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Numerical Modeling of the Charge Transfer Along 1D Molecular Chain "Donor-Bridge-Acceptor" at T = 300 K

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Abstract. We consider charge transfer along homogeneous chain of sites (such as DNA fragment) with the ends which imitate a donor and an acceptor. We performed direct numerical experiments based on the semi-classical Holstein model. To take into account the temperature, Langevin thermostat is used. Recently it has been shown that in homogeneous chains the charge distribution in thermodynamic equilibrium state (TDE) depends on the thermal energy of the lattice subsystem. Here, we have calculated dynamics of the system from the initial state "the charge is localized at the donor" over time intervals to the attainment of the TDE. The time intervals dependence on the length of the chain at fixed temperature is estimated. Part of parameter values are chosen as for DNA fragments of the GA…AGGG type. The results of the calculations are compared with the data of biophysical experiments on the hole transfer in DNA sequences.

Keywords: Holstein model · Langevin equation · Time to the attainment of the thermodynamic equilibrium state · DNA fragment

1 Introduction

At present, the attention of researchers is attracted to the possible mechanisms of charge transfer in quasy1D biomacromolecules, such as DNA, in connection with the potential using of this nano-objects in nanobioelectronics [1,2]. Studies of charge transfer in DNA also are of importance for biophysics; e.g., the propagation of excited charges along DNA is part of replication and reparation of DNA; movement of radicals over DNA molecules plays an important role in mutagenesis and cancerogenesis processes [3,4].

Biophysical experiments on the hole transfer from guanine G (donor) to guanine triplet GGG (acceptor), separated by adenine-thymine (A-T) bridges of various lengths [5–7], demonstrate that the rate of charge transfer between donor and acceptor decreases with increasing separation only if the guanines

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are separated by no more than three base pairs; if more bridging base pairs are present, the transfer rates exhibit only a weak distance dependence.

In this work we use a direct numerical experiment on the charge transfer from donor along bridge, consisting of homogeneous sites, to the acceptor. The model is based on the semi-classical Holstein Hamiltonian. The Holstein polaron model is simple and actual for explaining charge transfer in DNA [8–10]. To take into account the temperature, Langevin thermostat is used. Recently it has been shown that the charge distribution in the thermodynamic equilibrium state depends not only on the temperature, but also on the length of the chain, for homogeneous chains [11] and for the chain with a defect site in the center, which plays the role of a trap for the charge [12]. Here we have calculated dynamics of system from the initial state "the charge is localized at the donor" over time intervals to the attainment of the thermodynamic equilibrium. The time intervals dependence on the chain length N is estimated at fixed temperature $T = 300\,\mathrm{K}$.

2 Mathematical Model

We have considered the semiclassical Holstein model: quantum particle (an electron or a hole) moves along a chain of classical sites [13]. In the case of DNA a site – oscillator – corresponds to complementary base pair, its frequency ω is related to hydrogen bonds in the base pair. Choosing the wave function Ψ in the form $\Psi = \sum_{n=1}^{N} b_n |n\rangle$, where b_n is the amplitude of the probability of the charge occurrence at the n-th site ($n = 1, \ldots, N$, N is the chain length), we write the averaged Hamiltonian:

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{m,n} \nu_{nm} b_m b_n^* + \frac{1}{2} \sum_n M \dot{\tilde{u}}_n^2 + \frac{1}{2} \sum_n K \tilde{u}_n^2 + \sum_n \alpha' \tilde{u}_n b_n b_n^*. \tag{1}$$

Here ν_{nn} is the electron energy at the n-th site, ν_{mn} ($m \neq n$) are matrix elements of the transition between the m-th and the n-th sites (depending on overlapping integrals). We use the nearest neighbor approximation, i.e. $\nu_{mn} = 0$ if $m \neq n \pm 1$; the intrasite fluctuations $\tilde{u}_n$ are assumed to be small and can be considered to be harmonic; the probability $|b_n|^2$ of charge occurrence at the sites depends linearly on the sites displacements $\tilde{u}_n$, α' is the constant of coupling between quantum and classical subsystems, M is the effective mass of the site, K is the elastic constant.

Equations of motion obtained from Hamiltonian (1) and written in the dimensionless form are

$$i \frac{db_n}{dt} = \eta_{n,n-1} b_{n-1} + \eta_{n,n+1} b_{n+1} + \eta_{n,n} b_n + \chi u_n b_n, \tag{2}$$

$$\frac{d^2 u_n}{dt^2} = -\omega^2 u_n - \chi |b_n|^2 - \gamma \dot{u}_n + \xi Z_n(t). \tag{3}$$

Dimensionless values are related to dimensional parameters as follows. The matrix elements $\eta_{nk} = \nu_{nk} \tau / \hbar$ (τ is characteristic time, $\tilde{t} = \tau t$). Site frequency

$\omega = \tau\sqrt{K/M}$, coupling constant $\chi = \alpha'\sqrt{\tau^3/\hbar M}$. In subsystem (3) we added the term with friction (γ is a friction coefficient) and random force $Z_n(t)$ with the properties $\langle Z_n(t)\rangle = 0$, $\langle Z_n(t)Z_m(t+s)\rangle = \delta_{mn}\delta(s)$, $\xi^2 = (2k_B T^* \tau/\hbar)\gamma \mathrm{T}$ (T^* is characteristic temperature). This way of imitating the environmental temperature with the use of Langevin equations is well known [14,15].

To model the charge transfer dynamics, we computed a set of samples. Each sample is a trajectory of system (2, 3) with its own initial data and pseudorandom time series $\{Z_n(t)\}$, i.e. ODE system with random right-hand side. It is integrated by 2o2s1g-method [16]. Having obtained a number of samples we find averaged "by ensemble" functions of time, e.g., probability of charge localization on the n-th site $\langle P_n\rangle = \left\langle |b_n|^2\right\rangle$ and delocalization parameter $\langle R\rangle = \left\langle 1/\sum_n |b_n|^4\right\rangle$. If charge is localized at one k-th site, i.e. charge probability $|b_k|^2 \sim 1$, then $R \sim 1$. For homogeneous N-site chain, if charge is in delocalized state then $R \approx N/2$ [11].

3 On the Model Parameter Values

The characteristic time was chosen to be $\tau = 10^{-14}$ sec, the characteristic temperature $T^* = 1\,\mathrm{K}$.

For the quantum subsystem (2) the parameter values corresponding to nucleotide pairs are chosen as follows [17–20]. The matrix elements $\eta_{n,n\pm1}$ of the transition between sites are: $\eta_{\mathrm{GA}} = 1.352$ ($\nu_{\mathrm{GA}} = 0.089\,\mathrm{eV}$), $\eta_{\mathrm{AA}} = 0.456$ ($\nu_{\mathrm{AA}} = 0.030\,\mathrm{eV}$), $\eta_{\mathrm{AG}} = 0.744$ ($\nu_{\mathrm{AG}} = 0.049\,\mathrm{eV}$), $\eta_{\mathrm{GG}} = 1.276$ ($\nu_{\mathrm{GG}} = 0.084\,\mathrm{eV}$). The electron energy on the site $\eta_{n,n}$: $\eta_{\mathrm{G}} = 0$ ($\nu_{\mathrm{G}} = 1.24\,\mathrm{eV}$), $\eta_{\mathrm{A}} = 6.84$ ($\nu_{\mathrm{A}} = 1.69\,\mathrm{eV}$). For DNA the effective mass of a site is $M = 10^{-21}$ g; the rigidity $K = 0.062\,\mathrm{eV/\AA^2}$ and coupling constant $\alpha' = 0.13\,\mathrm{eV/\AA}$, i.e. $\omega = 0.01$ and $\chi = 0.02$. When performing calculations, for the classical subsystem (3) we chose the adapted values of the parameters that speed up the system's movement to the thermodynamic equilibrium state: $\omega = 0.5$ and $\chi = 1$. We suggest that not only the average values in the TDE are the same for two systems with the same ratio of parameters χ/ω [11], but the processes of reaching the TDE state from the same initial state (when the charge is localized at the first donor site) will be qualitatively similar.

The initial classical displacements u_n and velocities $\dot{u}_n$ of sites in the samples were chosen random from the TDE distribution of 1D oscillator at a given temperature; the charge is localized at the 1st site G: $b_1 = 1$, $b_n = 0$ ($n = 2, \ldots, N$).

Thermostat temperature $T = 300\,\mathrm{K}$. The length of the chain N varies from 5 (i.e. GAGGG – the bridge of one A) to 100 (i.e. GA…AGGG with 96 adenines).

4 On the Computational Method

For each N we have calculated the average probabilities $\langle P_n\rangle$ (for 100 samples) on time interval of reaching the TDE state. The time during which the system attains the TDE is estimated by the delocalization parameter $\langle R\rangle$ and by the probability values at the G sites. Figure 1 shows the $\langle R(t)\rangle$ curve and the average

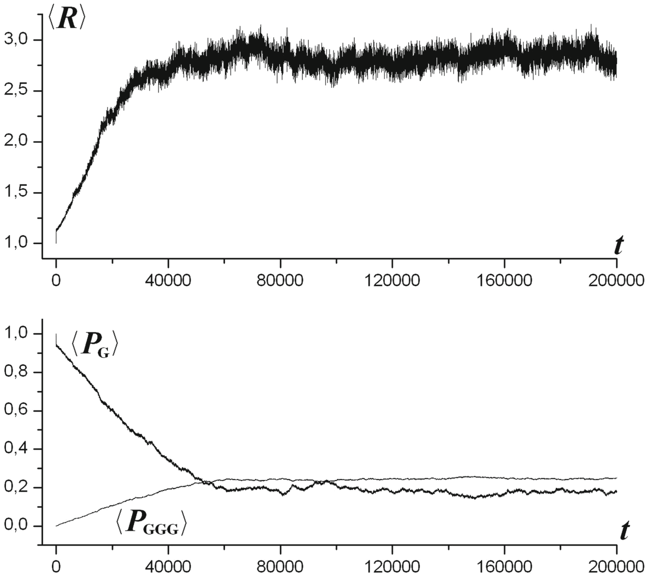

Fig. 1. Top: $\langle R(t)\rangle$. Bottom: average probability on donor (black curve) and on acceptor site (grey curve). The friction coefficient $\gamma = 4\omega$.

probabilities on donor $\langle P_G(t)\rangle$ and on acceptor $\langle P_{GGG}(t)\rangle = (1/3) \times \{$sum of probabilities on the sites of acceptor$\}$ for GAAGGG chain ($N = 6$).

Figure 1 demonstrates that at time $t \sim 60000$ the graphs become approximately constant, we take $t_{\mathrm{TDE}} = 60000$. In the TDE state the probability on the donor $\langle P_G\rangle \sim 0.18$ and the sum of probabilities on the acceptor sites $\sim$0.74. Increase in N leads to an increase in the time interval t_{TDE}. The time during which the system attains the state of TDE can be very long which raises the question of accumulation of a computing error. To clarify this question, we made test computations.

The system (2, 3) has the first integral: the total probability $\Sigma = \sum_{n=1}^{N} |b_n|^2$ must be equal to 1. As result of numerical integration Σ is not kept exactly. One of the ways that allows us to make computation intervals longer is forced normalization, when the variables b_n will be "corrected". After the integration step we obtain values b_n[old], calculate Σ[old] and $b_n[\mathrm{new}] = b_n[\mathrm{old}]/\sqrt{\Sigma[\mathrm{old}]}$, so new Σ will again be equal to 1. In doing so we do not come back to the same trajectory, but "overjump" to a new one (corresponding to the trajectory from other initial conditions), but individual trajectories are irrelevant when we are interested in the average by a lot of samples. The forced normalization means projection of all b_n onto a unit sphere in $\mathbb{C}^N$. This routine yields the same 2-nd order of accuracy as the scheme of integration.

In the programme this procedure is not performed at each step of integration. A "normalization error" $\varepsilon_{\rm norm}$ is specified. If at any moment t $|\Sigma - 1| > \varepsilon_{\rm norm}$, then $b_n = b_n/\sqrt{\Sigma}$. Similar methods are used in molecular dynamics modeling, e.g. for forced recover to the surface with a predetermined energy in microcanonical system [21].

For $N = 6, 8, 10$ we carried out some tests by integrating the system for large time intervals with different steps h and different values of $\varepsilon_{\rm norm}$. For $h \leq 0.0005$ and $\varepsilon_{\rm norm} \leq 0.0005$, the averaged curves $\langle R(t) \rangle$ are closed, and for $\langle P_n(t) \rangle$ we obtained the same result.

So, the problem of attaining the thermodynamic equilibrium can require huge integration time but we can expect that the averaged calculation values will not deviate greatly from the "ideal mean trajectory".

5 Simulation Results

Numerical experiments demonstrate that: for short chains ($N < 8$) the time interval $t_{\rm TDE}$ increases very fast (exponentially) with the increasing N. For $N \geq 8$, $t_{\rm TDE}$ is almost the same, and even decreases for $N > 20$. The calculations were performed for two friction values $\gamma = 1.8\omega = 0.9$, $\gamma = 4\omega = 2$ (periodic and aperiodic mode). In the aperiodic mode the time to reach the TDE decreases, but the quality picture is the same. The simulation results show that friction coefficient increasing accelerates the yield to the TDE of up to $\gamma \sim 4{-}5\omega$; with further growth of the γ $t_{\rm TDE}$ does not decrease.

In biophysical experiments for GA…AGGG fragments it was obtained [7], that the relative rate constants decrease exponentially for $N < 9$, and with further increase in N it remains almost unchanged. If we assume that the transfer rate is a reciprocal of the time $t_{\rm TDE}$, then a similar picture is obtained for modeling results. Figure 2 (left) shows the dependencies of $1/t_{\rm TDE}$ on the length of the chain N.

For the classical subsystem we chose the specific values of the parameters $\omega = 0.5$, $\chi = 1.$, that speed up the system's output to the TDE. We assume that not only the average values in the TDE are the same, but the processes of reaching the TDE from the same initial state (the charge is localized at the first donor site) will be qualitatively similar. We performed several test calculations with "more slow" parameters $\omega = 0.1$, $\chi = 0.2$ for chains with $N = 5 - 10$ sites (see Fig. 2, right), and the results of the tests do not contradict the assumption.

Figure 2 (right) shows that the time $t_{\rm TDE}$ of reaching the TDE increases with decrease of parameter values for classical subsystem (3); the ratio of classical frequencies is 5 and for $N \geq 8$ $t_{\rm TDE}$ increases hundreds of times. Qualitative picture of the time dependence on the length of the bridge is the same. Also this results demonstrate that for "DNA parameter values" ($\omega = 0.01$, $\chi = 0.02$) computational experiment will require a huge operating time.

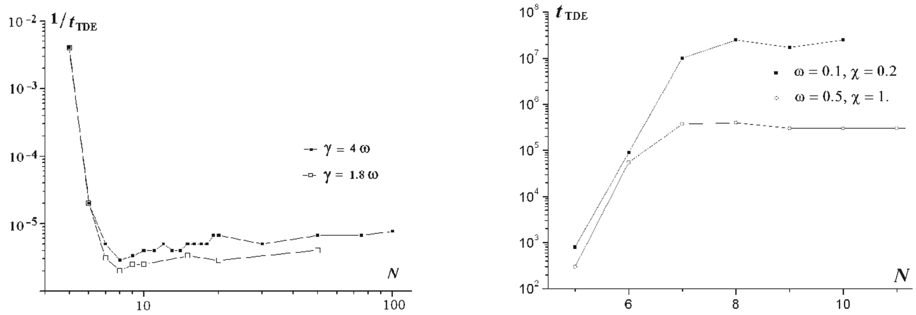

Fig. 2. Left: Dependencies of the transfer rate $1/t_{\mathrm{TDE}}$ on the chain length N for different friction coefficients, $\omega = 0.5$. Right: Dependence of the t_{TDE} on the N for two systems with the same ratio $\chi/\omega = 2$.

6 Discussion

In biophysical experiments [5–7], the transfer rate was not measured directly, the results are relative rate constants for different types of oligonucleotides. The authors obtained relative values of the reaction constants for hole transport from G to GGG, separated by bridges of different length. They found that for the chains with $N < 9$, lengthening the bridge on one site reduces the relative transfer rate by an order of magnitude. These values depend on oxidative damage at the G and GGG sites; the damage correlates with probability of the charge localization on the site.

We have modeled the system dynamics from the initial state "the charge is localized at the donor" over time intervals to the attainment of the thermodynamic equilibrium state and obtained dependence of the time intervals on the chain length. This dependence has the same properties as relative rate constants. Note that in the numerical experiments the values of probabilities of charge localization on the G and GGG sites in the TDE state are close. There is no direct correspondence between the data of biophysical experiments and simulation results, but we think that the results of numerical experiments are of interest.

In the thermodynamic equilibrium state, the value of $\langle R \rangle \sim N/2$ for chains $N \geq 20$, i.e. the charge is almost uniformly distributed along the chain. Based on the simulation results, it can be assumed that (similarly to the case of homogeneous chains) in short chains the charge is in the polaron state, and in long chains the charge is delocalized, and the charge transfer from the donor to the acceptor occurs by different mechanisms.

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