DNA molecule at Fermi energy 8.3eV in Fig. 4.8. At this Fermi energy, where the gap is opened by the strain, the transition from metallic to semiconducting behavior can be seen under stretching (see the blue dashed curve in Fig. 4.8a). From the enlarged plot of the I-V curve, depicted in the upper left insets of Fig. 4.8, the current increases linearly near the origin with no strain (black curve). With 10% stretching strain (blue dashed curve), however, the I-V behavior shows negligible current up to a threshold voltage, followed by a sharp rise of the current with a voltage gap ~0.4 V. In addition, the saturated current value is decreased due to stretching in comparison with relaxed equilibrium DNA. In contrast, compression
leads to higher saturated currents (see the red dashed curve in Fig. 4.8b). In the pre-saturation region, the current voltage curves nearly follow each other, except at ±10% strain for which the curve is slightly deflected. This change is related to the strain-based gap, and is less dominant for -10% strain compared to +10% strain.

Figure 4.8: Current-voltage and corresponding differential conductance curves (lower right insets) for the DNA molecule at Fermi energy $E_F = 8.3$ eV for selected strain percentages. (a) Stretching strain ($s_l = 0, 5,$ and 10) shows decreasing saturated current with strain. (b) Compression strain ($s_l = 0, -5,$ and -10) shows increasing saturated current with strain.

In addition, this gap causes a reduction in the conductance peak by about 40% for a percentage strain of +10%, while for the other values of strain, the
conduction peaks are of nearly the same order of magnitude (see insets in the right corner of Fig. 4.8a). Enlarged plots of the I-V curves near the origin are depicted in the upper left insets.

Figure 4.9: Current-voltage and corresponding differential conductance curves (lower right insets) for the DNA molecule at Fermi energy $E_F = 6.5\text{eV}$ for selected strain percentages. (a) Stretching strain ($s_l = 0, 5,$ and 10) shows decreasing saturated current with strain. (b) Compression strain ($s_l = 0, -5,$ and -10) shows increasing saturated current with strain.

Figure 4.9 shows the DNA I-V curves at a lower Fermi energy, close to the left band edge of transmission spectra, $E_F = 6.5\text{ eV}$. At this Fermi level, due to a lack of close available states in the transmission spectrum, the DNA molecule acts as a
semiconductor with a voltage gap. As the percentage strain decreases and becomes negative, the voltage gap shows a decreasing trend, which is related to the transmission spectrum broadening. The differential conductance at this Fermi level has two main peaks (see insets of Fig. 4.9), which is generally consistent with results for conductance at negative strain and a Fermi level of 8.3 eV, although for $E_F = 6.5$ eV the magnitude of the differential conductance peaks are reduced by approximately by 50%.
Chapter 5:

Summary and Conclusions

This work has examined molecular electronics of ds-DNA molecules. At the first step (Chapter 2), we have investigated the electron transport characteristics through both symmetric and asymmetric ds-DNA molecules using an advanced TB model which includes the NNN effects. In this system, the main conduction arises along the four long axes of the DNA with the sugar-phosphate backbone. We have calculated the transmission, the current-voltage characteristics, and the differential conductance as a function of the electron energy and source-drain voltage with a variation of the contact coupling between the leads and the DNA molecule. We have found that by considering the NNN effects, higher overall transmission and therefore enhanced current could be obtained.
As contact hopping symmetry is changed to an asymmetric configuration, the current values are increased as a result of an asymmetric contact hopping configuration. We have also presented the influence of the Fermi energy on the current-voltage characteristics, which demonstrates the I-V characteristics transitioning from semiconductor to Ohmic behavior (with no current gap) for the Fermi energy values which give maximum current. The NNN effects induce maximum current at lower Fermi energies than without the diagonal electron hopping between the sites.

In Chapter 3, the helical DNA conformation was included in the updated TB model. We have calculated the transmission and the current-voltage characteristics as a function of the electron energy and source-drain voltage with a variation of the contact coupling between the leads and the DNA molecule and DNA tilt angle. We have found that by considering the NNN effects, higher overall transmission and therefore enhanced current could be obtained. Also, we have presented results showing that the electron transmission and subsequently the current flow are diminished by increasing the tilt angle.

Lastly in Chapter 4, the electronic behavior of DNA molecules under the influence of axial mechanical strain was studied. Electronic band structure of the infinite poly(G)-poly(C) ds-DNA model disclosed a strain-induced energy gap beyond +5% strain. Regardless of the molecule length, this gap is observable and shows linear growth with positive (stretching) strains. LDOS’s revealed a key role for the sugar-phosphate backbone sites on the overall DNA electronic properties. As
backbones have relatively small hopping integrals, the localization and
delocalization of the states over these sites are very critical. Results for the
backbone LDOS clearly show that most of the states are localized over backbone
sites during DNA stretching. In other words, the transmission probability is
decreased (increased) by the localization (delocalization) of the backbone states.
Interestingly, the same strain-induced energy gap is seen in the transmission
spectrum of the coupled finite poly(G)-poly(C) ds-DNA as appears in the band
structure of the infinite repeating chain of ds-DNA. Further analysis shows the
length-independent nature of this energy gap. In agreement with band structure
results, transmission spectral broadening for the DNA molecule is seen under
compressing. Although the current vs. voltage behavior of DNA for low bias shows
minimal disturbance under application of small mechanical strains (in agreement
with molecular dynamics results [10]), the difference in saturated current values is
remarkable. This physical picture can provide interpretation of the variety of
experimental results obtained for DNA conduction.
References


[41] T. Chakraborty, Charge Migration in DNA: Perspectives from Physics, Chemistry and Biology (Springer Verlag, New York, 2007), and references therein.


