



Study of DNA conducting properties: Reversible and irreversible evolution

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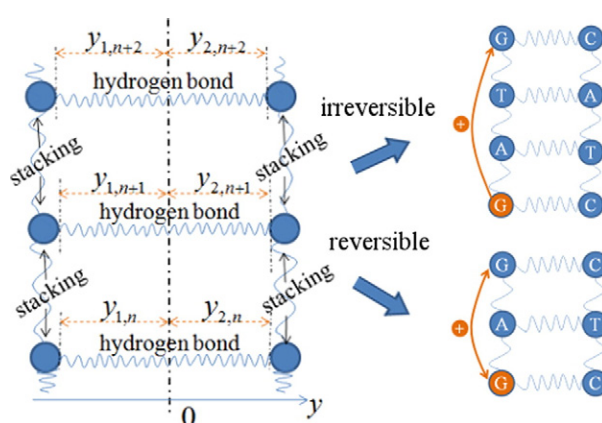
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HIGHLIGHTS

- The hole transport through DNA base sequences was modeled.
- The hopping and superexchange transfer mechanisms were discussed.
- The reversible and irreversible dynamics of the hole were described.
- Distance dependence of the hole transport relative rate was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

A hole transport through DNA base sequences was modeled. The fact that DNA consists of two polynucleotide strands was taken into consideration. Specific DNA base locations are determined in the model. The model predicts the behavior of a hole acting on the DNA chain, taking into account reversible and irreversible dynamics. It was shown that the transfer mechanisms depend on the sequence type and can be either of hopping nature or of superexchange one. Distance dependence of the hole transport relative rate on the number of hopping steps was investigated. The results obtained were compared with the experimental data. The investigation demonstrates the utilization of the formalism in practical problems for description of the charge migration through the different molecular sequences.

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1. Introduction

The idea of DNA having charge conducting properties has already been discussed for quite a while and proved in many experimental works [1–9]. Theoretically, different approaches modeling a charge transfer dynamics through DNA were suggested, among which there were polaronic transport [10–13], soliton-like dynamics [14],

superexchange and multistep hopping [15–19]. However, the problem of modeling a charge transfer through DNA still remains to be solved. It is first of all connected with the complexity of constructing a realistic mathematical model due to a large number of factors responsible for the charge transfer being involved.

As a rule, two sets of parameters are used to describe the process of a charge migrating through a DNA chain. The first one is that of ionization potentials – onsite base energies ϵ_n which determine the energy profile of DNA's strands. At present, it is known that guanine (G) possesses the smallest ionization potential, it being roughly speaking by 0.4–0.45 eV

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less than that of adenine (A) and by 0.7–1.5 eV less than those of cytosine (C) and thymine (T). That is why the migrating hole is most likely to locate on guanines and adenines rather than on thymines or cytosines. The second important energy parameter is the coupling matrix elements $\nu_{n,m}$ which determine the rate of charge transport between donor n and acceptor m nucleobases. Both ionization potentials and coupling matrix elements are not static values. They are gated by the structure and dynamics of DNA as well as by the DNA interaction with the environment (solvent) [20–22]. Thus, Kubar and co-authors determine several factors responsible for the charge transfer in DNA: 1) the environment factors, i.e., the electrostatic interaction of the charge with the remainder of DNA and solvent, the fluctuation of counterions; the DNA base fluctuation leading to the oscillations of ionization potentials in the order of 0.4 eV which has a crucial impact on the energy profile of the DNA's strands; 2) correlations between the onsite energies of neighboring bases which lead to the conformational gating type charge transport mechanism; 3) coupling matrix elements depend on DNA conformation and mutual base arrangement – twist, rise, stretch, etc. – and they are not affected by the solvent.

The hole migration process can be described by mean of a tight-binding Hamiltonian,

$$\mathcal{H}_Q = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{n \neq m} \nu_{n,m} |n\rangle\langle m|, \quad (1)$$

where the ionization potentials ϵ_n and coupling matrix elements $\nu_{n,m}$ are taken into account.

DNA models can be divided into several levels of complexity [23,24]. In the first level models, DNA is presented as an elastic rod or as disks bound together [25]. More complex models – those of the second level – make allowance for the fact that a DNA molecule consists of two polynucleotide strands. Here, each strand is modeled as an elastic rod or interconnected disks [26–29]. The third level models take additional details of either of DNA polynucleotide strands into consideration. Bonds inside atomic groups – bases, sugars, and phosphates – are considered [30]. In the fourth level models, a pair of nucleotides forms a DNA cell which is periodically reiterated through a DNA molecule making so-called lattice models [31]. The fifth level models make allowance for the most possible exact details [20–22,32].

The process of modeling a charged microparticle migration is of radically different kind from describing a DNA macromolecule dynamics because the former is in essence a quantum object. It has been found experimentally that the charge migration through the DNA chain can present two opposite processes: charge transport is reversible as in the experiments of Lewis et al. [3]. On the other hand, charge transport could be irreversible process as in the experiments of Giese et al. [1,2]. Today, there is no standard method to include irreversible dynamics in the theory. The description of the irreversibility is impossible on the basis of the classical laws of dynamics, since the latter are reversible in time [33]. For the same reason the exact description of irreversibility on the basis of fundamental quantum theory is impossible as well. It is a complex theoretic problem in itself.

As a rule, the irreversible evolution is described on the basis of different physical approximations such as the Pauli master equation, kinetic approaches, the Lindblad axiomatic formalism [13,34–37], and harmonic bath approach [12,13]. In the latter case polaron transport through DNA was investigated. In these cases of coarse-graining approximations, the distinction between an open system and its environment is used. Moreover the Feynman path-integral approach in the dissipative quantum mechanics is one of the interesting and constructively developed method for describing quantum dissipative systems [38–40].

The problem of describing irreversibility is currently being widely discussed in the literature [41–45], it being closely connected with the

investigation of such processes as decoherence in the biomolecular systems [34,42]; nuclear systems [43,44]; providing a theoretic basis for describing quantum computations [45], for which the reversibility/irreversibility problem is crucial. In this connection, selecting an appropriate system, or medium, or basis for conducting this kind of research is of vital importance. That is why building up a theory which could effectively describe the irreversible as well as reversible evolution processes on a unified basis is essential in this case.

One of the possible solutions to this problem can be achieved on the basis of the mixed quantum-classical nonlinear model, in which the charge migration through a base sequence is described by the Schroedinger equation, with DNA being considered as a classical object governed by the Hamilton equations [17,19,46].

In the paper, the charge evolution is determined on the basis of a tight-binding Hamiltonian (Eq. (1)), with coupling matrix elements $\nu_{n,m}$ being static and time-independent while ionization potentials ϵ_n being dynamic and determined by the dynamics of DNA as well as the DNA–environment interaction. In this case, the paper represents the ionization potentials as a sum $\epsilon_n = \alpha_n^0 + \alpha'_n r_n$ where the first term is static and corresponds to the ionization potentials of a separate base while the second one is dynamic and can depend on a number of reasons mentioned above. In this case α'_n being the constant of the relationship between the charge and shift r_n of the n -base. In our model the value of r_n depends on the viscosity of the surrounding DNA environment. DNA is viewed as a macroobject governed by one of the classical models [25–28].

The aim of our work consists in developing model that could predict the behavior of hole acting on the DNA chain, taking into account reversible and irreversible dynamics. We investigate the hole–DNA interaction on the basis of a quantum-classical nonlinear, double-stranded model. The fact that a DNA molecule is formed by two polynucleotide strands is taken into consideration. Stacking interactions through either DNA strand are also accounted for, and the hydrogen bonds are determined. The model clearly determines positions of separate DNA bases. Based on the model, results were obtained for a hole migration through DNA base sequences, such as GATGGG, GATGTGGG, GTTGGG, GTTGTGGG, and GTTGTTGTGGG.

The obtained relative transport rate values were compared with the experimental results [1] and [2]. Dependence of the relative rate $k_{CT,rel}$ of hole transport [2] on the number of hopping steps N

$$\ln k_{CT,rel} \approx -\eta \ln N \quad (2)$$

is discussed.

The work is organized as follows. In Section 2 the nonlinear double-stranded model is determined. In Section 3 we examine the nonlinear hole dynamics acting on the DNA chain. In Conclusion the results of the work are discussed in brief.

2. Model

\mathcal{H}_{Cl} model Hamiltonian presents a DNA macromolecule formed by two flowing strands (Fig. 1)

$$\mathcal{H}_{Cl} = \sum_n \left[M \frac{\dot{y}_{1,n}^2}{2} + M \frac{\dot{y}_{2,n}^2}{2} + k_h \frac{(y_{1,n} - y_{2,n} + l)^2}{2} + k_v \frac{(y_{1,n} - y_{1,n-1})^2}{2} + k_v \frac{(y_{2,n} - y_{2,n-1})^2}{2} \right], \quad (3)$$

with the first and second terms corresponding to the kinetic energy of the bases located on two different DNA strands with the coordinates of $y_{1,n}$ and $y_{2,n}$. We proceed from the assumption that $y_{1,n} < 0$ and $y_{2,n} > 0$. The bases are coupled together with hydrogen bonds, which are modeled by the third term. The last two terms form stacking interaction through each DNA strand. The DNA parameters are: M – effective base mass, k_h and k_v are force constants; l – horizontal

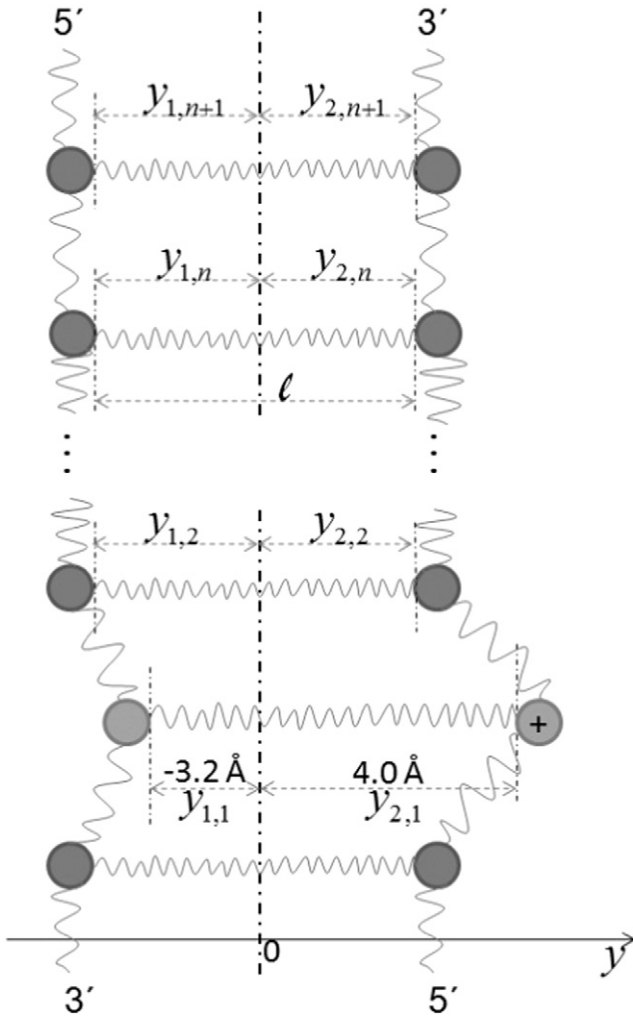


Fig. 1. DNA model at the initial time.

distance between the bases in equilibrium. The summation in expression (3) is over the number of base pairs in the strand under consideration.

\mathcal{H}_Q Hamiltonian determines the properties of the hole located on the bases in the state of $|n\rangle > |m\rangle$, where Dirac designation of a charged particle state was used. In this instance, the shift r_n is represented as $r_n = (y_{1,n} - y_{2,n} + l)$.

$$\mathcal{H}_Q = \sum_n \alpha_n^0 |n\rangle \langle n| + \sum_n \alpha'_n (y_{1,n} - y_{2,n} + l) |n\rangle \langle n| + \sum_{n \neq m} \nu_{n,m} |n\rangle \langle m|. \quad (4)$$

Thus, we consider the hole as a quantum object whose energy ϵ_n depends on the ionization potential value as a dynamic one changing with time and which consequently depends on the mutual arrangement of base pairs in a DNA strand and is a variable and changes depending on the environment as well as on DNA's dynamic ones determined by the Hamiltonian \mathcal{H}_{Cl} (Eq. (3)). The presence of the charge on one of the bases should apparently result in deforming the DNA structure. Taking into account the last fact, we assume that the bases of the G(+) – C pair had the coordinates $y_1 = 3.2 \text{ \AA}$ and $y_2 = 4.0 \text{ \AA}$ at the initial time (Fig. 1).

Let us restate Hamiltonians (3) and (4) by introducing new coordinates $x_{1,n}$ and $x_{2,n}$

$$x_{1,n} = \frac{y_{1,n} + y_{2,n}}{\sqrt{2}}, \quad x_{2,n} = \frac{y_{1,n} - y_{2,n}}{\sqrt{2}}. \quad (5)$$

Then, expressions for Hamiltonians (3) and (4) can be presented as

$$\mathcal{H}_{Cl} = \sum_n \left[M \frac{\dot{x}_{1,n}^2 + \dot{x}_{2,n}^2}{2} + k_h \frac{(\sqrt{2}x_{2,n} + l)^2}{2} + k_v \frac{(x_{1,n} - x_{1,n-1})^2 + (x_{2,n} - x_{2,n-1})^2}{2} \right], \quad (6)$$

$$\mathcal{H}_Q = \sum_n \alpha_n^0 |n\rangle \langle n| + \sum_n \alpha'_n (\sqrt{2}x_{2,n} + l) |n\rangle \langle n| + \sum_{n \neq m} \nu_{n,m} |n\rangle \langle m|. \quad (7)$$

In the new coordinates, expression (6) can be easily divided into a sum of terms, some of which depend on $x_{1,n}$ variable while the others are $x_{2,n}$ -dependent. In this case, Hamiltonian (7) only depends on $x_{2,n}$ variable. This new Hamiltonian's property will be used later on.

The dynamics of the charged particle is determined by the Schroedinger equation,

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \mathcal{H}_Q |\psi\rangle, \quad (8)$$

with $|\psi\rangle$ being a particle wave function. We will seek the solution to the Schroedinger Eq. (8) as

$$|\psi\rangle = \sum_n b_n(t) |n\rangle. \quad (9)$$

In expression (9), the coefficient $b_n(t)$ depends on time, while its squared module determines the probability of the charge location at the t moment on an n -base. Substituting the wave function (Eq. (9)) for the Schroedinger equation, the latter reduces to the equation which determines the temporal evolution of the coefficient $b_n(t)$

$$i\hbar \frac{\partial b_n(t)}{\partial t} = b_n(t) \alpha_n^0 + \sum_{m(n \neq m)} b_m(t) \nu_{n,m} + \alpha'_n b_n(t) (\sqrt{2}x_{2,n} + l). \quad (10)$$

The expression obtained can be reworked with the help of the nearest neighbor approximation. In this approximation, it is assumed that an n -base interacts vertically with the nearest neighboring $n - 1$ and $n + 1$ base sequence. In the nearest neighbor approximation, we will have

$$i\hbar \frac{\partial b_n(t)}{\partial t} = -i \left[b_n(t) \alpha_n^0 + \alpha'_n b_n(t) (\sqrt{2}x_{2,n} + l) + b_{n-1}(t) \nu_{n,n-1} + b_{n+1}(t) \nu_{n,n+1} \right]. \quad (11)$$

Let us introduce new undimensional parameters $\eta_n, n_{n,m}, \tilde{\epsilon}, \omega, \kappa$ and β , having dimensionality of length [17], which are related to Hamiltonian (7) parameters by the equalities

$$\alpha_n^0 = \frac{\hbar}{\tau} \eta_n; \quad \nu_{n,m} = \frac{\hbar}{\tau} \eta_{n,m}; \quad \alpha'_n = \frac{\beta M}{\tau^2}; \quad \kappa \omega^2 = \frac{\tau^3 \alpha_n'^2}{\hbar M}; \quad t = \tau \tilde{t}. \quad (12)$$

In equalities (Eq. (12)), the parameter $\tau = 10^{-14} \text{ s}$, $\omega^2 = \tau^2 \frac{k_h}{M}$.

Then, with the help of relationship (12), expression (11) is restated as

$$\frac{\partial b_n(t)}{\partial \tilde{t}} = -i \left[b_n(t) \eta_n + b_{n-1}(t) \eta_{n,n-1} + b_{n+1}(t) \eta_{n,n+1} + 2\kappa \omega^2 b_n(t) z_n \right], \quad (13)$$

where undimensional variable z_n is determined as follows $z_n = u_n + u_0$, with $u_0 = \frac{l}{2\beta}$, $u_n = \frac{x_{2,n}}{\sqrt{2}\beta}$.

Applying the Hamilton approach, a system of equations describing the dynamics of the DNA-charged particle interaction can be determined by expression (13), and Hamilton equation:

$$\frac{\partial p_n}{\partial t} = -\frac{\partial \mathcal{H}}{\partial y_n} + F_n, \quad (14)$$

with p_n being an n -base impulse; \mathcal{H} being a full Hamiltonian, and F_n being a damping term. The damping term for n -base can be determined as $F_n = -\gamma \frac{\partial y_n}{\partial t}$, where γ is the damping coefficient. The interaction of DNA with environment leads to energy dissipation. The Hamiltonian for dissipative system, in particular, can be written in the Caldirola–Kanai form $H = \exp(-\gamma t/M) p^2/2M + \exp(\gamma t/M) V$ [47], where the first-kinetic term is damped in the time, and the second-potential term is larger. As it was shown in the work [48] the damping term which has been put by hand (as in our case) is nothing else than the contribution of a damped kinetic term governed by the Caldirola–Kanai Hamiltonian. Thus, we determine our model with the dissipative effect on the basis of the Caldirola–Kanai approach.

The full DNA-charge Hamiltonian in expression (14) is determined as a sum of two terms

$$\mathcal{H} = \mathcal{H}_{Cl} + \langle \psi | \mathcal{H}_Q | \psi \rangle, \quad (15)$$

where the first-classical-part being determined by expression (6) while the second one – the matrix element of operator (7) – by a charged particle quantum dynamics. Taking into account expressions (7) and (9) for the matrix element, we can write down

$$\begin{aligned} \langle \psi | \mathcal{H}_Q | \psi \rangle = & \sum_n |b_n(t)|^2 \alpha_n^0 + \sum_n |b_n(t)|^2 \alpha'_n (\sqrt{2}x_{2,n} + l) \\ & + \sum_n (\nu_{n,n+1} b_n^*(t) b_{n+1}(t) + \nu_{n,n-1} b_n^*(t) b_{n-1}(t)). \end{aligned} \quad (16)$$

Hamiltonian's equations for the bases located on the either of the strands are as follows,

$$M \frac{\partial^2 y_{1,n}}{\partial t^2} = -\frac{\partial \mathcal{H}}{\partial y_{1,n}} - \gamma \frac{\partial y_{1,n}}{\partial t}, \quad (17)$$

$$M \frac{\partial^2 y_{2,n}}{\partial t^2} = -\frac{\partial \mathcal{H}}{\partial y_{2,n}} - \gamma \frac{\partial y_{2,n}}{\partial t}. \quad (18)$$

Eqs. (17) and (18) can be redefined by introducing $x_{1,n}$ and $x_{2,n}$. After a number of simple transformations (Appendix A) we obtain

$$M \frac{\partial^2 x_{1,n}}{\partial t^2} = -\frac{\partial \mathcal{H}(x_{1,n})}{\partial x_{1,n}} - \gamma \frac{\partial x_{1,n}}{\partial t}, \quad (19)$$

$$M \frac{\partial^2 x_{2,n}}{\partial t^2} = -\frac{\partial \mathcal{H}(x_{2,n})}{\partial x_{2,n}} - \gamma \frac{\partial x_{2,n}}{\partial t}, \quad (20)$$

with $\mathcal{H}(x_{1,n})$ and $\mathcal{H}(x_{2,n})$ Hamiltonians depending on different variables and appearing as

$$\mathcal{H}(x_{1,n}) = \sum_n \left[M \frac{\dot{x}_{1,n}^2}{2} + k_v \frac{(x_{1,n} - x_{1,n-1})^2}{2} \right], \quad (21)$$

$$\mathcal{H}(x_{2,n}) = \sum_n \left[M \frac{\dot{x}_{2,n}^2}{2} + k_v \frac{(x_{2,n} - x_{2,n-1})^2}{2} + k_n \frac{(\sqrt{2}x_{2,n} + l)^2}{2} \right] + \langle \psi | \mathcal{H}_Q | \psi \rangle. \quad (22)$$

While calculating Hamiltonian derivatives (Appendix A) the system of equations defining the DNA-charge dynamics may be written as

$$\frac{\partial b_n(t)}{\partial t} = -i \left[b_n(t) \eta_n + b_{n-1}(t) \eta_{n,n-1} + b_{n+1}(t) \eta_{n,n+1} + 2k\omega^2 b_n(t) z_n \right], \quad (23)$$

$$\frac{\partial^2 z_n}{\partial t^2} = \omega_v^2 (z_{n,n+1} - 2z_n + z_{n,n-1}) - |b_n(t)|^2 - 2\omega^2 z_n - \omega' \frac{\partial z_n}{\partial t}, \quad (24)$$

$$\frac{\partial^2 x_{1,n}}{\partial t^2} = \omega_v^2 (x_{1,n+1} - 2x_{1,n} + x_{1,n-1}) - \omega' \frac{\partial x_{1,n}}{\partial t}, \quad (25)$$

where undimensional frequency constants ω_v and ω' appearing as $\omega_v^2 = \tau^2 \frac{k_v}{M}$, $\omega' = \tau \frac{\gamma}{M}$.

The first three terms in expression (23) determine the reversible charge dynamics, while the charge interaction with DNA (the second term in Eq. (4)) leads to the fourth term. Thus, the charge evolution is described as the competition between two contributions that results in reversible or irreversible process.

As has been noted in the paper, introducing undimensional parameters (Eq. (12)) permits to reduce the Schroedinger Eq. (11) to the form of Eq. (23). In this instance, the ionization potentials ϵ_n which were initially determined by the expression $\epsilon_n = \alpha_n^0 + \alpha'_n (y_{1,n} - y_{2,n} + l)$, reduce to the undimensional sum $\eta_n + 2k\omega^2 z_n$, the second term of which is of dynamic nature and determines the Schroedinger equation's relationship with the DNA dynamics and the environment. It is this term that makes an impact on the nature of the hole evolution. The smaller it is in expression (23), the more reversible the hole evolution becomes. With the latter increasing, the hole evolution becomes irreversible in character.

The mutual influence of the two micro- and macrosystems in the model is determined by the second Eq. (24) as well, where the relationship between the charge (quantum) and DNA (classical) dynamics is determined. Eq. (24) describes the base shift with dissipative effect (the last term).

The third Eq. (25) corresponds to the classical $x_{1,n}$ value dynamics with the damping term.

3. Nonlinear hole dynamics

In accordance with experimental works [1] and [2], we investigate a hole migration through a DNA strand by the example of base sequences $G(+)$ ATGGG, $G(+)$ ATGTGGG, $G(+)$ TGGG, $G(+)$ TGTGGG, and $G(+)$ TGTGTGTGGG. It is assumed that the hole is located on guanine $G(+)$ base at the initial time. Thus, the $G(+)$ –C pair is displaced horizontally from equilibrium at the initial time (Fig. 1). The following model parameters were used in the study: the guanine energy $\alpha_G^0 = 1.24$ eV; the adenine energy $\alpha_A^0 = 1.69$ eV; the thymine energy $\alpha_T^0 = 1.90$ eV [8], $k_v = 2.50 \times 10^{-2}$ eV/Å², $k_n = 4.90 \times 10^{-3}$ eV/Å²; the base effective mass $M = 2.51 \times 10^{-25}$ kg [23,24,49], $\omega' = 4.50 \times 10^{-3}$ (see, for instance, the works [17,29,50,51]). In the position of equilibrium, the average distance l between the complementary base centers amounted to 7 Å. The matrix element values $\nu_{n,m}$ were averaged for all n,m base types and assumed to be equal to 0.12 eV. Certainly, the values of $\nu_{n,m}$ are different for the different n,m transitions. As have been shown by many calculations (for the more comprehensive data set, see [22,52–54]), the matrix elements could differ, depending on the nucleobase types and the relative nucleobase positions on the DNA strand. But as will be shown in our work the value 0.12 eV is a good approximation for the study of the nonlinear hole dynamics on the basis of the experimental results under consideration within the context of this paper.

Table 1

κ constant values and correspondent α' values for the different base sequences (see for comparison [19,46,50,51,56]).

Sequences	κ	α' (eV/Å)
GATGGG	16.50	7.31×10^{-2}
GATGTGGG	27.70	9.47×10^{-2}
GTTGGG	10.41	5.81×10^{-2}
GTTGTGGG	16.49	7.31×10^{-2}
GTTGTGTGTGGG	13.32	6.57×10^{-2}

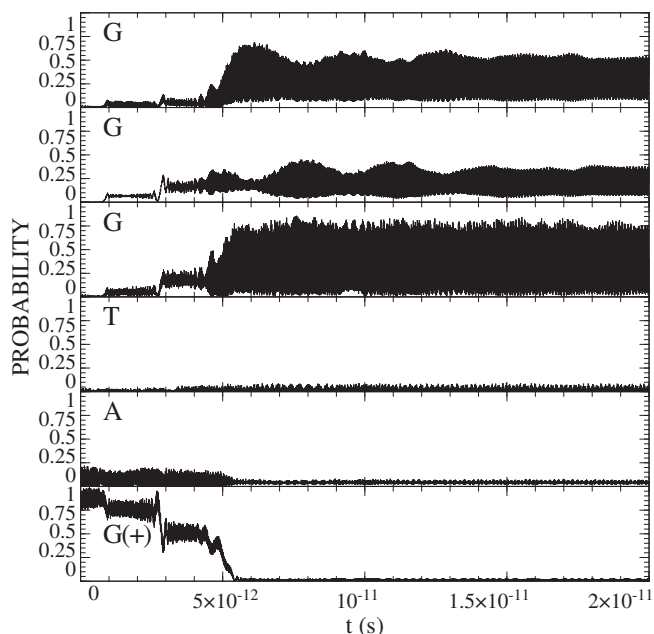


Fig. 2. Time-dependent probable hole location on the bases of the G(+)ATGGG sequence.

We selected the constant κ (Eq. (23)) so that the results of simulation will be in the best compliance with experiments [1] and [2] (Tables 1 and 2)).

All the computations in the present paper are numerical. The system of differential Eqs. (23)–(25) was solved on the basis of the Runge–Kutta method of 4–5 order. The precision control was exercised to suit the requirement $\left| \sum_n |b_n|^2 - 1 \right| < 5.00 \times 10^{-5}$.

Consider the results of solving the system of differential Eqs. (23)–(25).

Fig. 2 shows the probable hole location $|b_n(t)|^2$ on the bases of the sequence G(+)ATGGG (from the bottom upwards, respectively). In this case, 5.41×10^{-12} s later, the probability of the hole location on the first guanine falls considerably whereas the one of its location on the second, third, and fourth guanine rises. The probabilities of the charge location on the adenine and thymine are very low during the whole period of time. The charge is localized on the three following guanines oscillating between them. Since adenine's and thymine's ionization potentials are higher than a guanine's, they present a possible barrier to the hole migration. However, the hole migrates to guanines, whose ionization potentials are lower. The hole hops from the guanine G(+) to the guanines GGG, bypassing adenine and thymine. In this case result demonstrates irreversible hole dynamics being in a good agreement with the conclusions of the work [1]. We have a one-step hole transfer via a superexchange mechanism between G(+) and GGG bases.

Fig. 3 shows the dynamics of the hole–sequence G(+)ATGTGGG interaction. Here, initially we have the reversible process. The hole oscillates between the first two guanines, bypassing the adenine and thymine. Then 3.41×10^{-12} s later, it migrates to the second guanine and remains there for a short period of time. The process

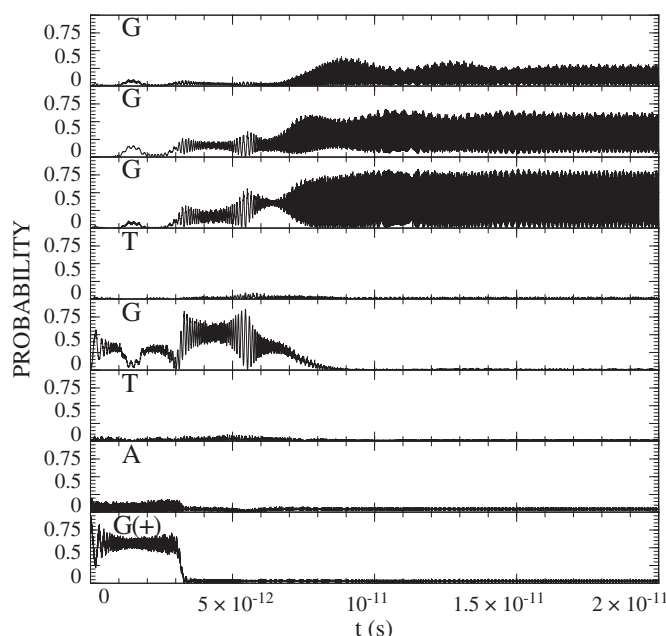


Fig. 3. Time-dependent probable hole location on the bases of the G(+)ATGTGGG sequence.

becomes irreversible in 8.00×10^{-12} s, after which the hole migrates to the GGG unit, bypassing the last thymine of the sequence. Here, we deal with a hopping mechanism, which correlates well with the experiment under consideration.

We defined the absolute transfer rate k_i for each i -th sequence, as the reciprocal of the migration time t of the hole from the guanine G(+) to GGG (Table 2). The direct comparison of the k_i values we obtained with those in works [1] and [2] is impossible since here a measurement of relative transfer rates $k_{CT,rel}$ for each sequence rather than absolute transfer rates k_i was taken through k_i comparison with k_{H_2O} . The latter, indicates the absolute rate of the H_2O reaction with the strand.

Let the ratio k_i/k_{H_2O} be a relative rate $k_{CT,rel}$. In our case we will determine the relative transfer rates k_{theor} taking up the sequence G(+)ATGGG as a reference sequence (see, for instance, Ref. [55]), the

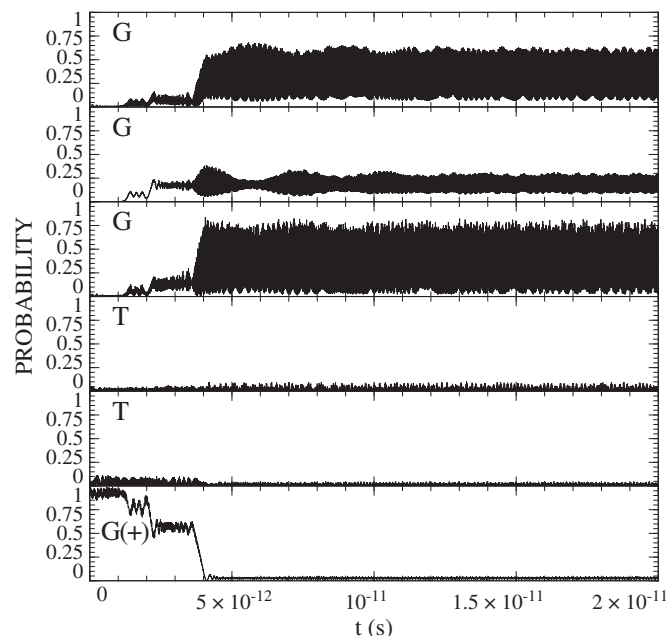


Fig. 4. Time-dependent probable hole location on the bases of the G(+)ITGGG sequence.

Table 2
Absolute k_i (s^{-1}) and relative transfer rates for the different base sequences: experimental [1,2] $k_{CT,rel}$ values and our results k_{theor} .

Sequences	k_i (s^{-1})	$k_{CT,rel}$ [1,2]	k_{theor}
GATGGG	1.85×10^{11}	3.20	3.20
GATGTGGG	1.25×10^{11}	3.40	2.16
GTGGG	2.45×10^{11}	8.90	4.24
GTGTGGG	1.49×10^{11}	2.80	2.58
GTGTGTGGG	6.25×10^{10}	0.88	1.08

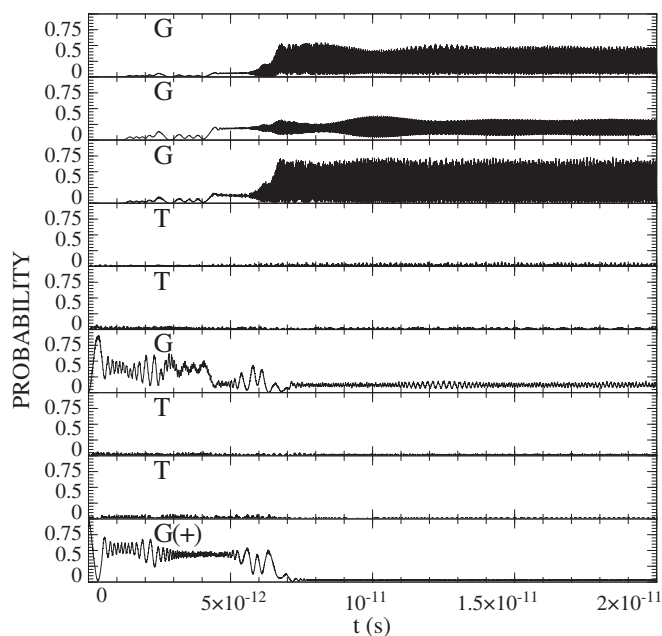


Fig. 5. Time-dependent probable hole location on the G(+)/TTGTTGGG sequence.

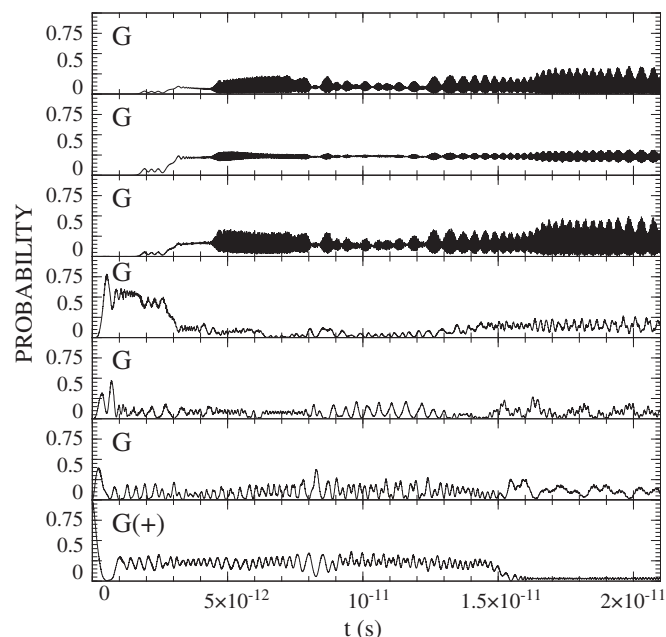


Fig. 6. Time-dependent probable hole location on the G bases of the G(+)/TTGTTGGTGGG sequence.

absolute transfer rate value $k_{G(+)/ATGGG}$ of which was selected as equal to $1.85 \times 10^{11} \text{ s}^{-1}$. Using the $k_{CT,rel} = k_i/k_{H_2O}$, determination, we obtain $k_{theor} = 3.20k_i/k_{G(+)/ATGGG}$, with the value 3.20 being the relative rate $k_{CT,rel} = k_{G(+)/ATGGG}/k_{H_2O}$ for the G(+)/ATGGG sequence from the work [1]. Table 2 shows the obtained values k_{theor} as compared to the experimental results $k_{CT,rel}$ [1,2].

Consider next a hole transfer dynamics through G(+)/TTGGG, G(+)/TTGTTGGG, and G(+)/TTGTTGGTGGG sequences (Figs. 4, 5, and 6). In the latter figure, only bases – guanines – on which the hole is localized while migrating are represented. The hole transfer is seen to be well-described by a superexchange, irreversible model for G(+)/TTGGG sequence (Fig. 4) and by a two- and four-hopping-step irreversible model in the cases of G(+)/TTGTTGGG (Fig. 5), and G(+)/TTGTTGGTGGG (Fig. 6) sequences. Following Eq. (2) the number of hopping steps N has the value of 1 and 2 for the strands G(+)/TTGGG and G(+)/TTGTTGGG, or 4 for the strand G(+)/TTGTTGGTGGG. In this case the calculation results for the relative rate k_{theor} obtained within the framework of our model are seen (Table 2) to be in good agreement with the experimental data of the work [2], Eq. (2) for $\eta = 1.7 \pm 0.2$.

4. Conclusion

The reversible and irreversible dynamics of hole acting on the DNA chain were described. Thus, the direction of the evolution process – reversible/irreversible evolution – depends on the base energy fluctuations and is dynamic in character.

The model considered above leads to the results which are in good agreement with the experiments [1] and [2] on the hole transfer through the DNA base sequences. The rate values k_{theor} obtained in the work correlate with the experimental data in order of magnitude. In accordance with the experiment, the hole transfer mechanisms were determined as the superexchange mechanism – the sequences GATGGG and GTTGGG, and the hopping mechanism – the sequences GTTGTGGG, GTTGTGTGGG, and GATGTGGG. The dynamics of the hole evolution through DNA in the cases GTTGGG, GTTGTGGG, and GTTGTGTGGG sequences corresponds to Eq. (2).

We assume that the investigation demonstrates the utilization of the formalism in practical problems for the study of charge migration through different molecular sequences that may be tested in experiments.

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Appendix A. Derivation of the expressions

Adding the left and right parts of expressions (17) and (18) we will have

$$M \frac{\partial}{\partial t} (\dot{y}_{1,n} + \dot{y}_{2,n}) = - \left(\frac{\partial}{\partial y_{1,n}} + \frac{\partial}{\partial y_{2,n}} \right) \mathcal{H} - \gamma \frac{\partial}{\partial t} (y_{1,n} + y_{2,n}). \quad (\text{A.1})$$

Rearranging

$$\begin{aligned} \left(\frac{\partial}{\partial y_{1,n}} + \frac{\partial}{\partial y_{2,n}} \right) \mathcal{H} &= \left(\frac{\partial x_{1,n}}{\partial y_{1,n}} + \frac{\partial x_{1,n}}{\partial y_{2,n}} \right) \frac{\partial}{\partial x_{1,n}} \mathcal{H} \\ &+ \left(\frac{\partial x_{2,n}}{\partial y_{1,n}} + \frac{\partial x_{2,n}}{\partial y_{2,n}} \right) \frac{\partial}{\partial x_{2,n}} \mathcal{H} \\ &= \sqrt{2} \frac{\partial}{\partial x_{1,n}} \mathcal{H}(x_{1,n}) \end{aligned} \quad (\text{A.2})$$

and using expression (5) we derive Eq. (19). Subtracting Eq. (18) from (17)

$$M \frac{\partial}{\partial t} (\dot{y}_{1,n} - \dot{y}_{2,n}) = - \left(\frac{\partial}{\partial y_{1,n}} - \frac{\partial}{\partial y_{2,n}} \right) \mathcal{H} - \gamma \frac{\partial}{\partial t} (y_{1,n} - y_{2,n}) \quad (\text{A.3})$$

and performing analogous transformations

$$\begin{aligned} \left(\frac{\partial}{\partial y_{1,n}} - \frac{\partial}{\partial y_{2,n}} \right) \mathcal{H} &= \left(\frac{\partial x_{1,n}}{\partial y_{1,n}} - \frac{\partial x_{1,n}}{\partial y_{2,n}} \right) \frac{\partial}{\partial x_{1,n}} \mathcal{H} \\ &+ \left(\frac{\partial x_{2,n}}{\partial y_{1,n}} - \frac{\partial x_{2,n}}{\partial y_{2,n}} \right) \frac{\partial}{\partial x_{2,n}} \mathcal{H} \\ &= \sqrt{2} \frac{\partial}{\partial x_{2,n}} \mathcal{H}(x_{2,n}) \end{aligned} \quad (\text{A.4})$$

we arrive at Eq. (20). Consider the Hamiltonian $\mathcal{H}(x_{1,n})$ and $\mathcal{H}(x_{2,n})$ derivatives. The Hamiltonian $\mathcal{H}(x_{1,n})$ derivative takes the form

$$\frac{\partial \mathcal{H}(x_{1,n})}{\partial x_{1,n}} = -k_v(x_{2,n+1} - 2x_{2,n} + x_{2,n-1}). \quad (\text{A.5})$$

Multiplying the obtained result by τ^2/M , we have Eq. (25). The Hamiltonian $\mathcal{H}(x_{2,n})$ derivative can appear as

$$\begin{aligned} \frac{\partial \mathcal{H}(x_{2,n})}{\partial x_{2,n}} &= k_v(x_{2,n} - x_{2,n+1} + x_{2,n} - x_{2,n-1}) \\ &+ k_h \sqrt{2}(\sqrt{2}x_{2,n} + l) + \sqrt{2}\alpha'_n |b_n|^2. \end{aligned} \quad (\text{A.6})$$

Going then to the variable $z_n = u_n + u_0$, where $u_0 = \frac{l}{\sqrt{2}\beta}$ and $u_n = \frac{x_{2,n}}{\sqrt{2}\beta}$ we obtain Eq. (24).

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