Modeling of the temperature and magnetic field dependence on the density of states of G4-DNA molecules

IOP Conf. Series: Materials Science and Engineering **496** (2019) 012016 doi:10.1088/1757-899X/496/1/012016

Modeling of the temperature and magnetic field dependence on the density of states of G4-DNA molecules

R Rahman and E Yudiarsah

Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA) Universitas Indonesia, Depok 16424, Indonesia

Corresponding author: e.yudiarsah@sci.ui.ac.id

Abstract. In this article, we investigate the charge-transport properties of G4-DNA molecules that are 32 base pairs long using the tight-binding Hamiltonian and Green function in numerical calculations. The transport properties are studied by calculating the density of states (DOS) of the G4-DNA model under the influence of various external magnetic field strengths and temperatures. We found that a shift in phase coherence lowers the DOS as the magnetic field increases. At zero temperature, the DOS spectrum is split into two bands of electron energies with a specific gap of zero values between them. Increasing the temperature decreases the DOS at all electron energies and narrows the energy gap in the DOS spectra when the frequency of the molecule's twisting motion is 0.77 meV.

Keywords: G4-DNA, magnetic field, temperature, DOS

1. Introduction

Nanotechnology can be used to improve the performance of electronic devices [1]. Biomolecular electronics are a promising application of nanotechnology, including the study of future electronic devices based on DNA molecules. DNA molecules can self-assemble into coherent structures, and they conduct electrical current, so that DNA and other chains of nucleic acids can form relatively large molecules for use in electronic devices in a bottom-up fashion. Nanowire structures, for instance, can be fabricated from chains of nucleic acids [2]. Interbase π–π coupling interactions mediate the charge-transport process in DNA molecules [3].

In addition to the standard double-stranded DNA (dsDNA) molecule that consists of adenine (A), cytosine (C), guanine (G), and thymine (T) bases, DNA chains can also be constructed by a variety of guanine-rich structures, such as guanine quadruplex (G4) structures that stack to form G4-DNA molecules [4]. The G4 structure consists of four G bases that are arranged in a square. G4 structures are stacked with separation of about 3.25 Å and are twisted with respect to the stack's symmetrical axis such that two adjacent G4 structures form an angle of about 30° [4]. A procedure for fabricating G4-DNA nanowires from poly(dG)-*n*(dC) was proposed by Borovok *et al.* [5]. The charge-transport capabilities of these G4-DNA nanowires open the possibility of using G4-DNA nanowires in electronic devices [5,6]. The four strands of a G4-DNA molecule allow more charge transport than the double strands of a dsDNA molecule do [7,8]. The counter ions present in a G4-DNA molecule, such as K^+, Na^+, and Mg^{2+}, offer stability in the π stack, which also improves the electronic properties of the structure [9,10].

In this study, we modeled G4-DNA molecules in order to study the molecule's charge-transport properties in the presence of varying applied magnetic field strengths and temperatures. The model system's charge-transport properties are modeled in terms of the density of states (DOS) at each electron energy, calculated using Green's function.

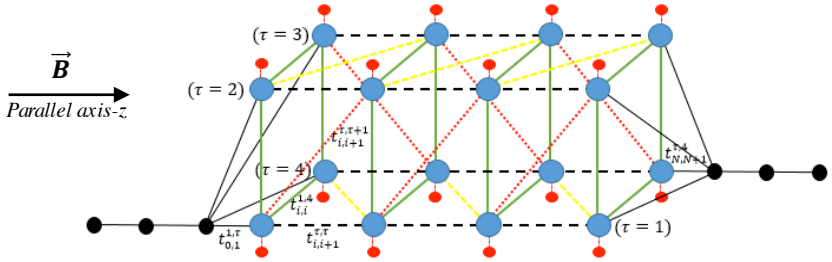

Figure 1: A schematic diagram of the G4-DNA molecule. The blue and red colors represent the guanine bases and the backbone, respectively. The black color represents the electrodes at the ends of the molecule.

2. Theoretical model

We used the tight-binding approach for numerical calculations. The DOS is calculated using Green's function. The charge transport that occurs within the molecule can be modeled using the tight-binding Hamiltonian. The tight-binding Hamiltonian of G4-DNA as depicted in figure 1, can be given by the following equation:

$$\begin{aligned} H_{\mathrm{DNA}} = \sum_{i=1}^{L}\Big[& \sum_{\tau=1}^{4}\left\{\left(\varepsilon_i^{\tau}+\varphi_i^{\tau}\right)\left|i,\tau\right\rangle\left\langle i,\tau\right| + t_{i,i+1}^{\tau,\tau}\left|i,\tau\right\rangle\left\langle i+1,\tau\right|\right\} \\ & + \sum_{\tau=1}^{4}\left\{B_i^{\tau,q}\left|i,\tau\right\rangle\left\langle i,q\right| + t_{i,i}^{\tau,q}\left|i,\tau\right\rangle\left\langle i,q\right|\right\} \\ & + \sum_{\tau=1}^{4}\left\{t_{i,i}^{\tau,\tau+1}\left|i,\tau\right\rangle\left\langle i,\tau+1\right| + t_{i,i+1}^{\tau,\tau+1}\left|i,\tau\right\rangle\left\langle i+1,\tau+1\right|\right\}\Big] + h.c. \end{aligned} \tag{1}$$

In equation (1), *h.c.* stands for Hermitian conjugate. The applied magnetic field induces a phase change in the electronic state, which affects the electron-hopping constant t_{ij} [11]. The electron-hopping constant can be calculated as a function of the applied magnetic field using the Peierls phase factor [12]. If B ≠ 0, the electron-hopping constant is given by the following equation:

$$t_{ij} = t_0 \exp\left(-i\frac{e}{h}\int_i^j \vec{A}.d\vec{l}\right). \tag{2}$$

In equation (2), t_0 is the electron-hopping constant when the magnetic field is zero, $\vec{A}$ is the vector potential, and $d\vec{l}$ is the electron displacement.

The DOS of the system in an external magnetic field can be calculated using the following equation:

$$\mathrm{DOS}(\varepsilon) = -\frac{1}{\pi}\sum_{\vec{k}} \mathrm{Im}\,\mathrm{Tr}\left[G^R(\vec{k},\varepsilon)\right], \tag{3}$$

where Im indicates that the imaginary part of the trace (Tr) of the Green function matrix $G^R(\vec{k},\varepsilon)$ is summed. The Green function matrix is given by the following equation:

$$\left[G^R(\vec{k})\right] = \left[\left(\varepsilon(\vec{k})+i\eta\right)[I] - H_{\mathrm{DNA}} - \Sigma_l^R - \Sigma_r^R\right]^{-1}, \tag{4}$$

where $\varepsilon(\vec{k})$, η, H_{DNA}, and Σ_l^R denote the electron energy as a function of the wave vector $\vec{k}$, an infinitesimal number, the Hamiltonian of the DNA molecule, and the retarded self-energy of the electrode, respectively.

The influence of temperature generates a phonon activity that changes the values of guanine-base on-sites and the electron-hopping constant. The effect of environmental temperature on the electron-hopping constant is modeled as in reference [3] by considering that the twisting angles of the bases follow a Gaussian distribution with zero mean and standard deviation $\sqrt{T/f}$, where T is the temperature and f is a parameter that depends on the twisting frequency of the bases.

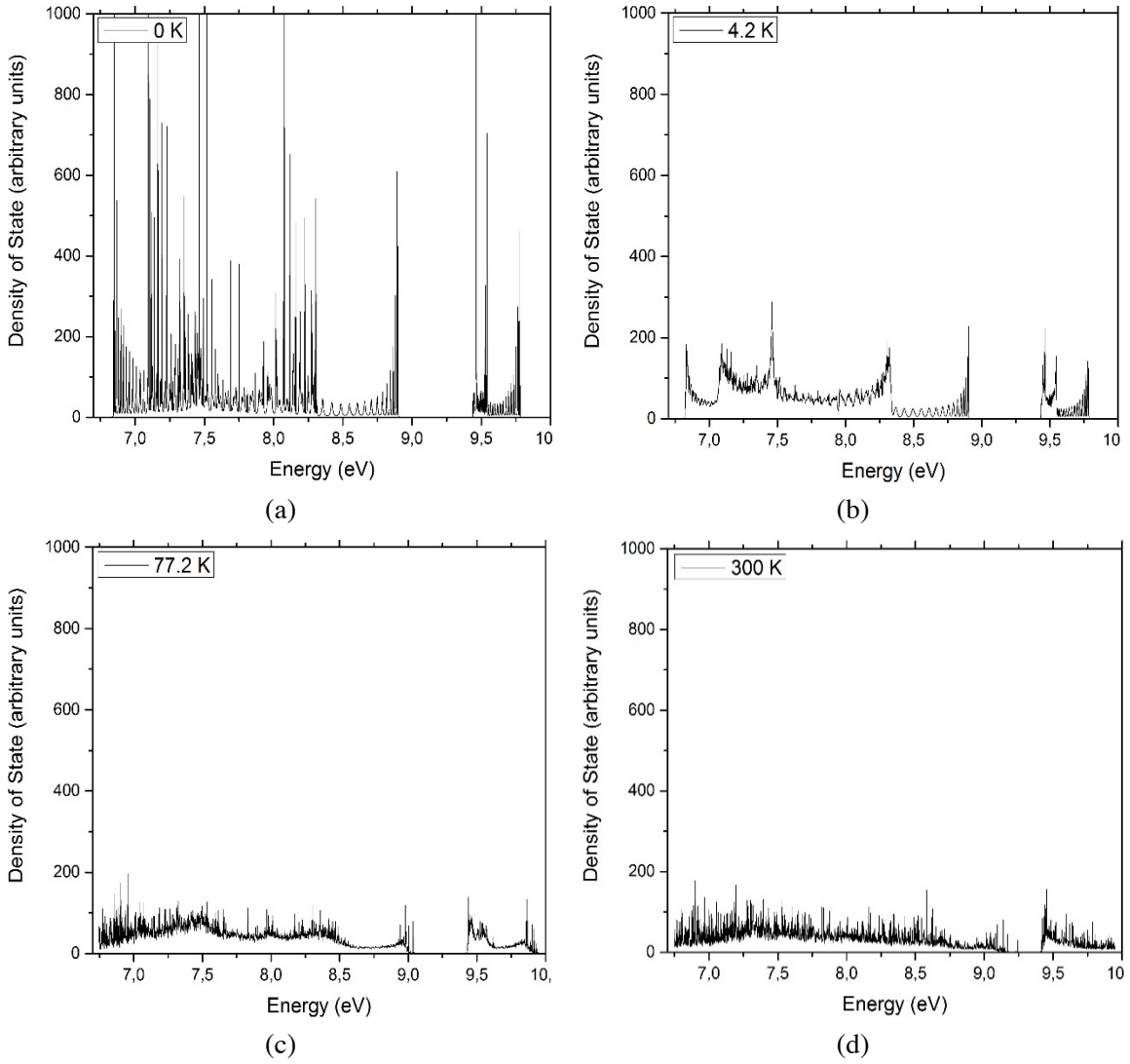

Figure 2. DOS as a function of electron energy under temperatures of (a) 0 K, (b) 4.2 K, (c) 77.2 K, and (d) 300 K for ω=*0.77* meV.

3. Results and discussion

The simulated DOS values are plotted for a range of temperatures and magnetic field strengths in figure 2 and figure 3, respectively. Figure 2 plots the DOS of the G4-DNA molecule against electron energy under temperatures in the range 0–300 K with a twisting frequency of f = 0.77 meV and B = 0 T. Temperature destabilizes the molecules, leading to thermal fluctuations that are expressed as phonons. In figure 2, two bands of nonzero DOS values appear across the spectrum of electron energy with an energy gap between them. At 0 K, the DOS is very high for all electron energies, and the DOS spectrum is not affected by the frequency of the twisting motion, since the standard of deviation $\sqrt{T/f}$ is zero if temperature is zero. A temperature of 300 K at f = 0.77 meV causes the electron-occupation state to change and generates many new phonon-induced states in the charge-transport process. As a result, the DOS decreases in certain energy ranges and the energy bands become irregularly shaped. The DOS energy bands also tend to widen, causing the energy gap to shrink. This result is consistent with the findings of Joe *et al.* [11] and Suhendro *et al.* [13] that nonzero temperatures tend to decrease the charge-transport capability of DNA molecules.

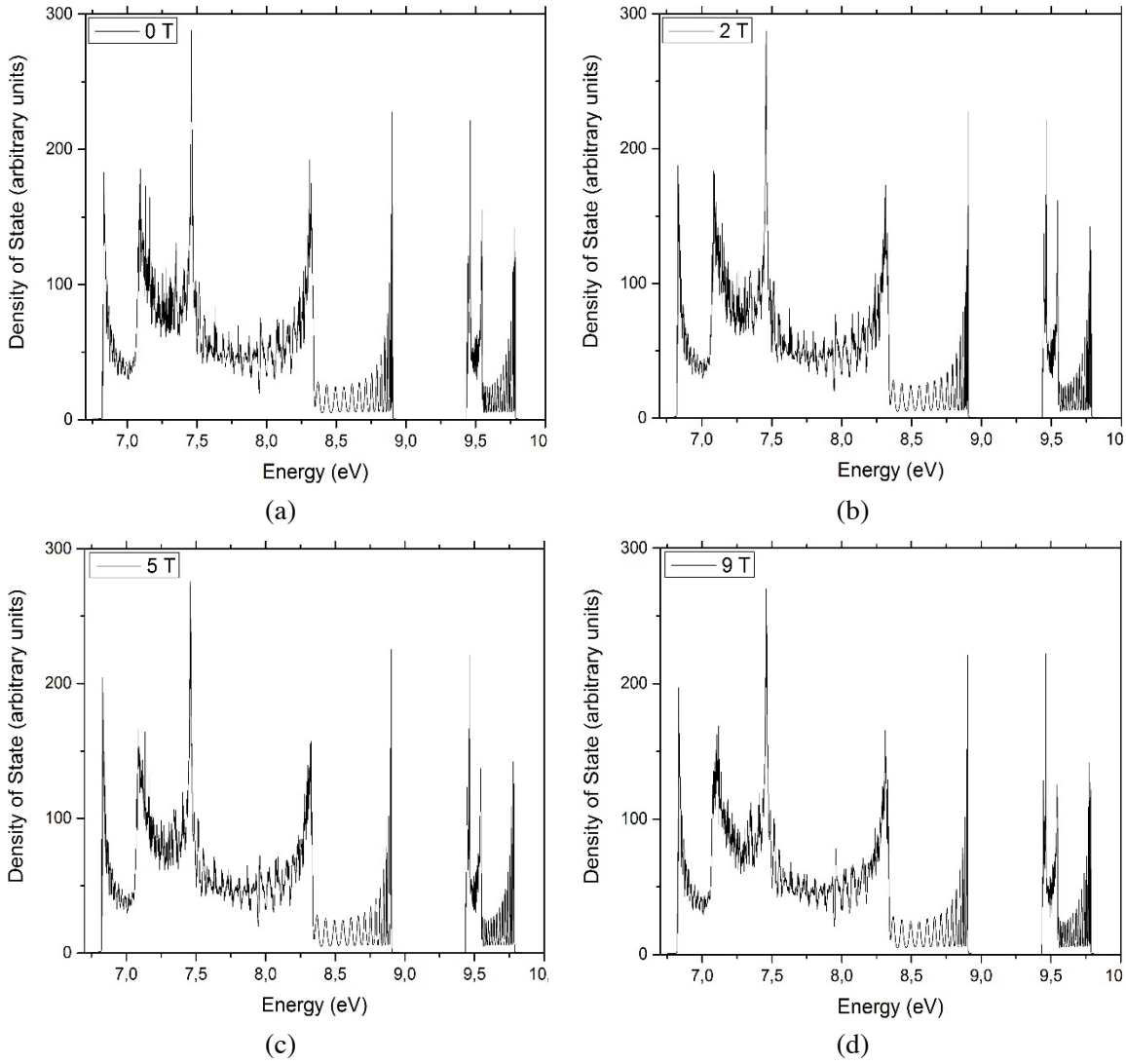

Figure 3. DOS as a function of electron energy in an applied magnetic field of (a) 0 T, (b) 2 T, (c) 5 T, and (d) 9 T for $T=4.2$ K with f=0.77 meV.

Next, a magnetic field is applied along the axis marked in figure 1. The applied magnetic field affects the physical properties of the system, leading to a shift in the phase coherence of the molecule [11,14]. Figure 3 shows plots of the calculated DOS as a function of electron energy with the applied magnetic fields varying from 0 to 9 T at a temperature of 4.2 K and f = 0.77 meV. A change in the electron state over the whole electron energy range corresponds to a strong applied magnetic field. The magnetic field shifts the electronic interference depending on the coupling configuration of the G4-DNA molecule. These results agree with those of Kang *et al.* [9], who found that an applied magnetic field changes the electronic state in a G4-DNA molecule.

4. Conclusions

The tight-binding Hamiltonian was used to model the influences of temperature and external magnetic field on a G4-DNA molecule. High temperatures deteriorate the electron state and create a new state occupied by phonons with irregularly shaped energy bands. This replacement tends to widen the energy bands, shrinking the gap energy for 0.77 meV. An external magnetic field affects the DOS by

causing a shift in phase coherence that changes the molecule's electronic state over the whole energy range that we tested.

Acknowledgements
This research was funded by PITTA Grant year of 2017 with the following contract number 649/U2.R3.1/HKP.05.00/2017. The authors wishing to thank Lab Cisco Department of Physics, FMIPA Universitas Indonesia for allowing the usage of the laboratory and Einago (www.einago.com) for the English language reviews.

References
[1] Wang F, Willner B and Willner I 2013 *Curr. Opin. Biotechnol.* **24** 562–74
[2] Endo M and Sugiyama H 2009 *Chembiochem.* **10**, 2420–43
[3] Endres R G, Cox D L and Singh R R 2004 *Rev. Mod. Phys.* **76** 195–214
[4] Guo A M and Xiong S J 2009 *Phys. Rev. B* **80** 035115
[5] Borovok N, Molotsky T, Ghabboun J, Porath D and Kotlyar A 2008 *Anal. Biochem.* **374** 71–8
[6] Zhang Y Q, Zhang W B, Liu C R, Zhang P, Balaeff A and Beratan D N 2016 *Surf. Sci.* **652** 33–8
[7] Calzolari A, Di Felice R, Molinari E and Garbesi A 2002 *Appl. Phys. Lett.* **80** 3331-3
[8] Woiczikowski P B, Kubař T, Gutiérrez R, Cuniberti G and Elstner M 2010 *J. Chem. Phys.* **133** 035103
[9] Kang D W, Sun M L, Zuo Z W, Wang H X, Lv S J, Li X Z and Li L B 2016 *Phys. Lett. A* **380** 977–82
[10] Guo A M, Yang Z, Zhu H J and Xiong S J 2010 *J. Phys. Condens. Matter* **22** 065102
[11] Joe Y S, Lee S H, Hedin E R and Kim Y D 2013 *J. Nanosci. Nanotechnol.* **13** 3889–96
[12] Peierls R 1933 *Z. Phys. A* **80** 763–91
[13] Suhendro D K, Yudiarsah E and Saleh R 2010 *Physica B* **405** 4806–11
[14] Kang D, Jiang H, Sun Z, Qu Z and Xie S 2011 *J. Phys. Condens. Matter* **23** 55302