A study of the poly(dA)-poly(dT) DNA electric field-dependence: density of states (DOS) analysis

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Abstract. Study of poly(dA)-poly(dT) DNA molecule electronic structure, by analysing its density of states (DOS), had been conducted. This research employed Green’s function method as tool to determine electron DOS of the DNA numerically. Electric field that was applied along z-axis is used as perturbation to modify electron hopping constant between sites in the molecule. In order to include electric field in the calculation, Miller-Abraham formula was used. Medium interaction with backbone molecules was considered as well within the calculation in the form of backbone disorder. By increasing electric field, the band in electron DOS spectrum appeared to become narrower and several states experience the decrement of DOS.

1. Introduction
Deoxyribonucleic acid (DNA) is a polymeric bimolecule that can be expected to perform a role in molecular electronics [1]. Some of its quality, which could be beneficial in molecular electronics application, are natural memory storage and self-organizational feature [2]. Moreover, nanoscale fabrication of DNA molecules can be precisely controlled, so it can be very distinctive among other molecular system such as thin-film transistor (TFT) with silver (Ag) nanoparticle inks, terphenyl oligomers, azurin monolayers, etc. [3]. The promising potency of DNA as building block in molecular electronics is one of the main reasons to study the charge transport in DNA [4]. For artificial periodic DNA systems (poly(dA)-poly(dT), poly(dG)-poly(dC), guanin quadruplex, etc.), theoretical approach can be used to determine the energy band structure. It could be a helpful strarter to understand experimental results such as semiconductivity and metal-insulator transition [5].

Theoretical modeling of DNA conductivity is a meticulous and complex task because many factors can alter the charge propagation process, therefore DNA charge transport is defined as highly sensitive to environmental changes. This high sensitivity of charge propagation in DNA is owing to extrinsic (electric and magnetic field, temperature, medium or environment [6]) and intrinsic (collective base fluctuations caused by phonon [7], sequence variability [8]) influences.

Some observations in electric and magnetic influence in DNA have been done at cellular level, and it showed that the structure of DNA is modified due to physical factors like electric and magnetic field especially in ultraviolet (UV) region [9]. Experimental research by Chunda Zhou et al shows that when double-stranded DNA is placed in AC electrical fields at frequencies of a few hundred Hertz, it exhibits collapses of DNA. The effect is reposed on the limited relaxation times of the counterion cloud, and the next partitioning of the molecule into the common attractive units [10]. Electric field’s influence on DNA also has been modeled theoretically by Ceron-Carrasco and Jacquemin [11]. They have computed DNA system affected by fields in the range of 0 to 5 GV/m. The mutagenic mechanism of a single guanine–cytosine DNA base pair is activated by an intense electric field, and might affect its hydrogen bonds in a partially controlled way [11].

In this paper we have analysed the electric field influence on the electron density of states (DOS) of poly(dA)-(dT) DNA molecule model. We also used temperature influence that can lead to fluctuation in twist angle between neighboring base pairs or distance between bases in base pair (bp) [7]. It could
be treated as a collective phonon vibration excitation in molecule. We also considered the presence of sugar-phosphate backbone of DNA. The result in our previous work with different type of DNA bases (poly(dG)-poly(dC)) illustrates how electric field influence can decrease conductivity due to voltage increment, it takes place due the application of electric field decreases the base and backbone on-site energy value in the first half of molecule linearly and raises it in the last half [12]. For theoretical model used in this research, we will elaborate it in the next section. Then, the results of our calculation will be expressed in terms of density of states that will be represented in third section. Finally, the paper will be concluded in the final section.

2. Theoretical model
The system observed was a double stranded DNA (ds-DNA) molecule contacted by two leads on each end to give a potential difference in between. As stated in the first section, we used ds-DNA, which consist of adenine (A) and thymine (T) base pair. We assume electron could travel from base to nearest bases within different strand (interstrand hopping), within the same strand (intrastrand hopping) through π orbital overlap [13], and also its pair (Watson-Crick hopping) through hydrogen bond [14]. Electron also can hop from bases to the nearest backbone or vice versa, as well as between backbone (see ref [15]). Therefore, we picture our model as having four strands (backbone-base pair-backbone), and each base is defined as a site, likewise each backbone.

The tight binding Hamiltonian model is expressed by Rahmi and Yudiarsah [15]:

\[
H = \sum_{i=1}^{L} \sum_{\tau,\sigma=1}^{4} (\epsilon_i^{\tau} + \phi_i^{\tau})|i,\tau\rangle\langle i,\tau| + \tau_{i,i+1}^{\tau,\sigma} |i,\tau\rangle\langle i+1,\sigma| + h.c
\]  

(1)

Symbol \( i \) (sites), \( \tau \) (base strands), and \( \sigma \) (backbone strands) are for representing electron position in the molecule. The length of the molecule sequence (\( L \)) we used is 32 base pairs. Parameter \( \epsilon_i^{\tau} \) is base onsite energy in site \( i \) and strand \( \tau \) (8.22 eV for A and 9.06 eV for T). \( \phi_i^{\tau} \) represents the effect of thermal agitation in the form of twisting vibrational motion around bases equilibrium position. Twisting angle of base is randomly distributed by Gaussian distribution. Medium and temperature are also considered randomly distributing backbone on-site energy around 9.36 eV with deviation 0.1 eV. Parameter \( \tau_{i,i+1}^{\tau,\sigma} \) is electron hopping value between each site. We also included metallic electrodes and molecule-electrode coupling in our tight-binding equation. Onsite energy value for both metallic electrode at each end is 8.45 eV, while hopping constant in metallic electrodes and among molecule-electrode is taken to be 0.75 eV.

External electric field was applied along helix axis of the system as perturbation where, theoretically, it will alter electron hopping constant from site \( i \) to \( j \) in the molecule. Miller-Abraham formula was used to incorporate electric field influence into our tight binding equation [16]. So, the electron hopping constant from site \( j \) to \( i \) becomes:

\[
t_{ij} = \begin{cases} 
  t_0 \exp \left( \frac{qE}{\hbar k_B T} (z_i - z_j) \right) & \text{if } (z_i - z_j) < 0 \\
  t_0 & \text{otherwise}
\end{cases}
\]

(2)

where \( z_i \) is z coordinate of site \( i \), \( q \) is electron charge, \( E \) is electric field amplitude, \( \kappa \) is the DNA and medium dielectric constant and \( k_B T \) is thermal energy at temperature \( T \).

This research employed Green’s function method as tool to calculate electron DOS of the DNA, numerically. Medium interaction with backbone molecules is considered as well in the calculation in the form of backbone disorder. The DOS is calculated using the following formula:

\[
\text{DOS}(\epsilon) = -\frac{1}{\pi} \text{Tr} \left[ G(\epsilon, i\hbar) \right]
\]

(3)

Furthermore, the presence of metallic electrodes at both end of DNA molecule is taken into account in the calculation through the self-energy (\( \Sigma \)) of the electrode. Within wideband approximation the self-energy can be formulated as:

\[
\Sigma_{\sigma,\ell}^{\tau,\tau} = -\text{Im} \left[ \frac{1}{\pi} t_{\ell,\sigma}^{\tau,\tau} \right]
\]

(4)
3rd International Symposium on Current Progress in Functional Materials

IOP Conf. Series: Materials Science and Engineering 763 (2020) 012067   doi:10.1088/1757-899X/763/1/012067

Figure 1. Electron density of states of poly(dA)-poly(dT) DNA in voltage of 0 – 0.6 volt at 4.2 K

Figure 2. Electron density of states of poly(dA)-poly(dT) DNA in voltage of 0-3 volt at 4.2 K

3. Results and discussion

In this research, the system is treated as wet DNA system, where dielectric constant $\kappa$ for water medium and DNA is set to 80 in the calculation. The results of the calculations at temperature 4.2 K and twisting motion frequency 0.51 meV for several voltages are shown in figure 1 and figure 2. Both figures show that the electron density of states (DOS) in DNA poly(dA)-(dT) spectrum has three bands, regions of energy in which DOS appears to be not zero or not approaching zero. Those three bands are around 7.6–8.0 eV (band I); 8.75–9.25 eV (band II); and 9.4–10 eV (band III). This means that electron could pass through this region of energy while transporting from one electrode to another. The states in these three bands can participate in the electron transport process. Besides that, in figure 1 and figure 2, it can be seen two regions with very low DOS (almost zero) that are in region 8.0–8.65
eV (gap 1) and 9.25–9.40 eV (gap 2). Because DOS values are very low, the contribution of the state of these two regions are minute on the transport process, since electrons at zero voltage can not occupy DNA states in this energy region.

Electric field applied parallel to the helix axis of the poly(dA)-(dT) DNA could change the electron hopping constant which accordingly change its DOS. The change can be seen from figure 1, as we set the value of electric field higher from 0 to 0.6 V. By increasing the electric field the bands appear to be narrowing where the width of energy gaps seems slightly widen. Figure 1 also exhibits the change of DOS values with electric field increment, some states experience DOS increment while other state experiences DOS decrement. However, most states experience DOS decrement. It shows that within the model used in this study, the electric field disturbs the DNA molecule, which in contradiction with conventional assumption that the electric field only drop at molecule-electrode contact. These results reflect that charge trasport in DNA poly(dA)-(dT) will be affected by the presence of electric field on the molecule. In figure 2, we set the electric field even higher (0–3) V, and it shows more significant constriction in band energy than at the lower voltage. Consequently, the energy gaps look significantly wider, especially in the influence of 3 V electric field. It also shows that several energy in the gap becomes accessible for the electron, since its DOS increases with the voltages.

4. Conclusions

Electron density of states in DNA Poly(dA)-poly(dT) molecule under the influence of electric field along its symmetrical axis at temperature of 4.2 K and twisting motion frequency of 0.512 meV has been studied. Within the model used in this study, the electric field changes the states in the molecule in the sense that the DOS spectrum changes. The width of the bands is narrower accompanied by wider gap with the increase of voltages and many states experience lesser density of states. These phenomenon means that molecule charge transport is compromised by electric field.

Acknowledgements

We would like to thank Daniel K. Suhendro for giving us calculation parameters. We would also give our gratitude to CISCO Laboratory, Physics Department, Universitas Indonesia for letting us using their computational facility. This research is supported by Hibah PITTA Universitas Indonesia 2018 with contract number: 2259/UN2.R3.1/HKP.05.00/2018.

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