Electron transmission probability and density of states of G4 DNA molecule in electric field

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Abstract. Electron density of states and transmission probability of G4 DNA molecule have been calculated. The calculation was carried out on G4 DNA consists of 32 G-quartets. G4 DNA molecule is represented mathematically by using Hamiltonian tight binding model and taking into account the electric field on electron hopping constants. The density of states and transmission probability as a function of energy is calculated using Green’s function method. The electric field applied parallel to the length of DNA leads to changes in electron hopping constants. The result shows that the increase in electric field causes electron density of states and transmission probability bands to shift.

1. Introduction

Charge transport on DNA molecules have attracted the attention of researchers [1] because it can be applied for molecular wires in nanotechnology applications [2,3] Charge transport along DNA molecule occurs through the overlap of π-π orbital on adjacent inter-pairs atoms [4,5]. Some variables, the environment and structure of DNA molecule itself, can affect the result of conductivity measurements on this molecule, that is DNA can act as insulator, semiconductor, and even superconductor [6,7].

Beside the canonical Watson-Crick model called the double-stranded DNA (ds-DNA), DNA molecule can be found or synthesized in other forms. One of these structures is G4-DNA called G-quadruplexes, which is formed by a planar arranged tetrad of G-bonded hydrogen base. DNA G4 has a longer size than ds-DNA, so that the charge transport on G4-DNA molecule occurs in a longer distance than on ds-DNA molecule [1]. In addition, the high G-nucleotide, known to have the lowest ionization potential among the nucleotides content makes this structure a highly promising candidate for future bottom-up nanoelectronic applications [8]. To this end, the understanding of charge transport on G4-DNA molecule becomes important.

In this study, we calculated transmission probability and density of states in G4 molecules under the influence of an applied electric field. This study is aimed to have an understanding on the effect of external electric field on DNA molecule, which will affect the charge transport process in it. This effect is rarely considered in the study of charge transport in DNA. The transmission probability and density of states are calculated using Green’s function method on G4-DNA molecule consisted of 32 stacks of guanine tetrads. Electric field affects the value of hopping electron constant on G4 DNA molecules based on Miller-Abrahams formula. The results show that both DOS and transmission probability spectra change with the voltage increment. The center of the bands, region with high values of DOS/transmission probability, in the spectra is shifted by the voltage.

2. Theoretical model

The arrangement of hydrogen bonds in G4-DNA molecule is different from the one on the Watson-Crick DNA. Each G base in tetrad G4 forms hydrogen bonds with neighboring two bases through Hoogsteen bonds [9]. The tetrad is stacked together in helix arrangement, with stack spacing and turning angles of 3.25 Å and 30 ° each, smaller than dsDNA. The figure of G4-DNA molecules can be
seen in the paper [9]. The Tight binding Hamiltonian model of single electron system on G4-DNA molecule can be stated as:

\[
H = \sum_{n=1}^{N} \sum_{\tau=1}^{4} \left\{ \epsilon_n^\tau |n, \tau) + \phi_n^\tau |n, \tau + t_{n,n+1}^\tau |n, \tau) (n + 1, \tau) \right\} + \sum_{q=u,d} \sum_{\tau=1}^{4} \left\{ B_{n,q}^\tau |n, \tau) (n, q) + t_{n,n+1}^\tau |n, \tau) (n, q) \right\} + \sum_{\tau=1}^{4} \left\{ t_{n,n+1}^\tau |n, \tau) (n, \tau + 1) + t_{n,n+1}^\tau |n, \tau) (n + 1, \tau + 1) \right\} + \text{h.c.} \tag{1}
\]

The parameters in equation (1) has been described in paper [10,11] External electric field is applied in direction of G4-DNA stack. Based on Miller-Abrahams [12,13], we wrote the electron hopping constant between two adjacent sites on G4-DNA molecule under the influence of electric field as follows:

\[
t_{n,n+1} = t_0 \exp \left( -eE \frac{Z(n+1) - Z(n)}{k_BT} \right), \tag{2}
\]

\[Z(n+1) - Z(n)\] is distance from site \(n+1\) to site \(n\), \(t_0\) is the value of electron hopping constant without electric field, \(t_{n,n+1}\) electron hopping constant affected by electric field from initial site \(n+1\) to final site \(n\). \(e\) is electron charge, \(k_B\) is Boltzmann constant, and \(T\) is temperature.

The retarded Green’s can be calculated from Hamiltonian of the system using

\[
G^r(E, \vec{k}) = [(E + i\eta)I - (\Sigma^r(\vec{k}) - \Sigma^a(\vec{k}))]^{-1}, \tag{3}
\]

where \(E\) is the electron energy, \(I\) is identity matrix, \(\eta\) is very small positive value close to zero, \(H(\vec{k})\) is Hamiltonian matrix of DNA molecule, \(\Sigma^r(\vec{k})\) is self-energy due to the contact of DNA molecules with left electrode and right electrode.

After obtaining the retarded Green’s function, DOS at each energy can be calculated using

\[
\text{DOS}(E) = -\frac{i}{\pi} \text{Im} [\text{Tr} G^r(E, \vec{k})]. \tag{4}
\]

Transmission probability is square of ratio between incoming and transmitted probability amplitudes. From retarded and advanced Green’s functions, \(G^a(E, \vec{k}) = [G^r(E, \vec{k})]^\dagger\), the transmission probability at each energy is calculated using Fisher-Lee relation [14]

\[
T(E, \vec{k}) = \text{Tr} [\Gamma^r L G^r(E, \vec{k}) \Gamma^a R G^a(E, \vec{k})], \tag{5}
\]

where \(\Gamma^r L\) represents the molecule coupling to electrode \(\Gamma^a L\) = \(i[\Sigma^r L - \Sigma^a L]\), index \(L\) for left electrode and \(R\) for right electrode.

3. Results and discussion

Density states as energy function on G4-DNA with 32 G-quartets has been calculated at temperature of 4.2 K and base twisting motion frequency of 4 meV for several voltages. The spectrum of DOS consists of energy region with nonzero DOS (band) and energy region with zero DOS (gaps). The bands represent energy region where the states can be occupied by electron in its way from an electrode to another electrode in the opposite end of DNA molecule. The states in the gap do not participate in the transport process since these states are forbidden for the electron. The density of states calculated in the presence of electric field with voltages of 0, 4.0 mV, 0.01 V, and 0.03 V are presented in figure 1. In the DOS spectrum there are two bands separated by a gap, except at voltage of 0.03 V. At zero voltage, the two bands are in the region of energy around 6.85 eV – 8.9 eV (band 1) and 9.45 eV – 9.8 eV (band 2) and the gap in the energy region around 8.9 eV – 9.45 eV. With voltage increment, the width of the bands becomes narrower and the center of the band is shifted. As a whole, the DOS spectrum becomes narrower and the gap becomes wider with the voltage. This occurs because the model used in this study guarantees that the electron hopping constants get smaller with the voltage. Other change is observed at voltage of 0.03 V, band 1 splits into two.
Figure 1. Electron density of states calculated at temperature 4.2 K and twisting motion frequency 4.00 meV for electric field of voltages 0, 4.0 mV, 0.01 V and 0.03 V.

The trend observed in the DOS spectrum is also observed in the transmission probability. The transmission probability is also calculated at temperature of 4.2 K and twisting motion frequency of 4 meV in the applied electric field of voltages 0, 4.0 mV, 0.01 V, and 0.03 V. Those transmission probabilities are presented in figure 2. Similar to the DOS case, at zero voltage transmission probability spectrum shows two regions with nonzero transmission probability (band) and a region with zero transmission probability (gap). Those features are reflection of electron density of states discussed before. The first band is shown in the energy range of around 6.85 eV – 8.9 eV (band 1) and the other around energy range of 9.45 eV – 9.8 eV (band 2). These two bands are separated by a gap in energy range of 8.9 eV – 9.45 eV. With the increase of electric field, the transmission probability spectrum becomes narrower and the width of the regions with nonzero transmission, in which the center band is shifted, also becomes narrower. However, the gap, energy region with zero transmission probability, widens. The gap at zero voltage already discussed in the previous section is the energy range in which the density of states is not affected by electric field. When electric field is increased the energy gap is widened and the energy band becomes narrow. Similar to the DOS spectrum, transmission probability spectrum at 0.03 V volt shows three bands, in energy range of 7.02 eV – 7.25 eV (band 1), 7.45 eV – 7.6 eV (band 2) and 9.45 eV – 9.65 eV (band 3), and two gaps, in energy range of 7.25 eV – 7.45 eV (gap 1) and 7.6 eV – 9.45 eV (gap 2). The increase of electric field causes the transmission probability spectrum to change, some states experience lesser transmission probability. The spectrum changes observed due to voltage increment indicates that lesser states with nonzero transmission probability are involved in the transport process. Nokhrin et al. [15] found 1 volt threshold voltage at distance of 5 nm decreases the conductivity of M-DNA by at least 10-fold.
Li et al. [12] measures the electrical character of transport hopping in organic semiconductors, in a very high electric field, an effective disruption of electron hopping so that causes a decrease in conductivity.

4. Conclusions
The effect of electric field increment on electron DOS and transmission probability of G4-DNA molecule have been studied. The electron DOS and transmission probability calculated at temperature 4.2 K and twisting motion frequency 4 meV showed the spectrum of DOS and transmission probability changes with the electric fields. The bands of nonzero DOS and transmission probability were shifted as the electric field increases. The effect of electric field on the molecule will affect the electron transport process across the molecule.

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