Dynamics of Proton and Electron conductivity in DNA Chains

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Abstract. The transport of energy, mass, and charge along quasi one-dimensional hydrogen-bonded systems is an extremely important scientific problem. We have studied proton mobility and electrical conductivity in DNA molecules using Peyrard-Bishop-Holstein model combined with proton transfer. For choosing the best values for system parameters in which the system behaves orderly, we have used the mean Lyapunov exponent. On the other hand, DNA shows a multifractal nature when electron together with proton flows through it. We have compared the multifractal behavior of two sequence of DNA when by considering the PCET using the Rényi dimension spectrum.

Keywords: Hydrogen-bonded systems, DNA nanowires, Proton coupled electron transfer, Chaos theory, Mean Lyapunov exponent, Multifractal, Renyi dimension. .

1 Introduction

DNA has become a key biological molecule in the study of genetics, medicine, and biotechnology. It possesses the natural ability to self-assemble and interacts with a wide range of molecules. Besides its importance in genetic studies and its application in various biological fields like biomedicine, cancer research, and genetic engineering, DNA has also become a preferred material for nanotechnologists because of its unique properties of structural stability, programmability of sequences, and predictable self-assembly. Electronic transport in DNA has recently attracted considerable interest in view of its possible use in nanoelectronics [1]. It is in close connection with basic properties of life, such as proton transport across biological membranes, and its implication to fundamental properties of condensed-matter materials, and proton mobility and electrical conductivity in DNA molecules. Charge transfer mechanism in DNA nanowires is studied through the different experimental and theoretical models. In this regard, Su-Schrieffer-Heeger (SSH) [2] and Peyrard-Bishop-Holstein (PBH) [3] models are the approaches considered the coupling of charge and DNA lattice. It seems that for a more comprehensive insight of charge transfer nature of DNA, we could consider the close relation between the electron and proton (Hydrogen atom) in lattice. We have focused attention on the proton coupled

electron transfer (PCET) mechanisms in DNA. PCET reactions are a particular type of charge transfer process that involves the simultaneous transfer of an electron and a proton. The coupled proton and electron transfer plays a vital role in electrochemistry, photosynthesis [4,5], respiration [6], numerous enzyme reactions [7], reactions in solid state materials [8].

In this work, we have tried to investigate charge conduction by regarding to the effect of proton transfer along DNA base pairs. We have taken into account the proton displacement and noted to the interaction of proton and DNA lattice. We have tried to improve the well-known PBH model by corrective terms related to proton transfer in DNA. In this regard, we have added the proton Hamiltonian to PBH Hamiltonian and considered the triple interactions of the electron, proton and DNA base-pairs. We have chosen the nonlinear dynamical systems methods and studied the system using the chaos theory. Mean Lyapunov exponent one of the most common tools of chaos theory shows the sensitivity of the system to initial condition and multifractal analysis studied the geometry of the system.

2   Mathematical Modeling

We have started the studying of charge transfer mechanism in DNA with N base-pairs and considering proton coupling using the following Hamiltonian:

$$H_{Tot} = H_e + H_p + H_{p-DNA} \tag{1}$$

where H_e is the electronic Hamiltonian of DNA based on the extended PBH model [3,9]. We could consider PBH Hamiltonian as following

$$H_e = H_{lat} + H_c + H_{c-lat} \tag{2}$$

that H_{lat} is the DNA Hamiltonian using the known PBD model [10]. In this model, Hamiltonian is written as

$$H_{lat} = \sum_n [\frac{1}{2} m \dot{y}_n^2 + V(y_n) + w(y_{n+1}, y_n)] \tag{3}$$

where

$$V(y_n) = D_n(e^{-a_n y_n} - 1)^2$$

is the Morse potential for describing the interaction of base-pairs along the hydrogen binding and

$$W(y_{n+1}, y_n) = \frac{k}{2}(1 + \rho e^{-b(y_{n+1}+y_n)})(y_{n+1} - y_n)^2$$

is the stacking interaction between the neighboring base-pairs in strand.

H_c is the carrier part of Hamiltonian that characterizes the hopping mechanism of the electron between the neighboring base-pairs as

$$H_c = \sum_n [\epsilon_n c_n^\dagger c_n - V_{n,n+1}(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n)] \tag{4}$$

where $c_n^\dagger(c_n)$ is the electron creation (annihilation) operator, ϵ_n is the on-site energy of each base-pair and $V_{n,n+1}$ the hopping parameter between them that is supposed to depend on the relative distance between two consecutive bases on the chain $V_{n,n+1} = V_0[1 - \beta_n(y_{n+1} - y_n)]$ [11]. The interaction between the electron and DNA lattice is represented by a Hamiltonian term as

$$H_{c-lat} = \chi_1 \sum_n y_n c_n^\dagger c_n \tag{5}$$

H_{c-lat} term states the coupling of the on-site energy with the base-pair displacements y_n and χ_1 is the carrier-lattice coupling constant.
For considering the proton transfer in DNA molecules, we could use the following terms in proton Hamiltonian [12,13]:

$$H_p = \sum_n [\frac{1}{2}m_p \dot{u}_n^2 + \frac{1}{2}m_p \omega_0 u_n^2 + V(u_n) - J u_{n+1} u_n] \tag{6}$$

where it contains an nonlinear potential and resonant or dipole-dipole interaction between the proton and its neighboring base-pair. $V(u_n)$ is a nonlinear potential arising from the interaction between the hydrogen atom and the bases which can be described by a Morse potential. The last term describes the resonant or dipole-dipole interaction of protons in the n-th base pair with the neighboring base pair. The strength of the interaction J is given by $J = q^2/4\pi\varepsilon_0 r^3$, where q is the net charge of proton, r is the distance between neighboring protons, and ε_0 is the dielectric constant of DNA.
The interaction Hamiltonian between the proton and its neighboring base-pairs is taken as

$$H_{p-lat} = \sum_n m_p \chi_2 u_n^2 (y_{n+1} - y_n) \tag{7}$$

It denotes the change of the position of the bases arising from the displacement of the hydrogen atom from its equilibrium position and χ_2 is the coupling constant.
It is worth mentioning that the system Hamiltonian is complex and it is difficult to study directly. In this regard, we have tried to move towards the phase space and studied it using the nonlinear dynamics theory. To this end, we have obtained the motion equations of the system as following:

$$\begin{aligned}
\ddot{y}_n =\ & \frac{2a_n D_n}{m} e^{-a_n y_n}(e^{-a_n y_n} - 1) \\
& + \frac{kb\rho}{2m}[e^{-b(y_n + y_{n-1})}(y_n - y_{n-1})^2 + e^{-b(y_{n+1} + y_n)}(y_{n+1} - y_n)^2] \\
& - \frac{k}{m}[(1 + \rho e^{-b(y_n + y_{n-1})})(y_n - y_{n-1}) - (1 + \rho e^{-b(y_{n+1} + y_n)})(y_{n+1} - y_n)] \\
& - \frac{V_0 \beta_n}{m}(c_{n-1}^\dagger c_n + c_n^\dagger c_{n-1} - c_n^\dagger c_{n+1} - c_{n+1}^\dagger c_n) - \frac{\chi_1}{m}|c_n|^2 \\
& + \frac{m_p \chi_2}{m}(u_2^2 - u_{n-1}^2) \tag{8a}
\end{aligned}$$

$$\dot{c}_n = -\frac{i}{\hbar}\{[\epsilon_n + \chi y_n - eEnd]c_n$$
$$- V_0[1 - \beta(y_{n+1} - y_n)]c_{n+1} - V_0[1 - \beta(y_n - y_{n-1})]c_{n-1}\} \qquad (8b)$$

$$\dot{u}_n = -\omega_0 u_n - \frac{\acute{V}(u_n)}{m_p} + J(u_{n+1} - u_{n-1}) - 2\chi_2 u_n(y_{n+1} - y_n) \qquad (8c)$$

3   Results

3.1   Parameter Selection

The dynamics of molecular structures is very sensitive to parameter values. Therefore, choosing the right values of parameters is difficult work. In such a way, it will be important to look at the system through another window that reflects the behaviour of the system as well. Since, any change in the system behaviour would be reflected in the change of trajectories distance in the phase space and as a result in the mean Lyapunov exponent (MLE) [14], we have tried to investigate the parameter range via MLE. The logical values of parameters for the better charge transport in the DNA model is where the MLE shows the minimum values in which system behaves orderly [15,16]. We have used the MLE to determine the range of some of these parameters. In all of them, it seems that increasing the parameter value corresponds to the growth of the MLE and hence the instability of the system (Figs. 1 and 2).
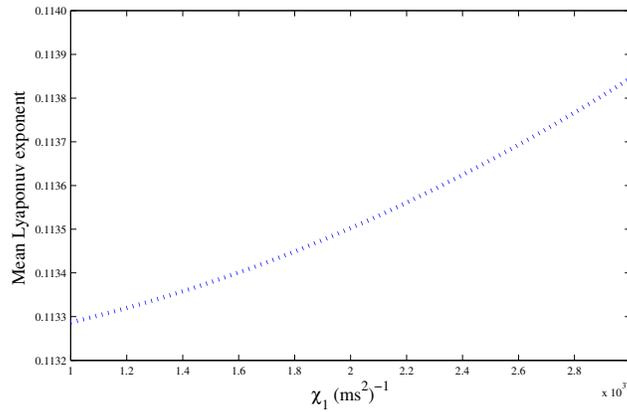
Fig. 1. Mean Lyapunov exponent with respect to the χ_1.

Therefore, we have chosen the smallest value previously offered to be closer to the actual results. The used parameters are according to Refs. [3,11,13]. Also, the effect of the external electrical field on the PCET phenomenon in DNA is obviously important. Then, one could determine the functional range of the field in which the system is regular. Figure 3 show the variation of MLE with respect to the external electrical field. It is obvious that the increasing of the field corresponds to increasing the MLE and then system disorder.
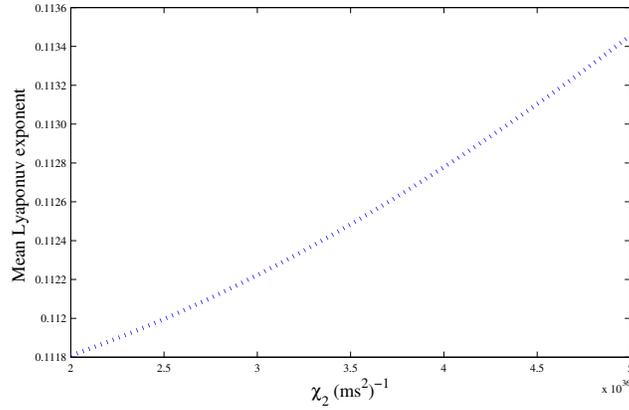
Fig. 2. Mean Lyapunov exponent with respect to the χ_2.
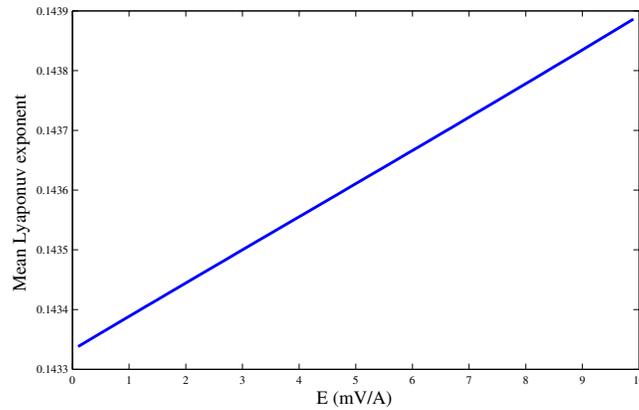
Fig. 3. Mean Lyapunov exponent with respect to the external electrical field.

3.2   Generalized Dimension

In more complex systems, such as DNA, where a great number of evolutionary processes have been involved, a single scaling exponent can not adequately describe the structure. A spectrum of exponents is more appropriate for the quantitative description of the structure and mechanism of system evolution. The continuous spectrum of exponents, each of which describes the local distribution of specific heights, is obtained through the multifractal description of the system. The q-th order exponent (D_q) is calculated as [17]

$$D_q = \frac{1}{q-1} \lim_{\epsilon \to 0} \frac{\log \sum_j p_j^q}{\log \epsilon} \tag{9}$$

where ϵ is the size of boxes that the surface is divided and p_j is the probability for capturing the trajectory in the j-th box. In the case of multifractal systems,

D_q is a decreasing function of q.

Previous studies show that the denaturation mechanism in DNA appears a multifractal nature [18]. It was confirmed in the studying the spin current in DNA wires using the multifractal analysis [19]. We have investigated the proton displacement in DNA using the Rényi fractal spectrum (D_q) [20]. An infinity of dimensions D_q is commonly used to describe the geometric and probabilistic features of the attractors.

D_q is derived for DNA proton transfer with different sequences. Two sequences are studied in the current work are presented in Table. 1.

Figure 3 shows the fractal spectrum for two sequences. Both of them exhibits

Name	The number of base pairs	DNA sequence
$CH22$	60 bp	AGGGCATCGCTAACGAGGTC
		GCCGTCCACAGCATCGCTAT
		CGAGGACACCACACCGTCCA
$L60B36$	60 bp	CCGCCAGCGGCGTTATTACA
		TTTAATTCTTAAGTATTATA
		AGTAATATGGCCGCTGCGCC

Table 1. The sequences used in calculation [21].

multifractal scaling behavior of PCET mechanism in DNA as it is already mentioned that in multifractals $D_q > D_{\acute{q}}$ for $q < \acute{q}$. But, it is clear that the variation of fractal dimension for L60B36 sequence is much more than CH22 sequence. This result is confirmed using the parameter $\tau = (q-1)D_q$. If τ is the linear function of q, then system will be a fractal. Each deviation from linearity corresponds to multifractal nature of system. Therefore, sequence $L60B36$ is more multifractal than another (see Fig. 4).
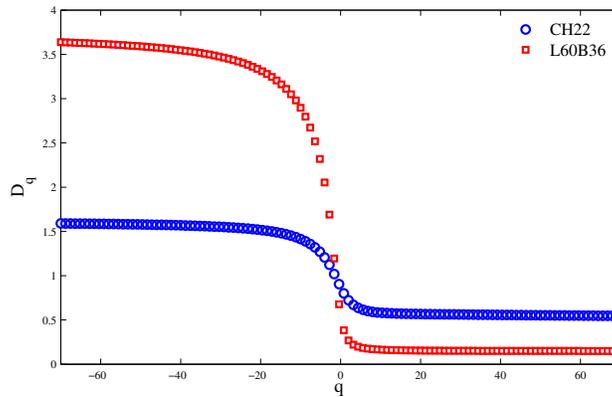
Fig. 4. Rényi dimension spectrum for two different sequence.
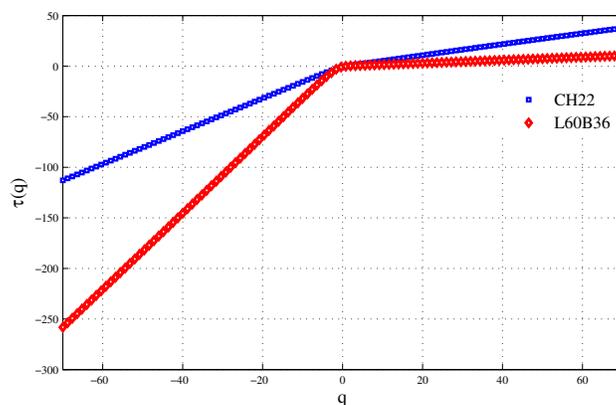
Fig. 5. τ_q for two different sequence.

4   Conclusion

We have considered the charge transfer coupled with proton mechanism in DNA using the proton-combined PBH model. Proton coupled electron transfer (PCET) events are going to stay in the heart of conductivity studies and radiation defects in DNA. The recent experimental results also show that the proton transfer is required for the long-range charge transfer in DNA. Therefore, elucidation of the dynamics of PCET electronic states is of fundamental importance to understanding DNA oxidative damage and to the design of DNA-based molecular devices. To reach the right results, we have selected the system parameters using the MLE theory. On the other hand, the external electrical field range is chosen using the MLE.

The multifractal dimension spectrum is used as another tool for distinguishing the different nature of proton displacement in DNA lattice with different sequence. The obtained results investigate that $L60B36$ sequence shows more multifractal nature than $CH22$.

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