Closed systems of equations of correlation functions of currents for heterogeneous DNA fragments and polarons

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ABSTRACT

A closed system of nonlinear differential equations is proposed for current correlation functions of the Kubo expression for conductivity. The chain of equations is closed by dropping the correlations of higher order. The approach allows estimating an error of the dropped correlations. A successive approximation technique can take account of the corrections and allow for subtle effects caused by DNA structure and identifies areas, where these corrections are significant. The local conductivity in one-dimensional case was shown to be defined by adjacent sites. Zone conductivity takes place for small electron-vibrational interactions. The conductivity decreases with temperature rise, but it may increase or decrease at low temperatures because of finiteness of polymer fragment. At low temperatures the zone conductivity persists for large electron-vibrational interactions, however the possibility of hopping appears, and hopping conductivity increases with temperature rise and becomes determinant at some temperature but starts decreasing with temperature rise at high temperatures.

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1. Introduction

Systems with strong interaction and small dimension become the main subject of research at the present time. The most interesting phenomena occur precisely in such systems. However, the description of such phenomena is more difficult, because the phenomena are more complicated than ordinary. Such systems cannot be appropriately described with simple change of part of variables for mean effective field. It is necessary to save part of generalized dynamic variables in such systems along with introduction of mean probabilistic characteristics of the systems [1]. The generalized coordinates depend on the Hamiltonian of the system and change during averaging according to its coarseness thus including the considerable dynamic properties of the system. The corresponding generalized variables could be the external fields obtained from computations. The initial conditions are believed to be Gibbs conditions, although it is not necessary. Such system is a quasi-one-dimensional chain of DNA. A DNA fragment of a special type of sequence is considered where the transfer occurs along one chain. A linear Hamiltonian of Fröhlich type can be used in this case. Hopping conductivity of holes in such system is investigated.

The problem of transfer in DNA occurred immediately after the discovery of helical structure of DNA by Watson and Crick [2]. This was due to the fact, that the reactions of charge transfer play an important role in replication, transcription and repair of DNA molecule in the processes of mutagenesis and carcinogenesis [3–5]. The advent of femtosecond technology and the method of covalent binding of complexes performing the donor and acceptor roles (a kind of "connectors") to the DNA fragment, allowed carrying out direct experiments on measurement of charge transfer [6,7]. In most experiments, electrons or holes (cation radicals) were created ad hoc on DNA fragments with a known sequence of bases. The transfer rate was determined either by quenching of fluorescence, or by the amount of damages in nucleotides induced with charge transfer in different parts of the DNA helix.

Studies of DNA frozen in water showed that the irradiation of DNA leads to migration of charges at a distance of less than 8 base pairs localized on the guanine G, [8,9]. Then it was shown that the migration at a distance of about 20 nm (60 base pairs) [10] exists with an efficiency which depends on distance of the migration.

The electron transfer at distances of 10.2, 13.6, 17.0 Å (3, 4, 5 base pairs between the donor and acceptor respectively) was studied in experiments [11]. An exponential decrease of the electron

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transfer rate was observed with increase of number of nucleotide pairs in these experiments. Similar results were obtained in research [12,13], where the transfer distance was 20.5 Å (8 nucleotide pairs). Unexpected results were shown in work [14], where the electron transfer at a distance of 15 nucleotide pairs (about 37 Å) was investigated and the transfer rate was three orders of magnitude greater than found in later work [15]. Further experiments showed that there are various mechanisms of transfer in DNA, and the transfer rate strongly depends on chain length, on sequence of nucleotides, on characteristics of donors and acceptors used in the experiments. Flickering is often observed [16]. Sometimes there is a trigger effect [17].

Study [14] showed that the charge moves mainly along one DNA strand. Then this strand is considered. The rate of charge transfer may vary by orders of magnitude in DNA chains of the same length, depending on type of chain sequence. The relative values of reaction constants were obtained in works [18,19] for hole transport from the donor (excited cation radical G^{*+}) to the acceptor (guanine triplet GGG), separated by a bridge of one, two, three and four (A/T) base pairs. Furthermore, there were investigated cases, when one (A/T) pair of the four pairs of bridge had been substituted for (G/C) pair. Theoretical estimates of the transport rate lead to the value of $10^{12} \ldots 10^{10}$ s^{-1}. However, measurements [20–22] showed that the rate is equal to $10^7 \ldots 10^8$ s^{-1}. The experiments showed that the DNA molecule with a random nucleotide sequence does not resemble a semiconductor at all [23]. However, DNA properties are close to properties of molecular wires in special cases, i.e. the transport rate depends weakly on the length of DNA sequence, for example, when DNA has artificially synthesized fragments with the same nucleotide pairs.

The electron-vibrational interaction is usually large in such systems. This leads to involvement of many vibrations in the transfer processes and to a strong influence of temperature on conductivity. The "crystal" is finite and heterogeneous in our case. Holstein analyzed this problem in 1959 [24,25] for a one-dimensional homogeneous infinite crystal and showed that there is a coherent (zone) and incoherent (hopping) transfer mechanism. We shall see below that they are parallel and overlap each other [26–28]. Contribution of both mechanisms was also observed [23].

The aim of this work is to develop an analytical method that enables to derive a closed system of equations, which would have a solution clarifying the mechanisms of the transport processes in heterogeneous linear polymers and DNA, explaining experiments and making predictions based on realistic models.

Such closed system of equations is obtained below for the current correlation functions included in the Kubo expression [29] for conductivity, and the approximations made are discussed.

2. A closed system of equations for the current correlation functions

We shall take the advantage of formalism of the density matrix and give the exact expression for the coefficient of electrical conductivity, the Kubo formula [29]. The conductivity tensor in x direction is equal to

$$\sigma_{xx} = \frac{1}{L} \lim_{s \to 0} \int_0^\beta d\lambda \int_0^\infty e^{-st} \langle J_x(-i\lambda) J_x(t) \rangle dt,$$

where $\langle \ldots \rangle$ denotes averaging with density matrix ρ, T is temporal ordering operator, $\rho = \rho' \exp[-\beta(H-F)]/\text{Sp}(\exp[-\beta(H-F)]\rho')$, L is the length of the DNA fragment, $\beta = (kT)^{-1}$, $J(t)$ is the current operator in the Heisenberg representation $\rho' = T \exp\left[\sum \int_0^\infty (\eta_q^+(t) b_q(t) + \eta_q^-(t) b_q^+(t)) dt\right]$. Auxiliary classical fields $\eta_q^\pm$ allow recording an infinite chain of differential equations as a

single functional derivative equation [30]. The classical fields vanish at the end of computations and there remains only averaging over the equilibrium states of the vibrational subsystem in the initial time. The system with only one charge carrier is considered.

Such complex structures as DNA can hardly be investigated analytically. A simplified model, which retains the basic properties of the original problem, is required. The model would be detailed enough to reproduce physical effects of interest to us, but not overdetailed. We will simulate B-form of DNA, because it is believed to be the most typical. The simplest Hamiltonian will be considered for DNA at low temperatures, i.e. before phase transition in a backbone. Consideration of more complex Hamiltonian does not lead to fundamental difficulties, but only the dependence of carrier mobility on temperature is of interest here. In this case

$$H = \sum_m \varepsilon_m a_m^+ a_m + \sum_m B_{m-1;m} a_{m-1}^+ a_m + \sum_m B_{m+1;m} a_{m+1}^+ a_m$$
$$+ \sum_q \omega_q b_q^+ b_q - \sum_m A_{mq} \omega_q (b_q + b_{-q}^+) a_m^+ a_m, \tag{1}$$

where $a_m^+(a_m)$ are the operators of creation (annihilation) of particles of electron subsystem, $b_q^+(b_q)$ are the operators of creation (annihilation) of particles of vibrational subsystem, A_{mq} is the parameter of electron-vibrational interaction. $A_{mq} = \gamma_q \left(\frac{1}{2N}\right)^{\frac{1}{2}} e^{iqm} = A_q e^{iqm}$ are the dimensionless values characterizing polarization of medium in the vicinity of site m in electronic state ε_m in quasi-one-dimensional case, N is the number of sites of the DNA fragment, ε_m is the energy of electron (hole) on node m, $B_{m\pm1;m}$ is the resonance integral of overlapping sites $m \pm 1$ and m, ω_q are the vibration frequencies, γ_q is the characteristic of electron-vibrational interaction.

This Hamiltonian is usually used in study of electron-hole conductivity. It consists of electronic part, vibrational part and describes interaction between electrons and backbone vibrations. The Hamiltonian considers the possibility of polarization of the DNA backbone. The Hamiltonian allows theoretical investigation of hole (or electron) transfer along the fragment considering the relaxation process [31,32] and enables to calculate the luminescence yield for recombination of the radical anion (localized electron) and radical cation (hole). The recombination time is related to the path hole takes and depends on structure of the fragment [33,34]. It allows to obtain the information about structure of the DNA fragment. The Hamiltonian parameters determined from the real systems are: $\varepsilon_G = 1.24$ eV, $\varepsilon_A = 1.69$ eV, $\varepsilon_Z = 0.95$ eV, $B_{GA} = B_{AG} = 0.09$ eV, $B_{AZ} = B_{ZA} = 0.05$ eV, $B_{GG} = 0.028$ eV, $\omega = 0.01 \ldots 0.03$ eV. For programming purposes a value of the order of 10^{-12} s is chosen as the time unit and Hamiltonian is passed to dimensionless parameters which are $\varepsilon_G = 16.74$, $\varepsilon_A = 22.79$, $\varepsilon_Z = 12.95$, $B_{GA} = B_{AG} = 1.35$, $B_{AZ} = B_{ZA} = 0.74$, $B_{GG} = 0.48$, $\omega = 0.1 \ldots 0.3$. Here G is guanine, A is adenine, Z is 7-deazaguanine. A_{mq} is estimated from experimental data.

The current operator is equal to

$$J_x = -ie \sum_m x_m (B_{m;m-1} a_m^+ a_{m-1} + B_{m;m+1} a_m^+ a_{m+1}), \tag{2}$$

where x_m is site coordinate.

This leads to expression for the coefficient of conductivity

$$\sigma_{xx} = -e^2 Re \left(\frac{1}{L} \lim_{s \to 0} \int_0^\beta d\lambda \int_0^\infty e^{-st} \sum x_m x_n \right.$$
$$< (B_{m;m-1} a_m^+ (-i\lambda) a_{m-1}(-i\lambda) + B_{m;m+1} a_m^+ (-i\lambda) a_{m+1}(-i\lambda))$$
$$\left. \times (B_{n;n-1} a_n^+ (t) a_{n-1}(t) + B_{n;n+1} a_n^+ (t) a_{n+1}(t)) > dt \right). \tag{3}$$

The correlation function (CF) is introduced

$$G_{n;n+g}(-i\lambda; t) = \langle a_{m_1}^+ (-i\lambda) a_{n_1}(-i\lambda) a_n^+ (t) a_{n+g}(t) \rangle$$
$$= G_{n;n+g}(0; t + i\lambda), \quad g = \pm 1.$$

The goal is to derive an equation for computation of CF for selected Hamiltonian (1). The motion equations for the operators have the form

$$i\frac{d}{dt}a_m^+ = -\varepsilon_m a_m^+ - B_{m-1;m}a_{m-1}^+ - B_{m+1;m}a_{m+1}^+ + \sum_q A_{mq}\omega_q(b_q + b_{-q}^+)a_m^+,$$

$$i\frac{d}{dt}a_m = \varepsilon_m a_m + B_{m-1;m}a_{m-1} + B_{m+1;m}a_{m+1}^+ - \sum_q A_{mq}\omega_q(b_q + b_{-q}^+)a_m,$$

$$i\frac{d}{dt}b_q^+ = -\omega_q b_q^+ + \sum_m A_{mq}\omega_q a_m^+ a_m,$$

$$i\frac{d}{dt}b_q = \omega_{qj}b_q - \sum_m A_{mq}\omega_q a_m^+ a_m.$$

(4)

The equation for CF has the form

$$i\frac{d}{dt}G_{m;n}(-i\lambda;t) = (-\varepsilon_m + \varepsilon_n)G_{m;n}(-i\lambda;t) - B_{m;m-1}G_{m-1;n}(-i\lambda;t)$$
$$- B_{m;m+1}G_{m+1;n}(-i\lambda;t) + B_{n;n-1}G_{m;n-1}(-i\lambda;t)$$
$$+ B_{n;n+1}G_{m;n+1}(-i\lambda;t) + \sum_q \omega_q(A_{mq} - A_{nq})\langle(b_q$$
$$+ b_{-q}^+)\widehat{G}_{m;n}(-i\lambda;t)\rangle,$$

(5)

where notation $\widehat{G}_{n;n+g}(-i\lambda;t) = a_{m_1}^+(-i\lambda)a_{n_1}(-i\lambda)a_n^+(t)a_{n+g}(t)$ is introduced.

Note, that CF of higher order $\langle b_q\widehat{G}_{m;n}(-i\lambda;t)\rangle$ and $\langle b_{-q}^+\widehat{G}_{m;n}(-i\lambda;t)\rangle$ were included in (5) for which their equations would be written down, latter will include CF of even higher order, and so on to infinity. We have

$$i\frac{d}{dt}\langle b_{q_1}\widehat{G}_{m;n}(-i\lambda;t)\rangle = \omega_{q_1}\langle b_{q_1}\widehat{G}_{m;n}\rangle$$
$$- \sum_{m_1}\omega_{q_1}A_{m_1q_1}\langle a_{m_1}^+ a_{m_1}\widehat{G}_{m;n}\rangle + (-\varepsilon_m$$
$$+ \varepsilon_n)\langle b_{q_1}\widehat{G}_{m;n}(-i\lambda;t)\rangle$$
$$- B_{m;m-1}\langle b_{q_1}\widehat{G}_{m-1;n}(-i\lambda;t)\rangle$$
$$- B_{m;m+1}\langle b_{q_1}\widehat{G}_{m+1;n}(-i\lambda;t)\rangle$$
$$+ B_{n;n-1}\langle b_{q_1}\widehat{G}_{m;n-1}(-i\lambda;t)\rangle$$
$$+ B_{n;n+1}\langle b_{q_1}\widehat{G}_{m;n+1}(-i\lambda;t)\rangle + \sum_q \omega_q(A_{mq}$$
$$- A_{nq})\langle Tb_{q_1}(b_q + b_{-q}^+)\widehat{G}_{m;n}(-i\lambda;t)\rangle,$$

(6)

$$i\frac{d}{dt}\langle b_{q_1}^+\widehat{G}_{m;n}(-i\lambda;t)\rangle = -\omega_{q_1}\langle b_{q_1}^+\widehat{G}_{m;n}\rangle + \sum_{m_1}\omega_{q_1}A_{m_1q_1}\langle a_{m_1}^+ a_{m_1}\widehat{G}_{m;n}\rangle$$
$$+ (-\varepsilon_m + \varepsilon_n)\langle b_{q_1}^+\widehat{G}_{m;n}(-i\lambda;t)\rangle$$
$$- B_{m;m-1}\langle b_{q_1}^+\widehat{G}_{m-1;n}(-i\lambda;t)\rangle$$
$$- B_{m;m+1}\langle b_{q_1}^+\widehat{G}_{m+1;n}(-i\lambda;t)\rangle$$
$$+ B_{n;n-1}\langle b_{q_1}^+\widehat{G}_{m;n-1}(-i\lambda;t)\rangle$$
$$+ B_{n;n+1}\langle b_{q_1}^+\widehat{G}_{m;n+1}(-i\lambda;t)\rangle$$
$$+ \sum_q \omega_q(A_{mq} - A_{nq})\langle Tb_{q_1}^+(b_q + b_{-q}^+)\widehat{G}_{m;n}(-i\lambda;t)\rangle.$$

(7)

New CF $\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m;n}(-i\lambda;t)\rangle$, $\langle Tb_{q_1}b_{q_2}\widehat{G}_{m;n}(-i\lambda;t)\rangle$, $\langle Tb_{q_1}^+ b_{q_2}^+\widehat{G}_{m;n}(-i\lambda;t)\rangle$, $\langle Tb_{q_1}b_{q_2}^+\widehat{G}_{m;n}(-i\lambda;t)\rangle$ appeared in (6) and (7). The equations for one of them have the form

$$i\frac{d}{dt}\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m;n}(-i\lambda;t)\rangle = (-\omega_{q_1} + \omega_{q_2})\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m;n}\rangle$$
$$+ \sum_{m_1}(\omega_{q_1}A_{m_1q_1}\langle b_{q_2}a_{m_1}^+ a_{m_1}\widehat{G}_{m;n}\rangle$$
$$- \omega_{q_2}A_{m_1q_2}\langle b_{q_1}^+ a_{m_1}^+ a_{m_1}\widehat{G}_{m;n}\rangle) + (-\varepsilon_m$$
$$+ \varepsilon_n)\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m;n}(-i\lambda;t)\rangle$$
$$- B_{m;m-1}\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m-1;n}(-i\lambda;t)\rangle$$
$$- B_{m;m+1}\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m+1;n}(-i\lambda;t)\rangle$$
$$+ B_{n;n-1}\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m;n-1}(-i\lambda;t)\rangle$$
$$+ B_{n;n+1}\langle Tb_{q_1}^+ b_{q_2}\widehat{G}_{m;n+1}(-i\lambda;t)\rangle$$
$$+ \sum_q \omega_q(A_{mq} - A_{nq})\langle Tb_{q_1}^+ b_{q_2}(b_q$$
$$+ b_{-q}^+)\widehat{G}_{m;n}(-i\lambda;t)\rangle.$$

(8)

A problem of breakage of the chain of equations of CF (Bogolyubov chain) has arisen. The chain can be broken for coordinates of the current carriers for the chosen Hamiltonian in the approximation of small-radius polarons $a_{m_1}^+(t)a_{m_1}(t)a_m^+(t)a_n(t) = \delta_{m_1;m}a_m^+(t)a_n(t)$ (approximation of small density of carriers). The dynamic lag of lattice relative to the electron can be taken into account and the Hartree approximation $a_{m_1}^+(t')a_{m_1}(t')a_m^+ a_n = \langle a_{m_1}^+(t')a_{m_1}(t')\rangle a_m^+ a_n = \langle a_{m_1}^+(0)a_{m_1}(0)\rangle a_m^+ a_n$ should be assumed for large-radius polarons, that also allows breaking the chain for coordinates of the current carrier. It remained to close the chain for the vibrational degrees of freedom. At the present time it is done by changing the force field of a very complex structure, which acts on a particle from the side of other particles, to an average constant field (molecular field). This field is determined from the self-consistency condition. Such approach is widely used, but it is justified only with a small interaction between subsystems. It does not allow for possible dynamic coupling. However, such coupling is considerable in quasi-one-dimensional systems. Uncoupling of the chain of equations and considering the dynamic coupling are possible if functional derivatives are used. Without loss of generality assumption (9) can be made.

$$\langle b_{q_1}(t)\widehat{G}_{m;n}(t)\rangle = \left(\langle b_{q_1}(t)\rangle + \frac{\delta}{\delta\eta_{q_1}^+(t)}\right)G_{m;n}(t)$$
$$= G_{m;n}(t)M_{q_1}(m_1, n_1, m, n; t).$$

(9)

The left equality in formula (9) is known widely, while the right equality has been devised by the author [35]. The last equation is the definition of functional M_q. Similarly, we have

$$\langle b_{q_1}^+(t)\widehat{G}_{m;n}(t)\rangle = G_{m;n}(t)M_{q_1}^+(m_1, n_1, m, n; t),$$

(10)

and

$$\langle Tb_{q_1}^+(t)b_{q_2}(t-0)\widehat{G}_{m;n}(t)\rangle = G_{m;n}(t)\left(M_{q_1}^+(m_1, n_1, m, n; t) + \frac{\delta}{\delta\eta_{q_1}^-(t)}\right)$$
$$\times M_{q_2}(m_1, n_1, m, n; t),$$

(11)

$$\langle Tb_{q_1}^+(t)b_{q_2}(t-0)b_{q_3}^x(t-0-0)\widehat{G}_{m;n}(t)\rangle$$
$$= G_{m;n}(t)\left(M_{q_1}^+(m_1, n_1, m, n; t) + \frac{\delta}{\delta\eta_{q_1}^-(t)}\right)$$
$$\times \left(M_{q_2}(m_1, n_1, m, n; t) + \frac{\delta}{\delta\eta_{q_2}^+(t)}\right)M_{q_3}^x(m_1, n_1, m, n; t).$$

(12)

The obtained expressions allow collapsing the infinite Bogolyubov chain and finding methods of its approximation. In fact, if the

operator of variational derivative is applied, and pass to limit $\eta_{qj}^x(t) \to 0$ is done, then (10) gives

$$\langle b_{q_1}^+(t)\widehat{G}_{m;n}(t)\rangle = M_{q_1}^+(m_1, n_1, m, n; t)G_{m;n}(t). \tag{13}$$

The latter expression means that the action of operator $b_{q_1}^+(t)$ inside the averaging is substituted for an external field, which is equivalent in effect and depends on time and on the type of CF considered. Accordingly, for the annihilation operator exists

$$\langle b_{q_1}(t)\widehat{G}_{m;n}(t)\rangle = M_{q_1}(m_1, n_1, m, n; t)G_{m;n}(t).$$

Field $M_{q_1}^+(m_1, n_1, m, n; t)$ differs from field $M_{q_1}(m_1, n_1, m, n; t)$, but meanwhile is uncertain, as well as field $M_{q_1 j_1}(m_1, n_1, m, n; t)$. The appropriate equations to define them will be obtained further. A new quality emerges when two vibrational states (operators) arise because a correlation between two fields is possible which must be taken into account. This was considered in expression (11). Passage to a zero limit for classical fields in this equation gives

$$\langle Tb_{q_1}^+(t)b_{q_2}(t-0)\widehat{G}_{m;n}(t)\rangle$$
$$= \left(M_{q_1}^+(m_1, n_1, m, n; t)M_{q_1}(m_1, n_1, m, n; t)\right.$$
$$\left. + \frac{\delta}{\delta\eta_{q_1}^-(t)}M_{q_2}(m_1, n_1, m, n; t)\right)G_{m;n}(t), \quad \{\eta_q^x\} \to 0.$$

Since $M_{q_1}^+(m_1, n_1, m, n; t)$ and $M_{q_1}(m_1, n_1, m, n; t)$ are fields in a physical sense acting on a particle (current carrier) with no regard for the correlations between them, taking the pairwise correlations between these fields into account reflects the pairwise correlations in the oscillating subsystem. These pairwise correlations will be denoted as

$$D_{q_1;q_2}^{+;-}(m_1, n_1, m, n; t) = \frac{\delta}{\delta\eta_{q_1}^-(t)}M_{q_2}(m_1, n_1, n, n; t), \quad \{\eta_q^x\} \to 0.$$

Consideration of only pairwise correlations between vibrations due to nonlinear interactions, or interactions through an intermediate carrier particle gives

$$\langle Tb_{q_1}^+(t)b_{q_2}(t-0)\widehat{G}_{m;n}(t)\rangle = (M_{q_1}^+(t)M_{q_1}(t) + D_{q_1;q_2}^{+;-}(t))G_{m;n}(t).$$

Hereinafter, the simplification of adopted notation is taken $M_{q_1}^+(m_1, n_1, m, n; t) = M_{q_1}^+(t)$, $M_{q_1}(m_1, n_1, m, n; t) = M_{q_1}(t)$, and $D_{q_1;q_2}^{+;-}(m_1, n_1, m, n; t) = D_{q_1;q_2}^{+;-}(t)$.

Values $M_{q_1}^+(t)$ and $M_{q_1}(t)$ take into account the effect from the first mode on the carrier, and $M_{q_2}^+(t)$, $M_{q_2}(t)$ — from the second mode without allowing for possible coordination of the first and second modes, and $D_{q_1;q_2}^{+;-}(t)$ takes into consideration the possibility of correlations between pairs of modes in interaction with the carrier. This approximation takes into account all pairwise correlations in the oscillating subsystem. Note that other correlations do not exist in the univariate case, and this representation is accurate.

Now the case of three modes will be considered, where pairwise correlations of the first mode with the second, the second mode with the third, the first mode with the third, and triple correlations are possible. Passage to limit $\{\eta_q^x\} \to 0$ transforms expression (12) into

$$\langle Tb_{q_1}^+(t)b_{q_2}(t)b_{q_3}^x(t)\widehat{G}_{m;n}(t)\rangle$$
$$= \left(M_{q_1}^+(t)M_{q_2}(t)M_{q_3}^x(t) + M_{q_1}^+(t)D_{q_2;q_3}^{-x}(t) + M_{q_2}(t)D_{q_1;q_3}^{+;x}(t)\right.$$
$$\left. + M_{q_3}^x(t)D_{q_1;q_2}^{+;-}(t) + \frac{\delta}{\delta\eta_{q_1}^-(t)}D_{q_2;q_3}^{-x}(t)\right)G_{m;n}(t), \quad \{\eta_q^x\} \to 0.$$

Expression $\frac{\delta}{\delta\eta_{q_1}^-(t)}D_{q_2;q_3}^{\pm,\pm}(t) = T_{q_1;q_2;q_3}^{+,\pm,\pm}$ describes the effect of triple correlations on travel of current carriers. There are no such correlations in one-dimensional case at all and they are hardly probable in general case because imply a collision of three particles at the same time. Correlations of any higher order can be similarly allowed for successive increase of the number of modes. The chain of the equations is closed by dropping the correlations of excessive order. The obtained system of nonlinear differential equations can be then solved numerically. The approach allows estimating the error of dropping of the part of correlations. The above approach is the improved method of functional derivatives [30,36–38].

3. Consideration of only pair correlations

The Bogolyubov chain equations will be broken in assumption of $T_{q_1;q_2;q_3}^{\pm,\pm,\pm} = 0$. Eq. (5) can be rewritten with consideration for agreed notations and approximations as

$$i\frac{d}{dt}G_{m;n}(t) = (-\varepsilon_m + \varepsilon_n)G_{m;n}(t) - B_{m;m-1}G_{m-1;n}(t) - B_{m;m+1}G_{m+1;n}(t)$$
$$+ B_{n;n-1}G_{m;n-1}(t) + B_{n;n+1}G_{m;n+1}(t)$$
$$+ \sum_q \omega_q(A_{mq} - A_{nq})(M_q + M_{-q}^+)G_{m;n}(t), \tag{14}$$

and Eq. (6) with consideration for (14) takes the form of

$$i\frac{d}{dt}M_{q_1} = \omega_{q_1}M_{q_1} - \omega_{q_1}\sum A_{m_2 q_1}\langle a_{m_2}^+(t)a_{m_2}(t)\rangle$$
$$+ \sum_q \omega_q(A_{mq} - A_{nq})(D_{q_1;q}^{-,-} + D_{q_1;q}^{-,+})$$
$$+ \{-B_{m;m-1}(M_{q_1}(m_1, n_1, m-1, n; t) - M_{q_1})G_{m-1;n} - B_{m;m+1}$$
$$\times (M_{q_1}(m_1, n_1, m+1, n; t) - M_{q_1})G_{m+1;n}$$
$$+ B_{n;n-1}(M_{q_1}(m_1, n_1, m, n-1; t) - M_{q_1})G_{m;n-1}$$
$$+ B_{n;n+1}(M_{q_1}(m_1, n_1, m, n+1; t) - M_{q_1})G_{m;n+1}\}G_{m;n}^{-1}(t). \tag{15}$$

The same operation will be implemented for Eqs. (7) and (8) which define functions $M_q(t)$, $M_q^+(t)$ and $D_{q_1;q_2}^{\pm\pm}(t)$. The expressions are not given here due to their complexity, but will be presented below after simplification. It would be possible then to write the equations for function $T_{q_1;q_2;q_3}^{\pm,\pm,\pm}(t)$ and so on, but it is assumed at the first approximation, that the consideration of triple correlations does not distort the result strongly, and supposed $T_{q_1;q_2;q_3}^{\pm,\pm,\pm}(t) = 0$. Then the system of nonlinear Eqs. (14), (15), etc. is simplified and can be solved numerically.

Members in braces can be taken into consideration to obtain a solution of desired quality via iterations. The system of equations will be simplified further. All braces, which appear in the system of equations, such as appeared in (15), take into account the change of frequencies or displacements of the term minima from the presence of current carriers in the system. There is a small amount of carriers in the system (just one per fragment) and their effect on a large number of vibrations leads to small corrections proportional to N^{-1} (N is the number of vibration modes). Nevertheless, these corrections can be taken into consideration using the method of successive approximations. It will allow for the subtle effects of the DNA structure and reveal areas where these corrections are significant.

4. Incomplete consideration of pair correlations

All the braces such as appeared in (15) can be omitted in the first approximation and then the functional equations for $G_{m,n}(t)$, $M_q^+(t)$, $M_q(t)$, $D_{q_1;q_2}^{\pm\pm}(t)$ will become much simpler. Then the func-

tional equations will be obtained in the form of a system of nonlinear equations.

$$
\begin{aligned}
i\frac{d}{dt}G_{m;n}(t) &= (-\varepsilon_m + \varepsilon_n)G_{m;n}(t) - B_{m;m-1}G_{m-1;n}(t) - B_{m;m+1}G_{m+1;n}(t) \\
&\quad + B_{n;n-1}G_{m;n-1}(t) + B_{n;n+1}G_{m;n+1}(t) \\
&\quad + \sum_q \omega_q (A_{mq} - A_{nq})(M_q + M^+_{-q})G_{m;n}(t).
\end{aligned}
\tag{16}
$$

If considered, that the carrier is localized on neighbouring sites, i.e. $a_m^+ a_m + a_n^+ a_n = 1$, then

$$
\begin{aligned}
i\frac{d}{dt}M_{q_1} &= \omega_{q_1} M_{q_1} - \omega_{q_1}((A_{mq_1} - A_{nq_1})\langle a_m^+(t)a_m(t)\rangle + A_{nq_1}) \\
&\quad + \sum_q \omega_q (A_{mq} - A_{nq})(D_{q_1;q}^{-,-} + D_{q_1;q}^{-,+}),
\end{aligned}
\tag{17}
$$

$$
\begin{aligned}
i\frac{d}{dt}M_{q_1}^+ &= -\omega_{q_1} M_{q_1}^+ + \omega_{q_1}((A_{mq_1} - A_{nq_1})\langle a_m^+(t)a_m(t)\rangle + A_{nq_1}) \\
&\quad + \sum_q \omega_q (A_{mq} - A_{nq})(D_{q_1;q}^{+,-} + D_{q_1;q}^{+,+}),
\end{aligned}
\tag{18}
$$

and four linear equations with constant coefficients

$$
i\frac{d}{dt}D_{q_1;q_2}^{+,-}(t) = (-\omega_{q_1} + \omega_{q_2})D_{q_1;q_2}^{+,-}(t),
\tag{19}
$$

$$
i\frac{d}{dt}D_{q_1;q_2}^{-,+}(t) = (\omega_{q_1} - \omega_{q_2})D_{q_1;q_2}^{-,+}(t),
\tag{20}
$$

$$
i\frac{d}{dt}D_{q_1;q_2}^{+,+}(t) = (-\omega_{q_1} - \omega_{q_2})D_{q_1;q_2}^{+,+}(t),
\tag{21}
$$

$$
i\frac{d}{dt}D_{q_1;q_2}^{-,-}(t) = (\omega_{q_1} + \omega_{q_2})D_{q_1;q_2}^{-,-}(t).
\tag{22}
$$

Eqs. (19)–(22) have identical solutions $D_{q_1;q_2}^{\pm,\mp}(t) = D_{q_1;q_2}^{\pm,\mp}(0)$ $\exp[-i(\mp\omega_{q_1} \pm \omega_{q_2})t]$, differing from each other only by the initial conditions equal to $D_{q_1;q_2}^{+,-}(0) = \delta_{q_1;q_2} N_{q_1}$, $D_{q_1 J_1;q_2 J_2}^{-,+}(0) = \delta_{q_1;q_2}\delta_{j_1;j_2}$ $(N_{q_1 J_1} + 1)$, $D_{q_1;q_2}^{+,+}(0) = 0$, $D_{q_1;q_2}^{-,-}(0) = 0$.

Therefore

$$
\begin{aligned}
D_{q_1;q_2}^{+,-}(t) &= \delta_{q_1;q_2} N_{q_1}, \\
D_{q_1;q_2}^{-,+}(t) &= \delta_{q_1;q_2}(N_{q_1} + 1), \\
D_{q_1;q_2}^{+,+}(t) &= 0, \\
D_{q_1;q_2}^{-,-}(t) &= 0.
\end{aligned}
\tag{23}
$$

Substitution of the obtained solutions in (17), (18) gives

$$
\begin{aligned}
i\frac{d}{dt}M_{q_1} &= \omega_{q_1} M_{q_1} - \omega_{q_1}((A_{mq_1} - A_{nq_1})\langle a_m^+(t)a_m(t)\rangle + A_{nq_1}) \\
&\quad + \omega_{q_1}(A_{mq_1} - A_{nq_1})(N_{q_1} + 1),
\end{aligned}
$$

$$
\begin{aligned}
i\frac{d}{dt}M_{q_1}^+ &= -\omega_{q_1} M_{q_1}^+ + \omega_{q_1}((A_{mq_1} - A_{nq_1})\langle a_m^+(t)a_m(t)\rangle + A_{nq_1}) \\
&\quad + \omega_{q_1}(A_{mq_1} - A_{nq_1})N_{q_1}.
\end{aligned}
$$

Solutions of these equations with initial conditions $M_{qj}^+(0) = 0$, $M_{qj}(0) = 0$ will be

$$
\begin{aligned}
M_q(t) &= e^{-i\omega_q t}\{-(A_{mq} - A_{nq})[\langle a_m^+(t)a_m(t)\rangle + A_{nq} - (N_q + 1)]\} \\
&\quad + (A_{mq} - A_{nq})[\langle a_m^+(t)a_m(t)\rangle + A_{nq} - (N_q + 1)].
\end{aligned}
\tag{24}
$$

Similarly obtained

$$
\begin{aligned}
M_q^+(t) &= e^{i\omega_q t}\{(A_{mq} - A_{nq})[\langle a_m^+(t)a_m(t)\rangle + A_{nq} - N_q]\} - (A_{mq} \\
&\quad - A_{nq})[\langle a_m^+(t)a_m(t)\rangle + A_{nq} - N_q].
\end{aligned}
\tag{25}
$$

$\langle a_m^+(t_1)a_m(t_1)\rangle$ was removed from the integrand in point $t_1 = t$, because function $\langle a_m^+(t_1)a_m(t_1)\rangle$ weakly depends on time, and only two main members of the sum were kept. Consideration of members $\langle a_n^+(t)a_n(t)\rangle$ is important only when large-radius polarons are considered. When values $M_q(t)$, $M_q^+(t)$ possess the analytic form, the analysis of the system of equations of CF is reduced to numerical solution of linear Eq. (16) with variable coefficients.

5. The small-radius polarons

For the case of small-radius polarons we have

$$
i\frac{d}{dt}M_{q_1} = \omega_{q_1} M_{q_1} - \omega_{q_1} A_{nq_1} + \omega_{q_1}(A_{mq_1} - A_{nq_1})(N_{q_1} + 1), \quad M_q(0) = A_{nq},
$$

$$
i\frac{d}{dt}M_{q_1}^+ = -\omega_{q_1} M_{q_1}^+ + \omega_{q_1} A_{nq_1} + \omega_{q_1}(A_{mq_1} - A_{nq_1})N_{q_1}, \quad M_q^+(0) = A_{nq}.
$$

The solution of these equations is

$$
\begin{aligned}
M_q(t) &= e^{-i\omega_q t}\left\{ M_q(0) - i\omega_q(A_{mq} - A_{nq})\int_0^t e^{i\omega_q t_1}(N_q + 1)dt_1 \right. \\
&\quad \left. + i\omega_q \int_0^t e^{i\omega_q t_1} A_{nq}dt_1 \right\} = \\
&= e^{-i\omega_q t}\{(A_{mq} - A_{nq})(N_q + 1)\} - (A_{mq} - A_{nq})(N_q + 1) + A_{nq}.
\end{aligned}
\tag{26}
$$

Similarly

$$
M_q^+(t) = e^{i\omega_q t}\{-(A_{mq} - A_{nq})N_q\} + A_{nq} + (A_{mq} - A_{nq})N_q.
$$

Substitution of obtained solution (26) in (16) for the one-dimensional linear chain of N nodes (sites) gives the system of equations of Mathieu type.

$$
\begin{aligned}
i\frac{d}{dt}G_{m;m}(t) &= -B_{m;m-1}G_{m-1;m}(t) - B_{m;m+1}G_{m+1;m}(t) + B_{m;m-1}G_{m;m-1}(t) \\
&\quad + B_{m;m+1}G_{m;m+1}(t), \\
i\frac{d}{dt}G_{m-1;m}(t) &= (-\varepsilon_{m-1} + \varepsilon_m)G_{m-1;m}(t) - B_{m-1;m}G_{m;m}(t) \\
&\quad + B_{m;m-1}G_{m-1;m-1}(t) + \\
&\quad + \sum_q \omega_q(e^{-i\omega_q t}\{(A_{m-1q} - A_{mq})^2(N_q + 1)\} - (A_{m-1q} - A_{mq})^2 \\
&\quad + 2A_{mq}(A_{m-1q} - A_{mq}) + \\
&\quad + e^{i\omega_q t}\{-(A_{m-1q} - A_{mq})^2 N_q\})G_{m-1;m}(t), \\
i\frac{d}{dt}G_{m+1;m}(t) &= (-\varepsilon_{m+1} + \varepsilon_m)G_{m+1;m}(t) - B_{m+1;m}G_{m;m}(t) \\
&\quad + B_{m;m}G_{m+1;m+1}(t) + \\
&\quad + \sum_q \omega_q(e^{-i\omega_q t}\{(A_{m+1q} - A_{mq})^2(N_q + 1)\} - (A_{m+1q} - A_{mq})^2 \\
&\quad + 2A_{mq}(A_{m+1q} - A_{mq}) + \\
&\quad + e^{i\omega_q t}\{-(A_{m+1q} - A_{mq})^2 N_q\})G_{m+1;m}(t), \quad m = 1, 2, \ldots, N,
\end{aligned}
\tag{27}
$$

with initial conditions $G_{m;n}(0) = \delta_{n_1;m}\delta_{m_1;n}n_n$, where $\delta_{n_1;m}$ is Kronecker delta, and n_n is current carrier population of node n in initial time.

Such system can be solved with only numerical methods or via expanding into the resonance integrals on the perturbation theory. Expression (27) includes two different categories of transitions, namely, the phononless processes, which have a maximum for the homogeneous case at zero temperature when $\sum N_q = \sum N_{q_1} = 0$, and the phonon processes when $\sum N_q \neq \sum N_{q_1}$.

If system (27) is considered for the case of four sites ($m = 0, 1, 2, 3$) then the analysis of the current CF can be done for the hole tran-

Table 1
The parameters of sites 0 and 3.

№	ω_{01}	ω_{23}	E_{01}	E_{23}	$(A_0 - A_1)^2$	$(A_2 - A_3)^2$	Additives
1	0.3	0.7	−1	−3	4	2	0.003
2	0.4	0.7	−1	3	4	6	0.002
3	0.5	0.6	1	09	3	2	0.001
4	0.6	0.5	2	3	2	16	0.000

sition from site 1 to site 2, i.e. CF $G_{2;1}(t)$ can be computed. The probability of local transition in the case of one vibrational frequency can be calculated according to Kubo formula.

$$\sigma_{1\to2} = -e^2 Re\left(\frac{1}{L}\lim_{s\to0}\int_0^\beta d\lambda \int_0^\infty e^{-st}(x_1 - x_2)^2 B_{1;2}^2 \langle a_1^+(-i\lambda)a_2(-i\lambda)a_2^+(t)a_1(t)\rangle dt\right) =$$

$$= -e^2 Re\left(\frac{1}{L}\lim_{s\to0}\int_0^\beta d\lambda \int_0^\infty e^{-st}(x_1 - x_2)^2 B_{1;2}^2 G_{2;1}(t + i\lambda)dt\right).$$

(28)

The value $\sigma_{1\to2}(T)$ was calculated according to formula (28) when $\omega = 0.3$, $B_{1;2} = B_{2;1} = 0.5$, $E_{21} = 3.0$, $(A_1 - A_2)^2 = 16$ and $\sigma_0 = e^2 n_2 B_{1;2}^2 (x_1 - x_2)^2$ for different sites 0 and 3 the parameters of which are given in Table 1.

As shown in Fig. 1 change of parameters of sites 0 and 3 has almost no effect on the local hole transfer between sites 1 and 2. If the curves on the right side in Fig. 1 are considered, then the upper curve corresponds with case 1, the lower — with case 4, two intermediate curves correspond with cases 2 and 3 respectively. Additives are made to separate curves for different cases. If no additives are given, then the curves coincide. Analysis of the shape and size of the relative conductivity of link 1–2 for a set of parameter numbers 2–4 led to the same results, i.e. it turned out that the local conductivity is defined by adjacent sites and does not depend on the second neighbours. This unexpected result is related with quasi-one-dimensionality of the system [39,40].

The conductivity-temperature relation of link 1–2 strongly depends on parameter $(A_1 - A_2)^2$ (see Fig. 2). If you look at the curves in the region of 150 K (Fig. 2), then the upper curve corresponds with $(A_1 - A_2)^2 = 0.7$, medium with $(A_1 - A_2)^2 = 4$, bottom with $(A_1 - A_2)^2 = 10$. Fig. 2 shows that zone conductivity exists and decreases with temperature rise for small $(A_1 - A_2)^2$, and it may increase or decrease at low temperatures due to finiteness of the polymer fragment. This is related with the selection of one vibra-
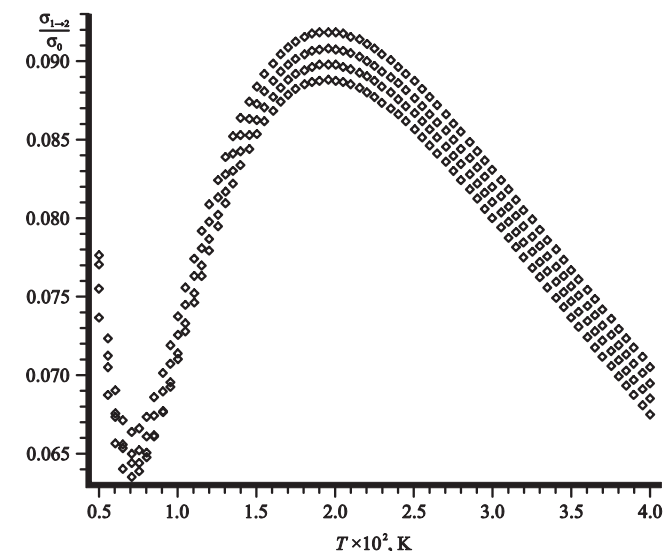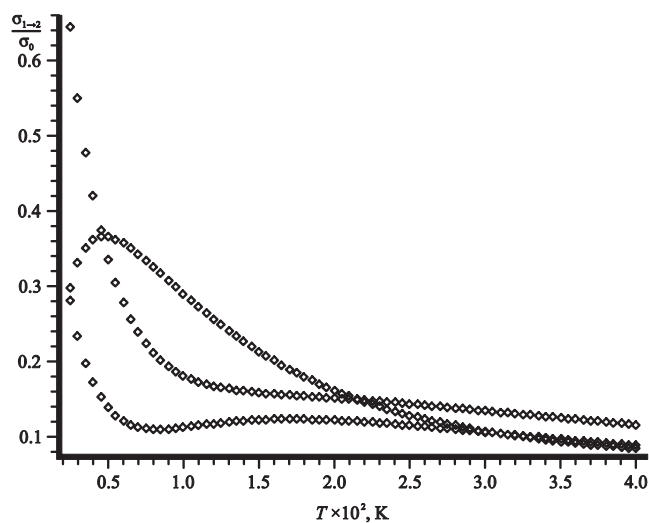

Fig. 2. The change of the temperature dependence of the local conductivity of 1–2 link on parameter $(A_1 - A_2)^2$ for number 1.

tion frequency and so the finite fragment does not allow achieving resonance of the initial and final states. Zone conductivity still exists for large $(A_1 - A_2)^2$ at low temperatures, but the possibility of hopping conductivity arises which increases with temperature then becomes determinative at some temperature, and also begins to decrease with temperature rise at high temperatures [41–43]. Numerical solution of the equation gives the same results as analytical solution [44]. The difference between the solutions is not significant. Therefore the dependence of hole mobility on temperature can be determined using analytical solution.

The diagram plotted from the numerical solutions of the equations qualitatively coincides with the diagram of analytical solution, but the quantitative difference between these diagrams is within 10%. Unlike the exact numerical solution the approximate analytical solution allows separation of the contributions to
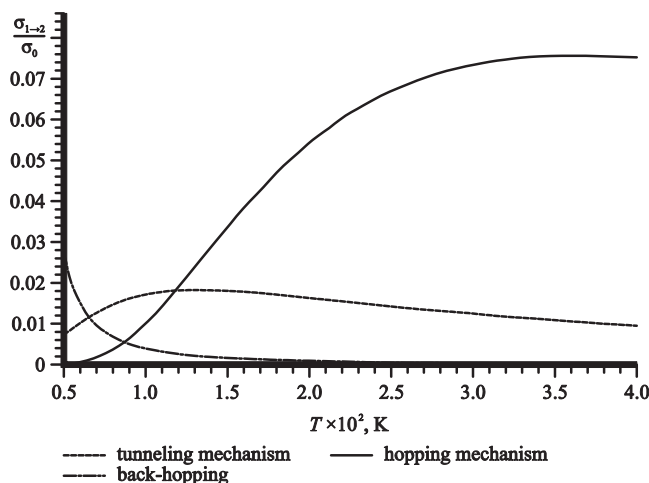

Fig. 1. The change of temperature dependence of the relative local conductivity of 1–2 link on parameters of nodes 0 and 3.

Fig. 3. Decomposition of the hole-transfer velocity by contributions from different mechanisms.

conductivity from different mechanisms [45,46] (Fig. 3). Conductivity caused by tunneling mechanism decreases with temperature rise because when the temperature increases the equality of the energies of the initial and final states, which is necessary for the tunneling process, is upset. Conductivity caused by the hopping mechanism increases with rising temperature, since the energy necessary to overcome the potential barrier by the charge carrier is obtained from thermal fluctuations. The probability of back-hopping or reflection from the barrier decreases with growing temperature.

6. Results and conclusion

The above method of obtaining the equations suitable for computational investigation of correlation functions (CF) is applicable for arbitrary systems including DNA and has an internal criterion of applicability. The analysis would be implemented taking into account CF of higher order for this purpose, and the relative correction would be determined to the previous specific-purpose result. It also allows identifying correlations that define the phenomenon (they are not necessarily two-particle or three-particle). The physical meaning of introduced functions $M_q^+(t)$, $M_q^-(t)$, $D_{q_1J_1;q_2J_2}^{+;-}(t)$, $D_{q_1J_1;q_2J_2}^{-;+}(t)$, $D_{q_1J_1;q_2J_2}^{+;+}(t)$, $D_{q_1J_1;q_2J_2}^{-;-}(t)$, etc., is introduction of the variables of self-consistent fields instead of operators under the sign of averaging. This leads to reducing of an infinite system of linear equations to an equivalent finite system of nonlinear equations. This allows making the best use of numerical solution methods. The proposed method allows considering non-exponential and non-monotonic change of CF with time. The idea to choose the self-consistent field is coming down to the fact that when the strong interaction takes place the field exerting effect on vibration of neighbouring particles from other particles is the same for the first and second particle and leads to additional correlation between particles. The results can be used in investigations of the mobility of charge carriers in a specially synthesized single-stranded nucleotide DNA and in investigations of the kinetic properties of DNA in living systems, where the parameters of the fragments are well known. Most interesting are the large-radius polarons, where new effects were discovered. Special experiments and modelling of processes are required for these systems. The mobility was found to depend strongly on fragment structure, temperature, method of polaron preparation (its velocity of travel along the chain), etc. The DNA system is heterogeneous in our case. The current is formed in a fragment by the energy absorbed from the electromagnetic field acting on the charge carriers in the medium. The energy levels are usually discrete in restricted isolated one-dimensional system. If interaction with the medium exists, they form a continuum with variable density of states described with Lorentzian curve. These non-monotonies reveal in conductivity and create an intricate picture of conductivity change caused by system parameters and external influences. There are also some slightly different approaches published [47–49].

The carrier mobility was ascertained to be determined mainly by neighbouring sites in heterogeneous DNA fragments. The mobility depends strongly on temperature and interaction parameters of electron and vibrational subsystems. Mobility results from three simultaneous processes changing the contribution according to temperature.

The scope of this work includes the qualitative behaviour of systems to identify capability of DNA fragments and the development of methods for property calculation. Both aims were attained. The DNA fragments have intricate but predictable dependence of conductivity behaviour on control parameters. It can be used if provided the study of the behaviour of each of the specific DNA fragment. The research and simulation technique

has been also developed and presented in this work. The effects of increasing or decreasing mobility of particles can be used in nanotechnologies for design of various nanodevices. They enable you to create nanoswitches, temperature controllers, temperature nanosensors, detectors of structure of the DNA fragments, the logical devices. A small-radius heteropolaron is considered in this work. But, the small-radius polaron cannot always be obtained. For example, it does not exist in (PolyG/PolyC) chain, which is not subject to Marcus theory. The Kubo formula describes the system behaviour in this situation. Application of DNA looks most promising. In this article, all the preparatory work has been carried out to formulate the problems of investigation of kinetic processes in the DNA fragments. So, there is obtained the closed system of equations for the current correlation functions, which can be solved numerically with estimated error of the discarded part of the system and considered corrections for the discarded members. The effect of backbone polarization on hole transfer in DNA is clarified.

References

[1] S.I. Kubarev, O.A. Ponomarev, The Effects of Dynamic Coupling in Statistical Physics, Nauka, Moscow, 1992 (in Russian).
[2] D.D. Eley, D.I. Spivey, Semiconductivity of organic substances. Part 9. -Nucleic acid in the dry state, Trans. Faraday Soc. 58 (1962) 411–415.
[3] M. Tubiana, J. Dutreix, A. Wambersie, Introduction to Radiobiology, Taylor & Francis, London, 1990.
[4] K. Frenkel, Carcinogen – mediated oxidant formation and oxidative DNA damage, Pharmacol. Ther. 53 (1992) 127–166.
[5] B.N. Ames, M.K. Shigenaga, T.M. Hagen, Oxidants, antioxidants and the degenerative diseases of aging, Proc. Natl. Acad. Sci. USA 90 (1993) 7915–7922.
[6] S.M.M. Conron, A.K. Thazhathveetil, M.R. Wasielewski, A.L. Burin, F.D. Lewis, Direct measurement of the dynamics of hole hopping in extended DNA G-tracts. An unbiased random walk, J. Am. Chem. Soc. 132 (2010) 14388–14390.
[7] M.A. Harris, A.K. Mishra, R.M. Young, K.E. Brown, M.R. Wasielewski, F.D. Lewis, Direct observation of the hole carriers in DNA photoinduced charge transport, J. Am. Chem. Soc. 138 (2016) 5491–5494.
[8] D. Becker, M.D. Sevilla, The chemical consequences of radiation damage to DNA, Adv. Radiat. Biol. 17 (1993) 121–180.
[9] M.G. Debije, M.T. Milano, W.A. Bernhard, DNA responds to ionizing radiation as an insulator, not as a "molecular wire", Angew. Chem. Int. Ed. 38 (1999) 2752–2756.
[10] M.E. Núñez, D.B. Hall, J.K. Barton, Long-range oxidative damage to DNA: effects of distance and sequence, Chem. Biol. 6, 85–97.
[11] A.M. Brun, A. Harriman, Dynamics of electron transfer between intercalated polycyclic molecules: effect of interspersed bases, J. Am. Chem. Soc. 114 (1992) 3656–3660.
[12] T.J. Meade, Electron transfer reactions through the DNA double helix, Met. Ions Biol. Syst. 32 (1996) 453–478.
[13] T.J. Meade, J.F. Kayyem, Electron transfer through DNA: site-specific modification of duplex DNA with ruthenium donors and acceptors, Angew. Chem., Int. Ed. Engl. 34 (1995) 352–354.
[14] S. Cluchi, S. Fratini, D. Mayou, Transient localization in crystalline organic semiconductors, Phys. Rev. B 83 (2011) 081202(R).
[15] Y. Zhang, C. Liu, A. Balaeff, S.S. Skourtis, D.N. Beratan, Biological charge transfer via flickering resonance, Proc. Natl. Acad. Sci. 111 (2014) 10049–10054.
[16] T. Hasegawa, J. Takeya, Organic field-effect transistors using single crystals, Sci. Technol. Adv. Mater. 10 (2009) 024314–024330.
[17] C.J. Murphy, M.R. Arkin, Y. Jenkins, N.D. Ghatlia, S.H. Bossmann, N.J. Turro, J.K. Barton, Long-range photoinduced electron transfer through a DNA helix, Science 262 (1993) 1025–1029.
[18] S.O. Kelley, J.K. Barton, Electron transfer between bases in double helical DNA, Science 283 (1999) 375–381.
[19] B. Giese, S. Wessely, M. Spormann, U. Lindemann, E. Meggers, M.E. Michel-Beyerle, On the mechanism of long-range electron transfer through DNA, Angew. Chem. Int. Ed. 38 (1999) 996–998.
[20] F.D. Lewis, X. Liu, J. Liu, S.E. Miller, R.T. Hayes, M.R. Wasielewski, Direct measurement of hole transport dynamics in DNA, Nature 406 (2000) 51–53.
[21] B. Giese, A. Biland, Recent developments of charge injection and charge transfer in DNA, Chem. Commun. (2002) 667–672.

[22] E. Meggers, M.E. Michel-Beyerle, B. Giese, Sequence dependent long range hole transport in DNA, J. Am. Chem. Soc. 120 (1998) 12950–12955.

[23] U. Lundin, R.H. McKenzie, Temperature dependence of polaronic transport through single molecules and quantum dots, Phys. Rev. B 66 (2002), 075303-075301-075303-075308.

[24] T. Holstein, Studies of polaron motion, Ann. Phys. 8 (1959) 325–342.

[25] T. Holstein, Studies of polaron motion, Ann. Phys. 8 (1959) 343–389.

[26] J.H. Schön, C. Kloc, B. Batlogg, Universal crossover from band to hopping conduction in molecular organic semiconductors, Phys. Rev. Lett. 86 (2001) 3843–3846.

[27] T. Sakanoue, H. Sirringhaus, Band-like temperature dependence of mobility in a solution-processed organic semiconductor, Nat. Mater. 9 (2010) 736–740.

[28] B.R. Landry, J.E. Subotnik, How to recover Marcus theory with fewest switches surface hopping: add just a touch of decoherence, J. Chem. Phys. 137 (2012) 22A513.

[29] R. Kubo, Statistical-mechanical theory of irreversible processes. I. General theory and simple applications to magnetic and conduction problems, J. Phys. Soc. Jpn. 12 (1957) 570–586.

[30] V.I. Klyatskin, Statistical Description of Dynamical Systems With Fluctuating Parameters, Nauka, Moscow, 1975 (in Russian).

[31] S.K. Min, F. Agostini, E.K.U. Gross, Coupled-trajectory quantum-classical approach to electronic decoherence in nonadiabatic processes, Phys. Rev. Lett. 115 (2015) 073001.

[32] L. Wang, D. Beljonne, Flexible surface hopping approach to model the crossover from hopping to band-like transport in organic crystals, J. Phys. Chem. Lett. 4 (2013) 1888–1894.

[33] W. Si, C.-Q. Wu, Decoherence and energy relaxation in the quantum-classical dynamics for charge transport in organic semiconducting crystals: an instantaneous decoherence correction approach, J. Chem. Phys. 143 (2015) 024103.

[34] J. Lee, J.W. Chung, D.H. Kim, B.-L. Lee, J.-I. Park, S. Lee, R. Häusermann, B. Batlogg, S.-S. Lee, I. Choi, I.W. Kim, M.S. Kang, Thin films of highly planar semiconductor polymers exhibiting band-like transport at room temperature, J. Am. Chem. Soc. 137 (2015) 7990–7993.

[35] S.I. Kubarev, O.A. Ponomarev, The non-simultaneous decoupling method for correlation functions, Phys. Lett. 26 (1968) 633–634.

[36] P.C. Martin, J. Schwinger, Theory of many-particle systems. I, Phys. Rev. 115 (1959) 1342–1373.

[37] P. Feynman, Statistical Mechanics, Massachusetts Institute of Technology, 1972.

[38] N.N. Bogolyubov, Lectures on Quantum Statistics, Radyanska Shkola, Kiev, 1949 (in Russian).

[39] D. Golež, J. Bonča, L. Vidmar, S.A. Trugman, Relaxation dynamics of the Holstein polaron, Phys. Rev. Lett. 109 (2012) 236402.

[40] A.K.C. Cheung, M. Berciu, Phonon-assisted carrier motion on the Wannier-Stark ladder, Phys. Rev. B 88 (2013) 035132.

[41] E.M. Conwell, Charge transport in DNA in solution: the role of polarons, Proc. Natl. Acad. Sci. USA 102 (2005) 8795–8799.

[42] S. Longhi, Low-frequency anomalies in dynamic localization, J. Phys.: Condens. Matter 26 (2014) 255504.

[43] I.K. Kominis, Quantum measurement corrections to CIDNP in photosynthetic reaction centers, New J. Phys. 15 (2013) 075017.

[44] S. Yang, P. Liu, S. Guo, L. Zhang, D. Yang, Y. Jiang, B. Zou, Negative differential resistance phenomena in colloidal quantum dots-based organic light-emitting diodes, Appl. Phys. Lett. 104 (2014) 033301.

[45] J. Dong, W. Si, C.-Q. Wu, Drift of charge carriers in crystalline organic semiconductors, J. Chem. Phys. 144 (2016) 144905.

[46] L. Wang, D. Beljonne, Charge transport in organic semiconductors: assessment of the mean field theory in the hopping reg, J. Chem. Phys. 139 (2013) 064316.

[47] C. Liu, D.N. Beratan, P. Zhang, Coarse-grained theory of biological charge transfer with spatially and temporally correlated noise, J. Phys. Chem. B 120 (2016) 3624–3633.

[48] C. Liu, L. Xiang, Y. Zhang, P. Zhang, D.N. Beratan, Y. Li, N. Tao, Engineering nanometre-scale coherence in soft matter, Nat. Chem. 8 (2016) 941–945.

[49] R.M. Young, A.P.N. Singh, A.K. Thazhathveetil, V.Y. Cho, Y. Zhang, N. Renaud, F.C. Grozema, D.N. Beratan, M.A. Ratner, G.C. Schatz, Y.A. Berlin, F.D. Lewis, M.R. Wasielewski, Charge transport across DNA-based three-way junctions, J. Am. Chem. Soc. 137 (2015) 5113–5122.