

# Localization Properties of Electronic States in Polaron Model of poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers

Hiroaki Yamada\*

Aoyama 5-7-14-205, Niigata 950-2002, Japan

Eugen B. Starikov†

Karolinska Institute, Center for Structural Biochemistry NOVUM, S - 14157 Huddinge, Sweden

Dirk Hennig‡

Freie Universität Berlin, Fachbereich Physik, Institut für Theoretische Physik, Arnimallee 14, 14195 Berlin, Germany

Juan F.R. Archilla§

Group of Nonlinear Physics, Departamento de Física Aplicada I, ETSI Informática, University of Sevilla, Avda Reina Mercedes s/n, 41012 - Sevilla, Spain

(Dated: November 23, 2013)

We numerically investigate localization properties of electronic states in a static model of poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers with realistic parameters obtained by quantum-chemical calculation. The randomness in the on-site energies caused by the electron-phonon coupling are completely correlated to the off-diagonal parts. In the single electron model, the effect of the hydrogen-bond stretchings, the twist angles between the base pairs and the finite system size effects on the energy dependence of the localization length and on the Lyapunov exponent are given. The localization length is reduced by the influence of the fluctuations in the hydrogen bond stretchings. It is also shown that the helical twist angle affects the localization length in the poly(dG)-poly(dC) DNA polymer more strongly than in the poly(dA)-poly(dT) one. Furthermore, we show resonance structures in the energy dependence of the localization length when the system size is relatively small.

PACS numbers: 87.15.-v, 63.20.Kr, 63.20.Ry

## I. INTRODUCTION

The recent development of the nanoscale fabrication let us expect the utilization of the DNA wire as a molecular device [1, 2] and the realization of DNA computing [3]. DNA is believed to form an effectively one-dimensional molecular wire, which is highly promising for diverse applications. Actually, the modern development of physico-chemical experimental techniques enables us to measure directly DNA electrical transport phenomena even in single molecules [2, 4]. Moreover, several groups have recently performed numerical investigations of localization properties of DNA electronic states based on realistic DNA sequences [5, 6, 7].

However, DNA transport properties still remain a controversial topic, mainly due to tremendous difficulties in setting up the proper experimental environment and the complexity of the molecule itself. Specifically, a distinctive feature of biological polymers is the complicated composition of their elementary subunits, and an apparent ability of their structures to support long-living non-

linear excitations. Although a number of theoretical explanations for DNA charge transfer/transport phenomena have been suggested on the basis of standard solid-state-physical approaches, like polarons, solitons, electrons or holes [1, 8, 9, 10, 11, 12, 13, 14, 15], the situation is still far from working out a unique, non-contradictory theoretical scheme.

In their polaron-like model, Hennig and coworkers studied electron breather propagation along DNA homopolynucleotide duplexes, i.e. in both poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers [8], and, for this purpose, estimated electron-vibration coupling strength in DNA using semiempirical quantum-chemistry [16, 17]. Chang *et al.* have also considered a possible mechanism to explain the phenomena of DNA charge transfer [9]. The charge coupling with DNA structural deformations can create a polaron and thus promote a localized state [9, 10]. As a result, the moving electron breather may contribute to highly efficient long-range conductivity. Recent experiments seem to support the polaron mechanism for the electronic transport in DNA polymers [18].

In the present paper, we investigate localization properties of electronic states in a stochastic bond vibration model of poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers by adopting the model by Hennig *et al.* [8]. Here we assume that the disorder is caused by DNA vibrational modes, and via electron-vibrational coupling

\*Electronic address: hyamada@uranus.dti.ne.jp.

†Electronic address: starikow@chemie.fu-berlin.de

‡Electronic address: hennigd@12move.de

§Electronic address: archilla@us.es

it influences the charge transfer/transport along DNA duplexes. Moreover, we discuss the difference in charge localization properties between poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers, as well as the peculiarities of the mixed (AT/GC) model.

The outline of the present paper is as follows. In the next section we introduce the DNA model to investigate subsequently the electronic states and their coupling to DNA vibrational modes. In the Sec. 3 we present numerical results concerning the influence of changes of the hydrogen-bond stretchings and twist angles as well as the effects of finite system size on the localization properties. The last section contains a summary and discussion.

## II. MODEL

This section reformulates the model Hamiltonian for DNA duplexes, as introduced by Hennig *et al.* [8] into a one-electron tight-binding adiabatic Hamiltonian with structural disorder, taking into account a nearest-neighbor electron hopping term. The latter model is actually akin to that proposed earlier by Dunlap-Kundu-Philips (DKP). Specifically, the general DKP model contains disorder induced by the proper vibrational modes, which shows up in both the diagonal and the off-diagonal parts of the electron Hamiltonian [19]. Generally, in the DKP model the transport can arise from a set of measure-zero unscattered states at a particular energy derived from the resonant transmission formula [19, 20], and the number of the unscattered states can be estimated by the resonance width in the system size.

The Hamiltonian for the electronic part in our DNA model is given by

$$H_{el} = \sum_n E_n C_n^\dagger C_n - \sum_n V_{nn+1} (C_n^\dagger C_{n+1} + C_{n+1} C_n^\dagger), \quad (1)$$

where  $C_n$  and  $C_n^\dagger$  are creation and annihilation operators of an electron at the site  $n$ . The on-site energies  $E_n$  are represented as

$$E_n = E_0 + kr_n, \quad (2)$$

where  $E_0$  is a constant and  $r_n$  denotes the fluctuation caused by the coupling with the transversal Watson-Crick H-bonding stretching vibration.

The transfer integral  $V_{nn+1}$  depends on the three-dimensional stacking-distance  $d_{nn+1}$  between adjacent bases labeled by  $n$  and  $n+1$ , along each strand and is given as,

$$V_{nn+1} = V_0(1 - \alpha d_{nn+1}). \quad (3)$$

The parameters  $k$  and  $\alpha$ , which describe the strength of the interaction between the electronic and spatial variable, have been previously calculated through quantum-chemical methods. Radial displacements bring about

also a variation of the distances between neighboring bases along each strand  $d_{nn+1}$ . The first-order Taylor expansion around the equilibrium positions is given by

$$d_{nn+1} = \frac{R_0}{\ell_0} (1 - \cos \theta_0) (r_n + r_{n+1}). \quad (4)$$

$R_0$  represents the equilibrium radius of the helix,  $\theta_0$  is the equilibrium twist angle between base pairs, and  $\ell_0$  the equilibrium distance between bases along a strand given by

$$\ell_0 = (a^2 + 4R_0^2 \sin^2(\theta_0/2))^{1/2}, \quad (5)$$

with  $a$  being the distance between neighboring base pairs in the direction of the helix axis. A sketch of the geometrical parameters  $R_0, \ell_0, \theta_0, r_{n+1}$  and  $d_{nn+1}$  is given in Fig.1.

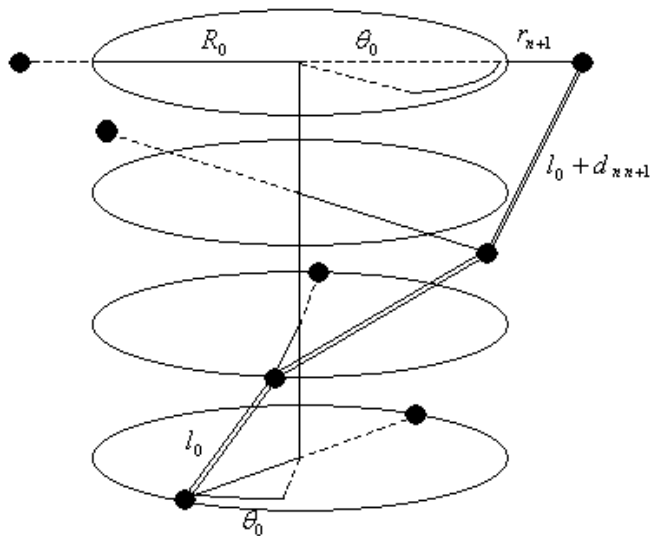


FIG. 1: Sketch of the structure of the DNA model. The bases are represented by bullets and the geometrical parameters  $R_0, \ell_0, \theta_0, r_{n+1}$  and  $d_{nn+1}$  are indicated.

We adopt realistic values of the parameters obtained from the semi-empirical quantum-chemical calculations;  $k = 0.778917[eV\text{\AA}^{-1}]$ ,  $\alpha = 0.053835[\text{\AA}^{-1}]$  for the coupling parameters of the poly(dA)-poly(dT) DNA polymer,  $k = -0.090325[eV\text{\AA}^{-1}]$ ,  $\alpha = 0.383333[\text{\AA}^{-1}]$  for the ones of the poly(dA)-poly(dT) DNA polymer. As to the other typical parameters for DNA molecules, we use:  $E_0 = 0.1[eV]$ ,  $V_0 = 0.1[eV]$ ,  $a = 3.4[\text{\AA}]$ ,  $R_0 = 10[\text{\AA}]$  and  $\theta_0 = 36^\circ$ .

Further, we consider  $\{r_n\}$  as independent random variables generated by uniform distribution with width ( $r_n \in [-W, W]$ ). Accordingly, fluctuations in both the on-site energies and the off-diagonal parts in the Hamiltonian (1) are mutually correlated because they are generated by the same random sequence  $r_n$ . (See Fig.2(c).) The typical value for  $W$  is  $W = 0.1[\text{\AA}]$ , which approximately corresponds to the variance in the hydrogen bond lengths

in Watson-Crick base pairs, as seen in X-ray diffraction experiments [21].

Figures 2(a) and (b) show a typical fluctuation pattern of  $E_n$  and  $V_{nn+1}$  for  $W = 0.1$  in poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers. Although the fluctuation of the on-site energy is almost of the same order in both poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers, the fluctuation of the transfer integral  $V_{nn+1}$  in the poly(dG)-poly(dC) DNA polymers is much larger than that of the poly(dA)-poly(dT) DNA polymers. This property ought to reflect the difference in the electron localization nature between poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers. We can see the correlation between the sequences,  $E_n$ ,  $V_{nn+1}$ , in the parametric plots in Fig.2(c).

In addition to the DNA homopolymer duplexes, we investigate the localization nature of the mixed sequence consisting of two types of the Watson-Crick pairs. Then, as a zero-order approximation, the electron-phonon coupling parameters for the mixed GC/AT stacks are taken here to be equal to the values obtained for poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers.

### III. NUMERICAL RESULTS

The Schrödinger equation  $H_{el}|\Phi\rangle = E|\Phi\rangle$  is written in the transfer matrix form,

$$\begin{pmatrix} a_{n+1} \\ a_n \end{pmatrix} = \begin{pmatrix} \frac{E - E_n}{V_{nn+1}} & -\frac{V_{nn-1}}{V_{nn+1}} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a_n \\ a_{n-1} \end{pmatrix}, \quad (6)$$

where  $a_n$  is the amplitude of the electronic wavefunction  $|\Phi\rangle = \sum_n a_n |n\rangle$  at the base pair site  $n$ . We use the localization length  $\xi$  and/or Lyapunov exponent  $\gamma$  calculated by the mapping (6) in order to characterize the exponential localization of the wave function. Originally the Lyapunov exponent (inverse localization length) is defined in the thermodynamic limit ( $N \rightarrow \infty$ ), however, in the present paper we use the following definition for the Lyapunov exponents of the electronic wave function for a large system size  $N$  [22, 23].

$$\gamma(E, N) = \xi^{-1}(E, N) = \frac{\ln(|a_N|^2 + |a_{N-1}|^2)}{2N}. \quad (7)$$

We use appropriate initial conditions  $a_0 = a_1 = 1$ , and for large  $N$  ( $\gg \xi$ ) the localization length and Lyapunov exponent are independent of the boundary condition. The system size dependence of the localization length is investigated in Subsect.3.3 in the relation with the resonance energy. The energy-dependent transmission coefficient  $T(E, N)$  of the system between metallic electrodes is given as  $T(E, N) = \exp(-2\gamma N)$  and is related to Landauer resistance via  $\varrho = (1-T)/T$  in unit of the quantum resistance  $h/2e^2$  ( $\sim 13[k\Omega m]$ ) [24].

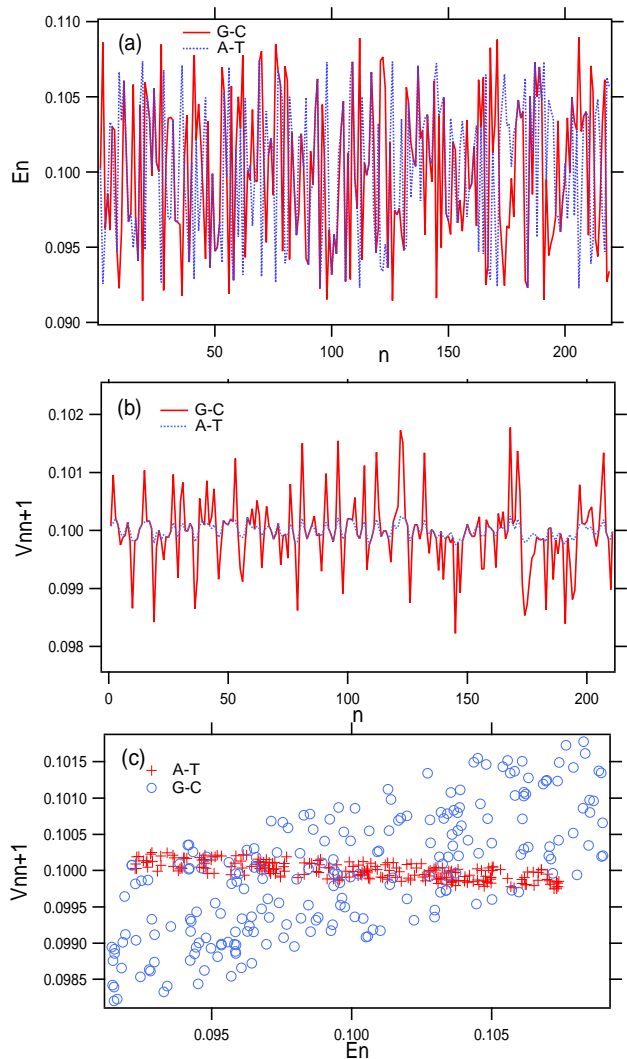


FIG. 2: (a) The on-site energy  $E_n$  [eV] and (b) transfer integral  $V_{nn+1}$  [eV] as a function of the base pair site  $n$ . The parametric plot  $E_n$  versus  $V_{nn+1}$  is shown in (c).  $W = 0.1$  and the other parameters are given in text. The unit of the energy and the spatial length are [eV] and the number of nucleotide base pair [ $bp$ ], respectively, throughout the present paper.

#### A. Fluctuation effect of stretching

Figure 3(a) shows the dependence of the localization length  $\xi$  on the energy for the cases of  $W = 0.1, 0.2, 0.4$  in the poly(dA)-poly(dT) DNA polymer. For the computation of the energy dependence of the localization length we used a energy subdivision of 800 points in the energy range. The extent of the localization depends on the Fermi energy of the electrodes when we measure the transmission coefficient or conductance. It is apparent that the localization length is reduced as a result of the increase of the fluctuation strength  $W$  of the hydrogen bond stretching. The small peaks for the resonance energy are suppressed in  $W \geq 0.2$  due to the large fluctua-

tion in the  $r_n$ .

Figure 3(b) and (c) show the localization length as a function of the energy in the case of poly(dG)-poly(dC) and the mixed DNA polymers, respectively. In Fig.3(b) the global behavior is almost the same as that illustrated in Fig.3(a) except for the shape of the energy dependence. The localization length in the poly(dA)-poly(dT) DNA polymer is globally larger than the one in poly(dG)-poly(dC) DNA polymer. The reason is simply because the fluctuation strength of  $V_{nn+1}$  in poly(dG)-poly(dC) DNA polymers is larger than the one in poly(dA)-poly(dT) DNA polymers as seen in Fig.2.

In the mixed case, the localization length in the mixed sequence shows the intermediate behavior between the poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers. The resonance peak structure in the energy dependence of the localization length is not as pronounced as in the case of poly(dA)-poly(dT) and poly(dG)-poly(dC) DNA polymers.

As a result, more disorder in the H-bond stretching (higher  $W$  values) renders the peak structure in the electronic states to disappear and makes the latter more localized. The finite system effect will be discussed in Subsect.3.3.

## B. Twist angle effect

In this subsection, we investigate how the localization length depends on the helical twist angle  $\theta_0$  of the DNA double helix. It is known that the allowed values of the angle range from ca.  $27^\circ$  till  $45^\circ$ .

Figure 4 shows the energy dependence of the localization length for some twist angles in the DNA models. We conclude, that in poly(dA)-poly(dT) polymers the change of the angle does virtually not affect the localization length, however, in the poly(dG)-poly(dC) polymer it does have an impact. The difference is caused by the  $\theta_0$  dependence of the fluctuation of the transfer energy  $V_{nn+1}$  which is smaller in the case of the poly(dG)-poly(dC) polymer than in its poly(dA)-poly(dT) counterpart as seen in Fig.2(b).

It follows that when the twist angle increases in the poly(dG)-poly(dC) DNA polymer the localization length becomes smaller (larger) in the low (high) energy region.

## C. System size effect on the resonance

Figure 5 shows the system size dependence of the localization length in the poly(dG)-poly(dC) polymer and the poly(dA)-poly(dT) polymer. Although the states for most of energies are exponentially localized, and have well-pronounced resonant maxima at discrete points correspond to the eigenenergies of each system when the system size is relatively small ( $N = 2^{16}$ ). Electronic states whose energy is close to resonance peaks have a

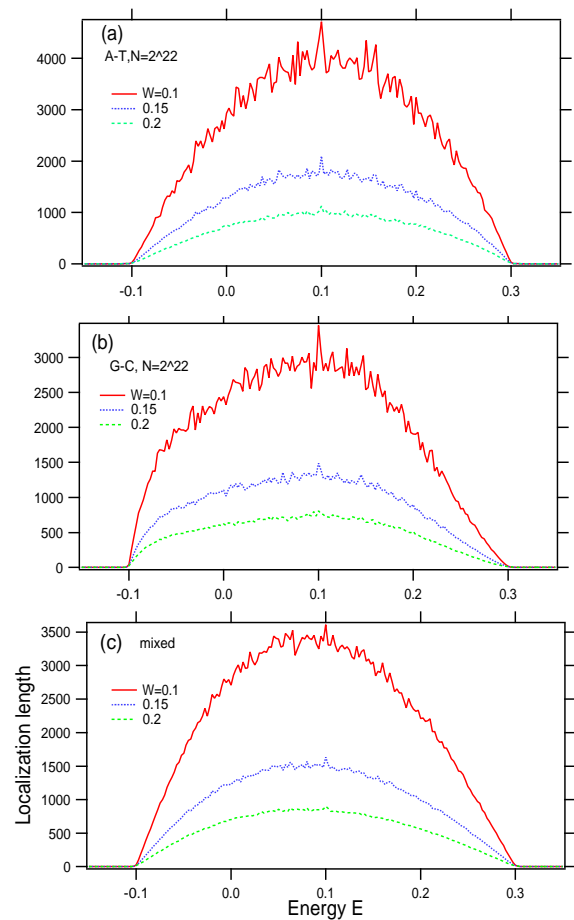


FIG. 3: The Localization length as a function of energy for several values of  $W$  ( $= 0.1, 0.15, 0.2$ ) in the (a) poly(dA)-poly(dT) DNA polymers, (b) poly(dG)-poly(dC) DNA polymers and (c) mixed DNA polymers. The system size is  $N = 2^{22}$  and  $\theta_0 = 36^\circ$ .

tendency to be extended in the sense that their localization length is larger than the system size. For the larger system size the energy dependence of the localization length converges.

In our definition of the localization length, when the system size  $N$  is smaller than the localization length, the sharp energy dependence of the resonance peaks appears, and the structure of the resonance depends on the randomness in  $r_n$  of each sample. Note that the resonance structure can be washed out if we take the ensemble average  $\langle \xi \rangle$  with regard to different configurations of  $r_n$  even for  $W = 0.1$ .

As a result we can say the transfer and transport of the electron sharply depend on the Fermi energy of the electrodes as the system size is relatively small. The extended states caused by the resonance can contribute to the transfer of the electron.

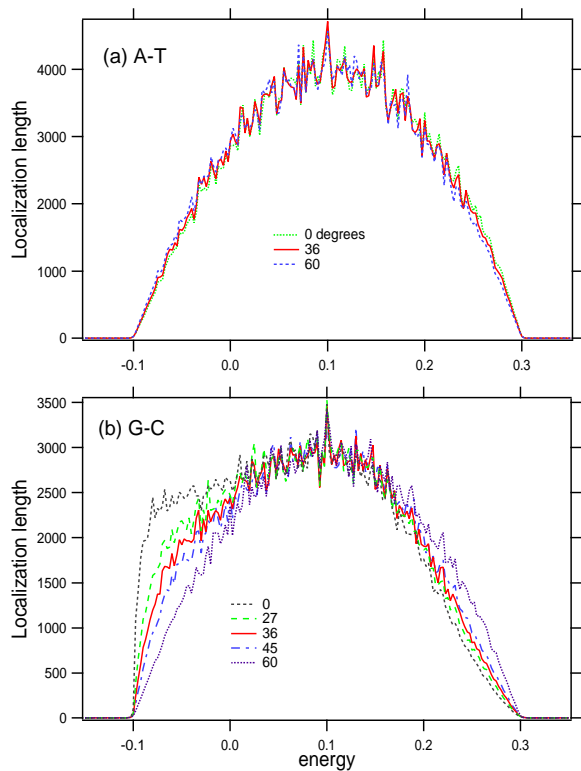


FIG. 4: The localization length as a function of energy for several values of the twist angle  $\theta_0$  ( $= 0^\circ, 27^\circ, 36^\circ, 45^\circ, 60^\circ$ ) in the (a) poly(dA)-poly(dT) DNA polymers, (b) poly(dG)-poly(dC) DNA polymers and (c) mixed DNA polymers. The system size is  $N = 2^{22}$  and  $W = 0.1$ .

#### IV. SUMMARY AND DISCUSSION

We have numerically investigated localization properties of electronic states in an adiabatic polaron model of poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA polymers with realistic parameters obtained using semi-empirical quantum-chemical calculations.

Now, we are in a position to compare the localization properties of the poly(dG)-poly(dC), poly(dA)-poly(dT) DNA polymers and the mixed case. Figure 6(a) and (b) show the localization length and Lyapunov exponent (inverse of the localization length) in the three types of the polymers with  $W = 0.1$ . In the low energy region, the localization length in the poly(dG)-poly(dC) DNA polymer is larger than that in the poly(dA)-poly(dT) DNA polymer. On the other hand, it is known from the experiments that poly(dG)-poly(dC) oligomer is a better semiconductor than poly(dA)-poly(dT) oligomer [18]. The difference is caused by the dynamical effect which is neglected in this paper and the system size effect. Indeed, the localization length of the DNA polymers is larger than  $\xi > 2000[bp]$  in almost all the energy band for all models, that is much larger than the system size of the oligomer used in the experiments. As seen in Fig.5 in the smaller system size the resonance peaks become complex.

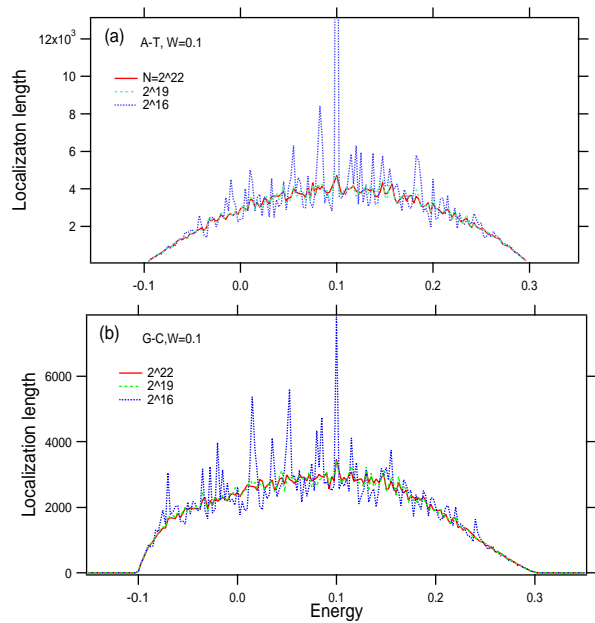


FIG. 5: The localization length as a function of the energy for several system sizes  $N$  ( $= 2^{16}, 2^{19}, 2^{22}$ ) in the (a) poly(dA)-poly(dT) DNA polymers, (b) poly(dG)-poly(dC) DNA polymers and (c) mixed DNA polymers.  $W = 0.1$  and  $\theta_0 = 36^\circ$ .

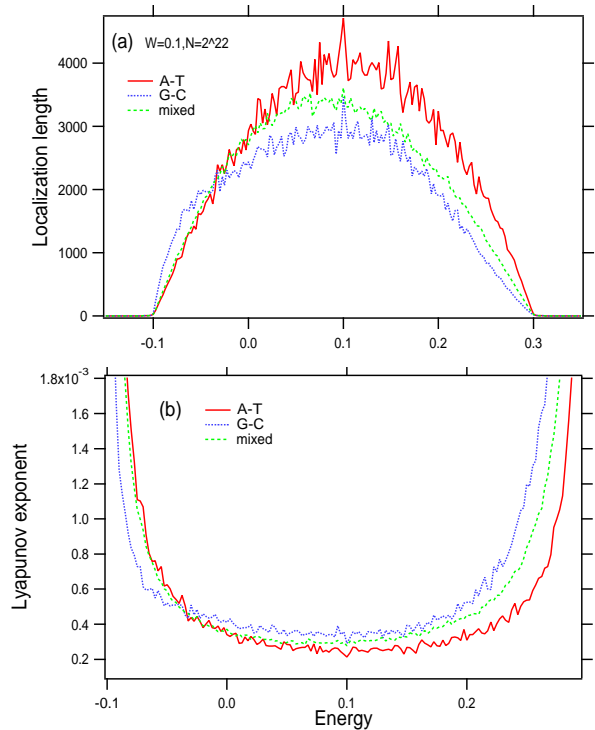


FIG. 6: Comparison (a) localization length and (b) Lyapunov exponent in poly(dG)-poly(dC), poly(dA)-poly(dT) and the mixed DNA polymers.  $W = 0.1$ ,  $\theta_0 = 36^\circ$  and  $N = 2^{22}$ .

### Acknowledgments

One of the authors (H.Y.) would like to thank Dr. Kazumoto Iguchi for his interest in this work.

- 
- [1] J.P. Lewis, T.E. Cheatham,III, E.B. Starikov, H. Wang and O.F. Sarkey, *J. Phys. Chem. B* **107**, 2581(2003).
- [2] D. Porath, G. Curiberti and R. Difelice, *Topics in Current Chemistry*, 1 (2004).
- [3] G. Paun, G. Rozenberg and A. Salomaa, *DNA Computing -New Computing Paradigms*, (Springer-Verlag, 1998).
- [4] P. Tran, B. Alavi, and G. Gruner, *Phys. Rev. Lett.* **85**, 1564(2000).
- [5] P. Carpena, P.B. Galvan, P.Ch. Ivanov and H.E. Stanley, *Nature* **418**, 955(2002); *ibid*, **84**, 764(2003).
- [6] S. Roche, *Phys. Rev. Lett.* **91**, 108101(2003); S. Roche, D. Bicout, E. Macia and E. Kats, *ibid*, **91**, 22810(2003).
- [7] H. Yamada, cond-mat/0406040.
- [8] D. Hennig, *Euro. Phys. J. B* **30**, 211(2002); D. Hennig, J.F.R. Archilla and J. Agarwal, *Physica D* **180**, 256(2003).
- [9] C. Chang, A.H.C. Neto and A.R. Bishop, cond-mat/0303250.
- [10] E.M. Conwell, S.V. Rakhmanova, *Proc. Natl. Acad. Sci. USA* **97**, 4556(2000).
- [11] D.K. Campbell, S. Flach and Y.S. Kivshar, *Physics Today*, Jan. 43(2004).
- [12] Z. Hermon, S. Caspi and E. Ben-Jacob, *Europhys. Lett.* **43**, 482(1998).
- [13] D. N. LeBard, M. Lilichenlo, Yu. A. Berlin, and M. A. Ratner, *J. Phys. Chem. B* **107**, 14509(2003).
- [14] K. Iguchi, *Int. J. Mod. Phys. B***11**, 2405(1997): *ibid*, **17**, 2565(2003); *J. Phys. Soc. Jpn.* **70**, 593(2001).
- [15] H. Yamada, *Int. J. Mod. Phys. B*, in press (2004). cond-mat/0401351.
- [16] D. Hennig, E. Starikov, J. F. R. Archilla, and F. Palmero, *J. Bio. Phys.* (2003), to appear, arXiv:mlin.PS/0308003.
- [17] E.B. Starikov, *J. Photochem. Photobiol. C* **3**, 147(2002).
- [18] K. -H. Yoo *et al.*, *Phys. Rev. Lett.* **87**, 198102(2001).
- [19] D. Dunlap, K. Kundu and P. Phillips, *Phys. Rev. B* **40**, 10999(1989); D. Dunlap, and P. Phillips, *J. Chem. Phys.* **92**, 6093(1990).
- [20] I. Varga and J. Pipek, *J. Phys. : Cond. Matt.* **10**, 305(1998).
- [21] W. Saenger, *Principles of Nucleic Acid Structure*, (Springer, New York, 1984).
- [22] A. Crisanti, G. Paladin, and A. Vulpiani, *Products of Random Matrices in Statistical Physics* (Springer-Verlag, Berlin, 1993), and references therein.
- [23] H. Yamada and T. Okabe, *Phys. Rev. E* **63**, 26203(2001).
- [24] See, for example, L.M. Lifshits, S.A. Gredeskul and L.A. Pastur, *Introduction to the theory of Disordered Systems*, (Wiley, New York,1988).