Modelling electric field influence on density of states (dos) and localization length of poly(da)-poly(dt) dna

F Rahmani and E Yudiarsah
1Department of Physics, FMIPA Universitas Indonesia, Depok 16424, Indonesia.
E-mail: e.yudiarsah@sci.ui.ac.id

Abstract. DNA based microelectronics technology have been developed in the last couple of years, but researchers found that its stability can be volatile to the change in its environment. In this research, electron transport in DNA poly(dA)-(dT) have been analysed by observing its density of states (DOS) and localization length. Retarded green function is used to calculate DOS, whereas transfer-matrix method is employed in calculating localization length in order to determine the electronic structure of the DNA. Along the z-axis of DNA electric field is applied, it will alter hopping constant between sites in DNA. Tight binding model is incorporated with Miller-Abraham expression to yield electric field and also temperature influence in DOS. Effect of medium is considered within the calculation. The results tell us that as the electric field increases, the value of DOS decreases, so that the localization length. The increment of temperature also shows similar trend.

1. Introduction
Charge transport properties in DNA molecule system has received interest in scientific community over the last two decades. The fact that there are similarity between the arrangement of $\pi$ orbital in DNA bases stacks and $\pi$ orbital in stacked metallic aromatic organic crystals, like Bechgaard salts [1], could motivate scientist to be assured of DNA conductive ability [2]. Barton et al. reported that charge transfer in DNA which is intercalated by transition metal complex is distance-independent [3]. The mechanism of charge transport in DNA can be explained by two major processes, that are superexchange and hopping mechanism, both have been verified experimentally [4]. Variety of results has been occured and studied extensively both theoritically and experimentally [5-9]. Ab initio calculations predict dry poly(dG)-poly(dC) DNA to be a wide-gap semiconductor [5], and it is in agreement with experimental result that show it has 2.0 V voltage gap under low temperature [6]. Experiment performed by Yoo et al. concludes that poly(dA)-poly(dT) could behave as an n-type semiconductor, while poly(dG)-poly(dC) has a p-type semiconductor characteristic [7]. This behaviour owing to base-pair-sequence-dependence of the observed molecule.

The environment impacts (i.e electric field [7], magnetic field [8], and temperature [9]) also play important role in altering DNA charge properties, due to its sensitivity. Research conducted by Wong et al indicates higher efficiency in magnetic field induced radical cation propagation which leads to more electron conductivity in DNA duplexes [8]. Phonon excitation in DNA due to temperature effect can be treated as base pair twisting and stretching modes, and it affected on its localization length decrement. This outcome caused by the widening of twist angle distribution width [9]. Electric field can also modify DNA charge transport process. Experimental research by Chunda Zhou et al shows
that when double-stranded DNA is conducted with AC electrical fields at frequencies of a few hundred Hertz, it exhibit breakage of the DNA conformation [10]. Study by Malyshev argue that perpendicular gating electric field could generate potential harmonic modulation on the base on-site energy along helical axis, so in consequence it leads to effective increase of transmission and voltage gaps [11]. Theoretical work by Li et al. reckon when electric field exists, it could transform hopping constant amplitude of an organic semiconductor [12], which in this study becomes a major influence of our DNA energy band calculation.

Numerical calculation in understanding qualitative properties of the poly(dA)-poly(dT) DNA in electric field influence has been done in this research. We studied its electron transport by examining electron density of states (DOS) and also localization length. Temperature effect is seen as collective phonon vibration excitation, wherein leads to fluctuation in twist angle and distance between base pair [9]. Miller-abraham formula is used in modelling the electric field influence on the molecule system [12]. Both incorporated into our Hamiltonian tight-binding expression [13]. In this work we account contribution of backbone disorder, watson-crick hopping constant amplitude, and homogeneous interelectrode field.

2. Theoretical Method

Periodic nucleotide chains consist of adenine (A) and its complementary base, thymine (T), is sandwiched between two electrodes to provide different potential in both ends. Charge can propagate along DNA base pairs and its backbone (sugar-phosphate). The pathway of charge propagation described as interstrand, intrastrand, and in addition we also consider in watson-crick pairs hopping. Electron charge also can hop from bases to the nearest backbone or vice versa, and the backbones are interconnected. Each base and each backbone is viewed as one site. Parameter $t_{i,j}^{\tau,\sigma}$ describes electron hopping between each site. Environment contact related effect is not considered in our calculation, since we treat our molecule as dry DNA system. The tight-binding Hamiltonian model is given by [13]

$$H = \sum_{i=1}^{L} \left[ \sum_{\tau,\sigma=1}^{4} (\epsilon_{i} + \phi_{i}) |i, \tau\rangle \langle i, \tau| + t_{i,i+1}^{\tau,\sigma} |i, \tau\rangle \langle i+1, \sigma| + t_{i,i}^{\tau,\sigma} |i, \tau\rangle \langle i, \sigma| + t_{i,i+1}^{\tau,\sigma} |i+1, \tau\rangle \langle i+1, \sigma| \right] + h.c$$

(1)

The length of the molecule is represented by $L$ (pairs). Electron position in molecule is represented by $i$ (sites), $\tau$ (base strands), and $\sigma$ (backbone strands) symbols. Onsite energy at each site in a particular strand is denoted as $\epsilon_{i}^{\tau}$ (8.22 eV for A, 9.06 eV for T, and 9.36 eV for backbone). Phonon vibration excitation is given by $\Omega_{i}^{\tau}$ parameter, namely twisting mode effect on the onsite energy, where it is assumed to decrease with twist angle increment. This parameter contains not only electron-phonon coupling, but also the change of twist angle of the $i$-th base in strand $\tau$ [9]. Helical structure of DNA is not neglected in this work and preserved in the form of relative twist angle between neighboring base pairs in equilibrium, and the value is constant for all base pairs (36°). Gaussian distribution is used to randomly distribute the twisting angle of bases on temperature with zero mean and standard deviation proportional to $\sqrt{\frac{T}{f}}$; temperature (T) used in this study are 30 K and 77 K. $f$ is proportional to the square of twisting frequency ($\omega$ ) [9]. Onsite energy value for both metallic electrode is 8.45 eV, while molecule-electrode hopping constant is 0.75 eV.

The molecule is influenced by gated electric field along its helix axis. This perturbation will modify electron hopping constant ($t$) from site $i$ to $j$ in molecule site, according to Miller-Abraham formula [14]. So, the electron hopping constant will become

$$t_{ij} = \begin{cases} t_{0} \exp \left( \frac{q^{2}E}{nk_{B}T} (z_{i} - z_{j}) \right) & \text{if } (z_{i} - z_{j}) \leq 0 \\ t_{0} & \text{otherwise} \end{cases}$$

(2)
where $z_i$ is $z$ coordinate of site $i$, $q$ is electron charge, $E$ is electric field amplitude which represented by voltage difference (V) across molecule, $\kappa$ is the DNA in medium dielectric constant and $k_BT$ is thermal energy at temperature $T$.

Transfer matrix method is employed to calculate localization length. However, this method will produce large number of matrices multiplication, where multiplication of exponentially small number with exponentially large number is inevitable. In consequence, there would be numerical error. To avoid this problem we use Gram-schmidt orthonormalization method to obtain coefficient value that is used to calculate Lyapunov exponents ($\delta$). Then the smallest value of $\delta$ is taken to yield localization length ($\lambda$) \cite{12}.

$$
\lambda = \frac{1}{\delta}
$$

DOS of the molecule will be generated numerically by Green’s function method. Furthermore, metallic electrodes at both end of DNA molecule is evaluated within calculation through the self-energy ($\Sigma$) matrices that will be substituted into DOS formula. The DOS formula is given by

$$
DOS(\varepsilon) = \frac{\pi}{\hbar} Tr [\mathcal{G}(\varepsilon, \vec{k})]
$$

3. Results and Discussion

![Figure 1.](image)

Figure 1. Electron localization length of poly(dA)-poly(dT) DNA in voltage of 0 – 3 volt, calculated at temperature of (a) 30 K and (b) 77 K

Equation (2) shows hopping constant amplitude $t_{i,j}^{\sigma}$ are modified by electric field, so that later will change electron energetic movement that have been incorporated into the tight-binding Hamiltonian used in this work. This change appears in Figure 1 and Figure 2 through the widening of band gap,
region in which DOS and localization length are almost zero, by the presence of electric field. We can also see the energy bands, where both aforementioned values are larger than zero, are narrowing. In Figure 1 the localization length do not show extended states, valued less than N (102 pairs), that being said electron can not reach the end of electrode. Work by Suhendro et al. argue if localized states emerge by disorder in backbone onsite energy together with thermal fluctuation, and it caused disorder in effective bases onsite energy, so that the difference between backbone onsite energy and bases onsite energy in few electronic energy states are quite minuscule to yield extended states [9]. The widening of band gap in Figure 1a imply that charge trasport in DNA poly(dA)-(dT) is compromised by the influence of electric field. A similar trend also occurs for DOS as seen in Figure 2a, where the peaks of energy band near gaps are degrading, in consequences it widen the band gaps. It interprets that within the framework used in this research, electric field disturbs the DNA molecule, defying the conventional assumption that electric field merely drop at molecule and electrode contact.

The electric field effect is visibly more prominent for 30 K temperature in either localization length (Figure 1a) or DOS (Figure 2a), but moment when temperature increase to 77 K (Figure 1b and 2b) the effect is no longer seen. From Figure 1 we can see that along with the increasing magnitude of temperature, localization length drops quite significantly. In high temperature standar deviation of twist angle distribution will be affected, and makes it wider. In accordance, it causes variation in both intrastrand and interstrand hopping amplitudes between sites, so it provide onsite energy disorder which hinder charge transport in the molecule [14].

![Figure 2](image_url)

Figure 2. Electron density of states of poly(dA)-poly(dT) DNA in voltage of 0 – 3 volt, calculated at temperature of (a) 30 K and (b) 77 K

Thermal energy transforms the onsite energy of bases that would obtain negative impact on molecule energy structure. Thermal fluctuation have primary effect in localization length decrement than electric field. This could be seen in Figure 1b where voltage increment makes insignificant
change to the localization length. As in DOS when the temperature is 77 K (Figure 2b) the earlier gap created by electric field now have been filled by several new states. This new states is analysed to be phonon excitation states which emerge by force of thermal energy. The electric field effect cannot also be seen affecting DOS in Figure 2b in terms of widening or narrowing band region. In addition, as the temperature rise up the DOS shows the molecule to be more disordered.

4. Conclusion

Theoritical work in calculating electric field influence on DOS and localization length of poly(dA)-poly(dT) DNA had been done. In 30 K temperature, higher electric field results in the widening of localization length and DOS band gap, but when the molecule is in 77 K the effect is no longer visible. The field effect occurs because electric field could modify hopping constant amplitude according to Miller-Abraham formula [12]. However, phonon excitation activated by thermal energy is more prominent than field effect.

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References

[1] Roth S R and David C 2015 One-Dimensional Metals: Conjugated Polymers, Organic Crystals, Carbon Nanotubes and Graphene (Germany: VCH Verlagsgesellschaft, Weinheim) pp 31-34
[2] Eley D D and Spivey D I 1962 Trans. Farad. Soc. 58 411–415
[3] Murphy C J, Arkin M R, Jenkins Y, Ghatlia N D, Bossmann S H, Turro N J, and Barton J K 1993 Science 262 1025–1029
[4] Jortner J, Bixon M, Langenbacher T, and Michel-Beyerle M E 1998 Proc. Natl. Acad. Sci. USA. 95 12759–12765
[5] Mertig M, Bixon M, Pompe W, and Engelhardt H 1999 Eur. Phys. J. D. 9 45-48
[6] Storm AJ, van Noort J, de Vries S, and Dekker C 2001 Appl. Phys. Lett. 79 3881
[7] Yoo K H, Ha D H, Lee J O, Park J W, Kim J, Kim J J, Lee H Y, Kawai T, and Choi H Y 2001 Phys. Rev. Lett. 87, 198102
[8] Wong J R, Lee K J, Shu J J, and Shao F 2015 Biochemistry 54, 3392–3399
[9] Suhendro D K, Yudiarsah E, and Saleh R 2010 Phys. B Cond. Matt. 405 4806-4811
[10] Zhou C, Reisner W W, Staunton R J, Ashan A, Austin R H, and Riehn R 2011 Phys. Rev. Lett. vol. 106 pp. 248103
[11] Malyshev A V 2007 Phys. Rev. Lett. 98 096801
[12] Ling L, Meller G, and Kosina H 2007 Microelec. Jour. 38 47–51
[13] Rahmi K A and Yudiarsah E 2016 AIP Conf. Proc. 1729 020037
[14] Yudiarsah E, Suhendro D K, and Saleh R 2014 AIP Conf. Proc. 1617 35–38