

Translation of the original article

Vinogradov G.A., Lakhno V.D. *Mathematical Biology and Bioinformatics*. 2025;20(2):269–286.

doi: [10.17537/2025.20.269](https://doi.org/10.17537/2025.20.269)

===== TRANSLATIONS OF PUBLISHED ARTICLES =====

On Charge Transfer in DNA

Vinogradov G.A.^{*1}, Lakhno V.D.^{†2}

¹*Emanuel Institute of Biochemical Physics RAS, Moscow, Russia*

²*Institute of Mathematical Problems of Biology RAS, Keldysh Institute of Applied Mathematics RAS, Pushchino, Russia*

Abstract. The paper examines various mechanisms of charge transfer in DNA. Some of them, tunneling and the hopping mechanisms, are impossible due to a rapid decrease in probability with increasing transfer distance. Two models of charge transfer due to polarons are considered in detail. In both models (Peyrard-Bishop-Holstein and Su-Schrieffer-Heeger), the polaron is unstable with respect to destruction due to large amplitudes of thermal fluctuations. Based on the available experimental results, an alternative charge transfer mechanism is considered, which is weakly sensitive to temperature changes.

Key words: charge transfer, DNA, polaron

INTRODUCTION

Charge transfer (CT) is of great importance in such biochemical processes as photosynthesis [1, 2], where the absorption of a quantum of light causes primary charge separation; respiration [3, 4], as well as in many other biological reactions [5, 6].

Along with vital reactions, CT can lead to oxidative damage of DNA [7]. Guanine (G) oxidation is one example of oxidative stress, since G has the lowest ionization potential of all four DNA bases.

On the other hand, there is an interesting assumption that there are DNA sequences that “sacrifice themselves” (sacrificial nucleobase sequences), thereby protecting more important parts of the genome from oxidative damage [8]. Charge transfer also plays a key role in this mechanism. It is reported [9] that it is possible to “heal” several damages on the DNA chain, formed as a result of UV irradiation with the help of a single electron “traveling” along the DNA chain.

When discussing possible mechanisms of CT, the molecular structure of the DNA chain should be taken into account. This structure is similar to a spiral staircase, in which the steps are approximately parallel oriented conjugated heterocyclic DNA bases. Their π - π interaction provides the exchange electron interaction of the bases and the stability of the entire structure. A similar organization of π -orbitals is typical for some molecular crystals consisting of organic aromatic molecules and possessing a metallic type of conductivity. This analogy suggests that DNA conductivity can be carried out along a chain of π -conjugated bases [10, 11] and gives grounds to believe that DNA can be used as a molecular conductor.

There are several mechanisms that claim to explain the nature of conductivity. Historically, the first one was the Marcus theory [12, 13]. However, it was shown [14] that in the D-(b)_n-A system, consisting of a donor D, *n* repeating structural units b (a conducting

^{*}gvin@deom.chph.ras.ru

[†]lak@impb.ru

bridge of DNA bases or peptide groups) and an acceptor A, the probability of charge transfer decreases exponentially with increasing distance between D and A. Therefore, it turned out to be difficult to explain the charge transfer over long distances using the Marcus theory.

A hopping mechanism of charge transfer in DNA has been proposed [15]. For the hopping mechanism, the probability of charge transfer also decreases rapidly with the distance R over which this charge is transferred, but according to a power law with a constant $k \sim R^\alpha$, where $\alpha < 1$ is the attenuation parameter for hopping charge transport. Tunneling is also an unlikely process of transport over long distances with an exponentially rapid decrease in the probability of charge transfer with distance.

The polaron theory of charge transfer in DNA has become widespread. Apparently, the first mention of the possibility of charge transport by means of polarons is contained in works [16, 17]. In turn, these studies were based on the first experimental results on charge transfer in DNA [18, 19]. Recently, it is the polaron paradigm that has been considered as the main mechanism of charge transfer.

Below we will consider some experimental results on charge transfer in biological systems[‡]. The object of study for CT is a natural or artificial DNA biomacromolecule. A donor and an acceptor are attached to it on both sides: D-(b)_n-A. The donor serves to inject a charge into the chain, and the acceptor registers the charge that has reached it in one way or another. The bridge consists of n structural units b, which are DNA bases or peptide groups. Charge transfer involves three main stages: 1) generation of a charge on D and its transfer to the chain; 2) charge transport along the chain and 3) charge capture by the acceptor and its registration.

Donors and acceptors should satisfy certain requirements. First, the donor should interact well with the DNA bases so that the charge transfer from the donor to the chain occurs efficiently. Given that access to the bases is shielded by peripheral phosphate groups, one possibility is to attach D and A molecules directly to the DNA bases at the ends of the chain. Another convenient way is to insert D molecules between the DNA bases by intercalation. In addition, the donor should initiate the charge transfer with a good quantum yield. The acceptor should serve as an efficient charge transfer detector.

The charge transfer in this experimental technique is shown schematically in Figure 1. The attached molecules D and A are metal complexes (MC). The MC ligands, usually planar aromatic heterocyclic molecules, are inserted (intercalated) between two adjacent DNA bases. This ensures sufficient electron π - π overlap between the π orbitals of the MC ligand and the DNA bases for efficient charge transfer.

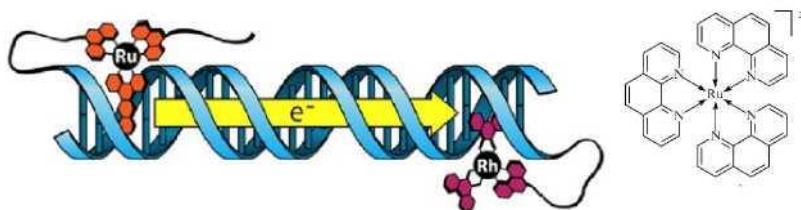


Fig. 1. Schematic illustration of charge transfer in an artificial DNA fragment. On the left is an intercalated Ru metal complex. On the right is an intercalated Rh metal complex. Upon photoexcitation, an electron from the Ru metal complex is transferred to the DNA helix, moves along the chain, and is captured by the Rh metal complex followed by registration. The right panel shows one of the variants of the Ru metal complex in more detail.

[‡] Work led by Jacqueline Barton on charge transfer and related biochemical processes was recognized by the highest US award for achievements in science, with the wording: “For discovery of a new property of the DNA helix, long-range electron transfer, and for showing that electron transfer depends upon stacking of the base pairs and DNA dynamics. Her experiments reveal a strategy for how DNA repair proteins locate DNA lesions and demonstrate a biological role for DNA-mediated charge transfer.”

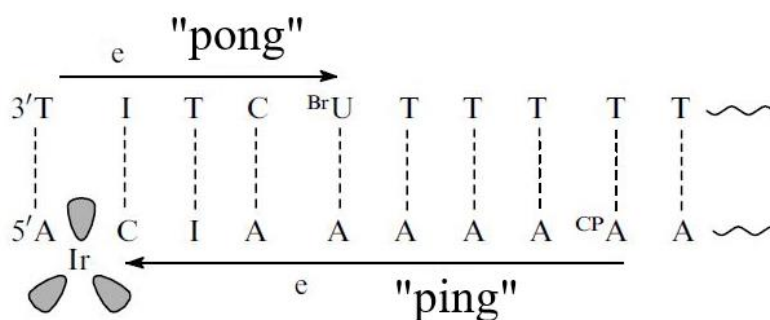


Fig. 2. Schematic representation of the ping-pong reaction. In this diagram, ‘I’ stands for the synthetic analogue of adenine. The directions of the arrows are opposite to the directions of the electron motion.

From the analysis of the mechanisms of natural biochemical reactions and numerous experiments on model systems, it follows that the place where the charge is born and the place where this charge, after migration along the DNA chain, causes a photophysical response or biochemical reactions, can be separated in space. Such reactions are called “chemistry at a distance” [20].

Another experiment worthy of attention is the so-called “ping-pong” reaction, which proves that charge transfer occurs via the π - π conjugation of parallel bases of only one DNA helix [21]. This is shown schematically in Figure 2.

The mechanism of the “ping-pong” reaction is as follows. An artificial fragment of the DNA chain shown in Fig. 2 was synthesized. The metal complex Ir is intercalated into the adenine sequence of the DNA helix. Cyclopropyl adenine ^{CP}A (a synthetic analogue of adenine) is embedded into the same sequence at some distance from the metal complex. Bromuridine ^{Br}U (a synthetic analogue of thymine) is embedded in the complementary helix of thymine bases. Upon photoexcitation of the Ir complex (365 nm), electron transfer occurs with the reduction of ^{CP}A : $Ir^{2+} \xrightarrow{e^-} Ir^{3+}$ and $^{CP}A + e^- \rightarrow ^{CP}A^-$. This is a “ping” reaction of direct electron transfer.

The reverse “pong” reaction occurs via the thymine pathway with the transfer of an electron from ^{Br}U back to the Ir complex and restoration of its initial charge +2. Both compounds ^{CP}A and ^{Br}U undergo irreversible chemical transformations, which allows one to make necessary quantitative measurements with the reaction products.

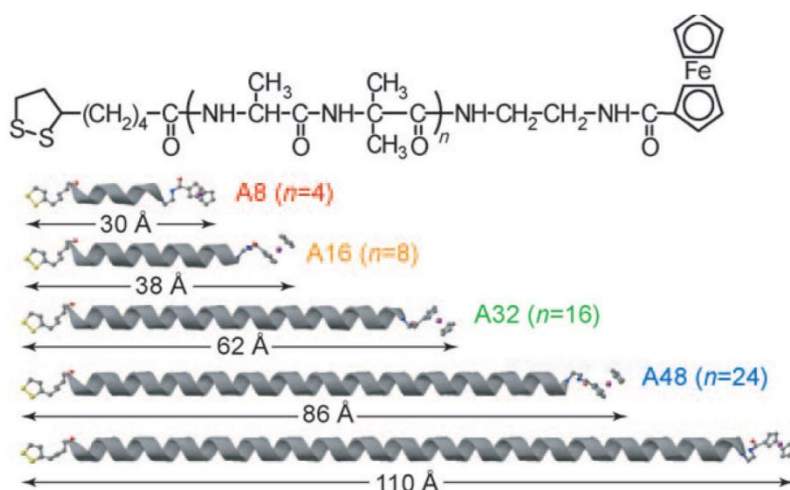


Fig. 3. Chemical structure and schematic illustrations of helical peptides of different lengths.

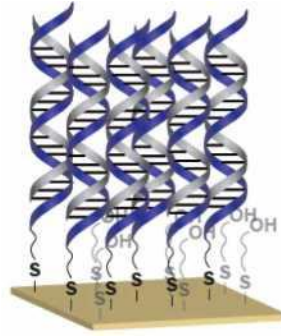


Fig. 4. Monolayer of DNA oligomers on a gold substrate.

Another important result [22] is the almost complete absence of dependence of the probability of charge transfer on the chain length for helical α -proteins (Fig. 3). Their parallel functional groups are very similar to biological systems. In this work, monolayers of helical peptides on a gold substrate with peptide lengths from 8-mers to 64-mers were prepared. The attachment of peptides was carried out by coupling sulfur-containing cycles with the gold substrate.

Monolayers of DNA oligomers with a base sequence consisting only of adenine-thymine pairs of 40 base pairs long and attached to a gold substrate were obtained (Fig. 4) [23]. This technique made it possible to carry out thorough quantitative measurements of the charge transfer probability. And, in contrast to earlier experiments, a dependence of the charge transfer probability on the DNA chain length was nevertheless revealed.

More detailed information on charge transfer in DNA can be found in a number of reviews [23–27].

IS THE POLARON CHARGE TRANSFER MECHANISM IN DNA EFFICIENT?

A possible semiclassical polaron model of charge transfer in DNA could be the use of the Peyrard Bishop Holstein (PBH) approximation [28] (more precisely, the Peyrard-Bishop-Daxous-Holstein model, see, for example, [29]), where the classical energy functional is:

$$H^{PBH} = \sum_j v_0 \left(1 - e^{-\alpha y_j}\right)^2 + \frac{k}{4} \left[2 + e^{-\beta(y_j + y_{j+1})}\right] (y_j - y_{j-1})^2 \quad (1)$$

with the parameter values: $\alpha = 4.45 \text{ \AA}^{-1}$, $\beta = 0.35 \text{ \AA}^{-1}$, $k = 0.04 \text{ eV \AA}^{-2}$. Newton's equations of dynamics in an electric field are: $m\ddot{y}_j = -(\partial H^{PBH})/(\partial y_j) - \chi |\psi_j|^2$, where the first term is the derivative of functional (1).

The Schrödinger equation for a polaron in an electric field has the form:

$$i\hbar\psi_j = -|e|E(ja)\psi_j - t_0(\psi_{j-1} + \psi_{j+1}) + \chi y_j \psi_j, \quad (2)$$

where the first term is the interaction of an electric field of intensity E (V/Å) with the charge of the polaron e (numerically equal to one), the second term is the exchange interaction with the hopping integral $t_0 = 0.1 \text{ eV}$ and the third one is the electron-phonon interaction with the parameter $\chi = 0.6 \text{ eV \AA}^{-1}$.

The parameter a , the distance between lattice sites, is not included in either the dynamics equation or the Schrödinger equations. By default, it is assumed that distances along the chain are measured in lattice sites. The reason is that all variables are indexed by site numbers. Without loss of generality, for convenience, we can set $a = 1 \text{ \AA}$, which numerically coincides with the difference in the numbers of adjacent sites. If we are interested in the real values of coordinates and velocities, then for DNA, for example, we can $a = 3.4 \text{ \AA}$. Thus, a is an arbitrary parameter.

In addition to numerous results on the study of polaron dynamics in an electric field, we will make one addition. Figure 5 shows the dependences of the polaron coordinates on time for several values of the electric field intensity. After some acceleration time, depending on the electric field intensity, the polaron velocity acquires a steady-state value. If $E = 5 \cdot 10^{-6} \text{ V/\AA}$, then $v_1 = 6.8 \cdot 10^{-3} \text{ \AA/fs}$. If $E = 10^{-4} \text{ V/\AA}$, then $v_2 = 9 \cdot 10^{-3} \text{ \AA/fs}$. With an increase in the field intensity by 20 times, the velocity increases only by ≈ 1.3 times. Detailed studies of the dependence of the velocity on the external electric field intensity for the Holstein polaron were performed in [30].

At short times, when the polaron is accelerated, the dependence of the coordinate on time obeys with very good accuracy the law $x(t) = x_0 + at^2/2$ for all electric field intensities. In Figure 5 this is shown by the dotted line for $E = 10^{-5} \text{ B/\AA}$. For this field intensity, the acceleration is $a = 1.6 \cdot 10^{-6} \text{ \AA/fs}^2$. Such kinematics of motion follows from the Newtonian relation $F = m_p a$, where m_p is the polaron mass and is $F = E|e|$ the force acting on the polaron charge from the electric field. And the polaron mass is $m_p = 6 \text{ eVfs}^2\text{\AA}^{-2}$. The ratio $E|e|/a$ which determines the polaron mass, is practically the same for all field intensities, which means that the polaron mass is independent of E .

The effective mass of a polaron m^* is usually expressed as a ratio to the mass of an electron: $m^* = m_p/m_e$. The mass of an electron is $m_e = 0.0057 \text{ eV fs}^2 \text{ \AA}^{-2}$. Moreover, the polaron turns out to be very “heavy”, – $m^* \approx 10^3 \div 10^4$ [30]. For comparison, the effective mass of a polaron in polyacetylene is $m^* \approx 1.29$.

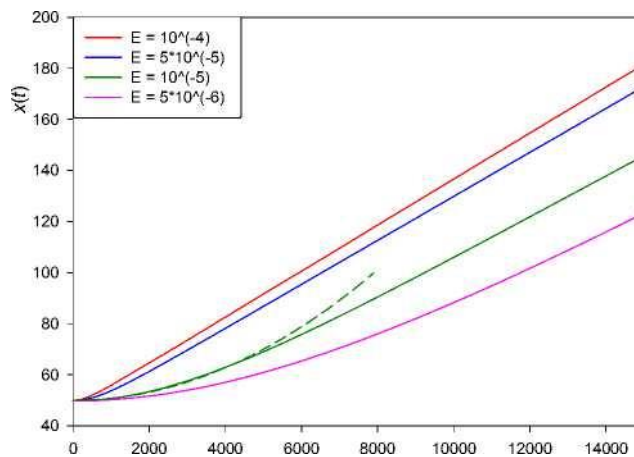


Fig. 5. Polaron coordinates depending on the electric field intensities (the intensity values in $\text{V/\AA}$ units are shown in the inset). The dotted line shows the dependence $x(t) = x_0 + at^2/2$, where $x_0 = 50$ is the initial coordinate of the polaron.

Figure 6 shows a “photograph” of a polaron after evolution for 15000 fs in a field with intensity of $E = 10^5 \text{ B/\AA}$. The polaron is translationally invariant, its shape practically does not change (the dotted line shows the initial condition for a polaron with the center at $j_0 = 50$). The polaron is followed by lattice oscillations. These oscillations are monochromatic and the wave number k of these oscillations does not depend on the electric field intensity and is determined only by the polaron velocity. The explanation for the occurrence of lattice oscillations is as follows: the electric field performs the work of moving the charge and the energy transmitted to the entire system from the electric field is converted only into the energy of monochromatic lattice oscillations [31] with a constant value of the wave number. An increase in the field intensity (an increase in the energy imparted to the lattice) leads only to an increase in the amplitudes of monochromatic oscillations without changing their dispersion. This effect is similar to that observed for polyacetylene [32]. The presence of an oscillating monochromatic “tail” following the polaron is an inherent property of the polaron being supersonic. In contrast to the case considered, for the Holstein polaron, in the absence

of dispersion in the spectrum of the chain oscillations, the polaron is always followed by a “tail” [33].

The PBH polaron is destroyed quite quickly in electric fields with intensity of $E > 3 \cdot 10^{-4} \text{ V/\AA}$.

Although very interesting results were obtained for the polaron in the PBH model at $T = 0$, it turned out that the polaron is unstable at physiological temperatures [34]. Previously, for the Holstein model, the temperature instability of the polaron was investigated in [35–37], and at physiological temperatures, the polaron in DNA also collapses very quickly [37]. For this reason, such a naive picture can hardly be used to describe charge transfer in biological systems. The reason for the instability can be illustrated by Figure 7. Panel a) shows a polaron in the PBH model at a temperature of $T = 200 \text{ K}$ after thermalization for 4 ps. The initial state of the polaron is shown in panel b). It follows from the figure that already at $T = 200 \text{ K}$ the amplitudes of thermal fluctuations are greater than the amplitude of displacements of sites from equilibrium positions in the steady-state state of the polaron. Therefore, these random high-amplitude thermal fluctuations play a leading role in the dynamics of the wave function and the stability of the polaron is violated.

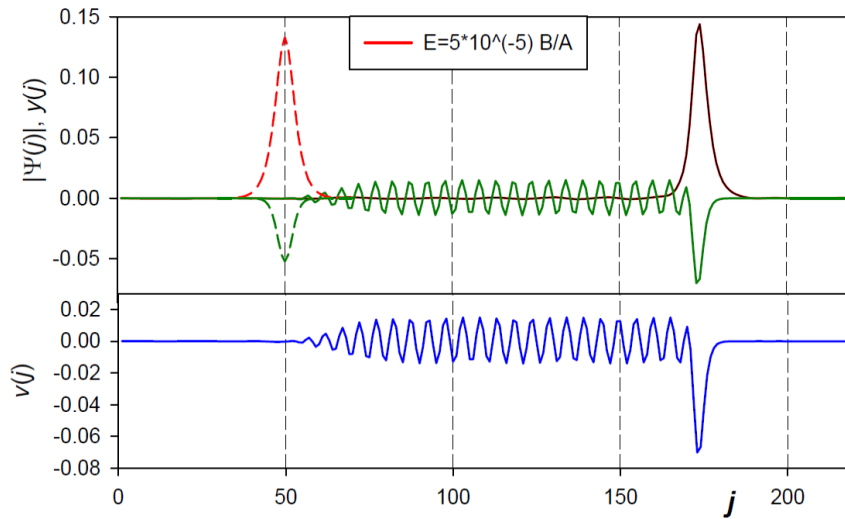


Fig. 6. A polaron in an electric field of intensity $E = 10^{-5} \text{ B/\AA}$. The upper panel shows the moduli of the wave functions (red line) and the values of the displacements from the equilibrium positions z_j (green lines). The lower panel shows the values of the corresponding velocities. The polaron is initially centered on the site $j_0 = 50$ (shown by the dotted line).

Based on the above-mentioned experimental results on “ping-pong” charge transfer, an alternative polaron model of charge transfer can be formulated. It follows from the experiments that the charge is transferred along a chain of $\pi - \pi$ conjugated parallel-oriented heteroaromatic bases of **one** DNA helix. In this case, the electron-phonon interaction is much stronger than in the PBH model, and it can be expected that the polaron will be more stable.

The simplest and most effective way to consider such systems is the Su-Schrieff-Heeger (SSH) approximation [38, 39] for the wave function of a charge in an electric field. In this approximation, the electron energy functional has the form (see, for example, [40]):

$$H^{el} = -\sum_j \left[t_0 - \alpha(x_{j+1} - x_j) \right] e^{-iBt} \psi_{j+1}^* \psi_j + \left[t_0 - \alpha(x_j - x_{j-1}) \right] e^{iBt} \psi_j^* \psi_{j-1}, \quad (3)$$

where x_j is the longitudinal deviation of the j -th particle (DNA base) from the equilibrium position, t_0 is the hopping integral at equilibrium, α is the electron-phonon interaction parameter.

Here, another method is used to account for the interaction of the polaron with the electric field – the multiplier $\exp(-iBt)$ is introduced and $B = Eea / \hbar$, where E , e is the electric field

intensity and the electron charge, a is the distance between the lattice sites. The parameters of the quantum functional [41] are: the hopping integral at equilibrium $t_0 = 0.3$ eV and the electron-phonon interaction parameter $\alpha = 0.6$ eV Å⁻¹.

The multiplier $\exp(-iBt)$ depends only on time and affects the phases of the partial wave functions ψ_j at the lattice sites. Thus, the classical dynamics of the polaron is additionally determined by the phases of the wave function. Apparently, the importance of taking phases into account was first pointed out in [42]. The influence of the phases of the wave functions on the dynamics of a supersonic polaron in polyacetylene is considered in more detail in [32].

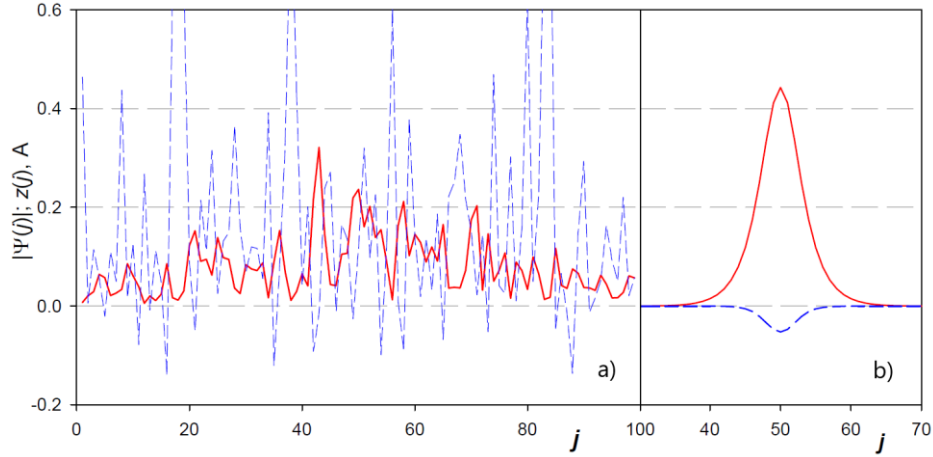


Fig. 7. Panel **a)**: the modulus of the wave function in the PBH model (solid red line) and thermal fluctuations - deviations of bond lengths from equilibrium positions (dashed blue line) at $T = 200$ K and $t = 4$ ps after the start of thermalization. Panel **b)**: the initial condition for the polaron is shown for comparison. The scale along the y-axis is the same for both panels.

Schrodinger equation for the wave function of a charge in an electric field:

$$i\hbar\psi_j = -\left[t_0 - \alpha(x_j - x_{j-1})\right]e^{-iBt}\psi_{j-1} - \left[t_0 - \alpha(x_{j+1} - x_j)\right]e^{-iBt}\psi_{j+1} \quad (4)$$

Below, by analogy with the classical harmonic potential [43], we will use the expression for the classical energy functional:

$$H^{cl} = \frac{m}{2} \sum_{j=1}^N \dot{x}_j^2 + \sum_{j=2}^N D_0 \left(1 - e^{-\beta(x_j - x_{j-1})}\right)^2 \quad (5)$$

with the Morse potential taking into account the $\pi - \pi$ interactions of adjacent parallel DNA bases. The parameters of the classical potential are: $m = 15510$ eV fs² Å⁻² ($m = 150$ Da is the average mass of the base of one helix). $D_0 = 0.3$ eV, $\beta = 1.2$ Å⁻¹ [43, 44].

The equations of lattice dynamics, taking into account the interaction of a charge with an electric field, have the form:

$$m\ddot{x}_j = \frac{-\partial H^{cl}}{\partial x_j} + \alpha \left[e^{iBt} (\rho_{j-1,j} - \rho_{j,j+1}) + e^{-iBt} (\rho_{j-1,j} - \rho_{j,j+1}) \right], \quad (6)$$

where the first term is the dynamic forces from functional (5) and $\rho_{j,i} = \psi_j^* \psi_i$.

Noteworthy is the importance of the influence of the wave function phases on the polaron dynamics during the charge transport in an electric field. This follows from the fact that the real right-hand sides of equation (6) are a combination of complex expressions of the type $(e^{iBt}\psi_{j-1}\psi_j^* + e^{-iBt}\psi_{j-1}^*\psi_j)$ and it is obvious that the dynamic forces also depend on the phases of the wave functions (the expression in square brackets depends on the amplitudes of the wave functions and their phases).

There are two ways to account for the interaction of a charge with an electric field. The

first one is used above for the problem with the PBH functional. The second way is to introduce the phase multiplier $\exp(-iBt)$. It is possible to show the equivalence of both approaches to account for the influence of the electric field [45–47], which is a consequence of the gauge invariance of the vector potential.

Since the phase multiplier $\exp(-iBt)$, responsible for the interaction with the electric field, does not contain coordinates, it is convenient to use it for lattices with cyclic boundary conditions. Then it is possible to monitor the dynamics of the polaron, which can “spin” along a closed circular trajectory an unlimited number of times.

The initial condition for the polaron is determined as follows. In the steady state, the velocities are zero and the wave functions are real. Then expressions (3) and (5) can be rewritten as:

$$H^{el} = -\sum_j (t_0 - \alpha z_{j,j-1}) \psi_j \psi_{j-1}, \quad (7)$$

where ψ_j is a real wave function, and

$$H^{cl} = \sum_{j=2}^N D_0 \left(1 - e^{-\beta z_{j,j-1}}\right)^2. \quad (8)$$

For brevity, the notation has been introduced above $z_{j,j-1} = (x_j - x_{j-1})$. Having minimized the sum of expressions (7) and (8) over $z_{j,j-1}$, we have:

$$2\alpha \psi_j \psi_{j-1} + 2\beta D_0 \left(1 - e^{-\beta z_{j,j-1}}\right) e^{-\beta z_{j,j-1}} = 0. \quad (9)$$

The solution of this equation for $z_{j,j-1}$ has the form:

$$z_{j,j-1} = \frac{1}{\beta} \ln \left(\frac{\beta D_0 + \sqrt{\beta^2 D_0^2 + 4\alpha\beta D_0 \psi_j \psi_{j-1}}}{2\beta D_0} \right). \quad (10)$$

The initial state of the polaron is found as follows. Some trial values $z_{j,j-1}$ are specified. 1) The $(N \times N)$ -matrix is filled with the values of the elements on the secondary diagonals $G(j, j-1) = G(j-1, j) = -(t_0 - \alpha z_{j,j-1})$. 2) This matrix is diagonalized (the eigenvalue problem is solved). 3) The wave function receives the eigenvector values corresponding to the ground state (the eigenvalue with the lowest energy). 4) New values of $z_{j,j-1}$ are calculated from equation (10). 5) The energy ε is calculated, equal to the sum of the energy functionals (7) and (8). And the iteration process returns to point 1). The criterion for completing the iteration process is the difference in energies ε at two subsequent iteration steps. Usually it is sufficient for the difference to be 10^{-6} . Upon completion of the procedure, the initial condition for the polaron is obtained. The wave function gets the values of the eigenvector at the last iteration cycle, and the relative coordinates are determined as follows: $x_1 = 0$, $x_j = x_{j-1} + z_{j,j-1}$ ($j = 2, 3, \dots, N$).

The iterative process converges quite quickly and gives a very accurate initial state of the polaron. This method for finding the initial state of the polaron can be used for other types of functionals of electron and classical energies. A necessary condition for the implementation of the iterative process is the presence of a relationship between the relative displacements and the wave function.

Some properties of polaron dynamics for the PBH and SSH models are qualitatively similar. The effective mass of the SSH polaron was estimated in the same way as for the PBH polaron. It turned out that the effective mass is very large, $m \approx 1.2 \times 10^4$. Compared to the PBH polaron, the steady-state velocity is slightly less, 10^{-3} Å/fs.

The speed of sound on a lattice with functional (5) in the harmonic approximation is

$v_{snd} = a\sqrt{k/m}$, where k is the rigidity of the harmonic coupling and the distance between the lattice sites is $a = 1 \text{ \AA}$. The expansion of the Morse potential (5) into the Taylor series is $0.432x^2 - 0.518x^3 \pm \dots$ with the coupling rigidity coefficient $k = 0.864 \text{ eV \AA}^{-2}$. Then the speed of sound $v_{snd} \approx 3.7 \times 10^{-3} \text{ \AA/fs}$. And the velocity of the polaron is less than the speed of sound. Note that if in model (5) the polaron is subsonic, then the polaron will lack an oscillating “tail”.

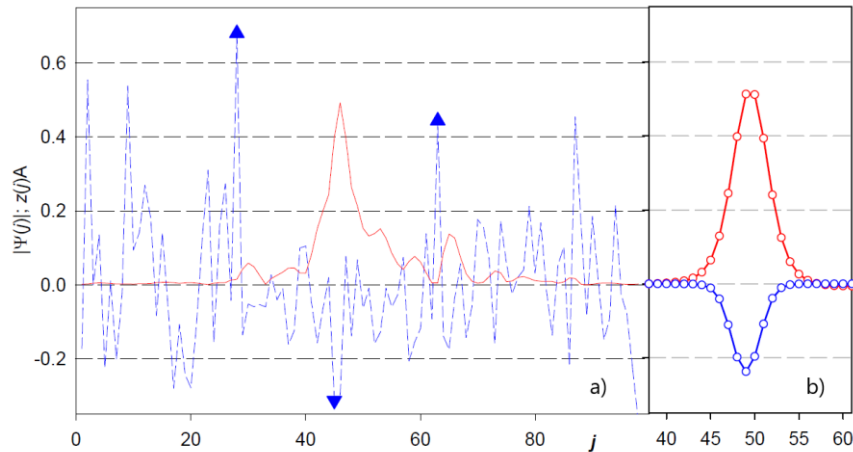


Fig. 8. Panel **a)**: The modulus of the wave function in the SSH model (solid red line) and thermal fluctuations – deviations of bond lengths from the equilibrium positions (dashed blue line) at $T = 300 \text{ K}$ and $t = 4 \text{ ps}$. Panel **b)**: the initial condition for the polaron is shown for comparison. The scale along the y-axis is the same for both panels.

Figure 8 shows a polaron in the SSH approximation on a thermalized lattice (similar to Figure 7). It is evident that the polaron is more stable (the amplitude of the lattice deformation in the polaron region is greater than in the PBH model due to the greater electron-phonon interaction – panel b). And this “polaron deformation” is commensurate with thermal fluctuations). The maximum of the wave function is determined by the minimum value of the parameter z (in the figure – the triangle with the apex down). A significant part of the wave function is limited on both sides by positive fluctuations (the triangles with the apex up). These fluctuations prevent the propagation of the wave function. At long times ($t > 10 \text{ ns}$), the polaron finally loses stability.

In addition to the temperature instability, there are additional factors that make the polaron mechanism of charge transport require further investigation. Apparently, the main obstacle is the process of polaron formation. It is not known what the wave function of the charge looks like after transfer to the lattice, i.e. what the initial conditions for the polaron formation are. Detailed modeling of the process of formation of the polaron state in the Holstein model was carried out in [48, 49]. Thus, it is necessary for a “well” of negative relative displacements of the lattice to form and for the wave function to become an eigenfunction of this well. Two factors hinder the implementation of this mechanism. First, the slow dynamic subsystem does not have time to coordinate its dynamics with the fast dynamics of the quantum subsystem (see Fig. 9 below). And secondly, the chaotic dynamics of thermal fluctuations destroys the coherent dynamics necessary for the formation of a polaron and is an additional factor preventing the formation of polarons.

For a long time, the electrical conductivity of polyacetylene was a classic example of the applicability of the polaron theory. However, it turned out that polarons in polyacetylene in the SSH approximation are also temperature unstable [50, 51].

Therefore, there is a need to develop a model that would be able to describe charge transport in DNA in accordance with experimental results.

Evolution of the charge wave function after transfer to the DNA chain

In charge transfer experiments, the initial process is the photoexcitation of the donor and the subsequent charge transfer to the DNA helix. It can be assumed that the charge from the donor “hops” to the DNA chain in the form of a highly localized wave function. The limiting case is the δ -function at the first lattice site and the initial state of the wave function is $\psi(t = 0) = (1, 0, 0, \dots, 0)$. First, let us consider the dynamics of the wave function with this initial condition at $T = 0$ K.

Figure 9 shows the evolution of the wave function. The wave function is formed as a moving wave packet[§]. The wave packet is reflected several times from the boundaries of the lattice. At the moments of reflection, a partial localization of the wave function occurs.

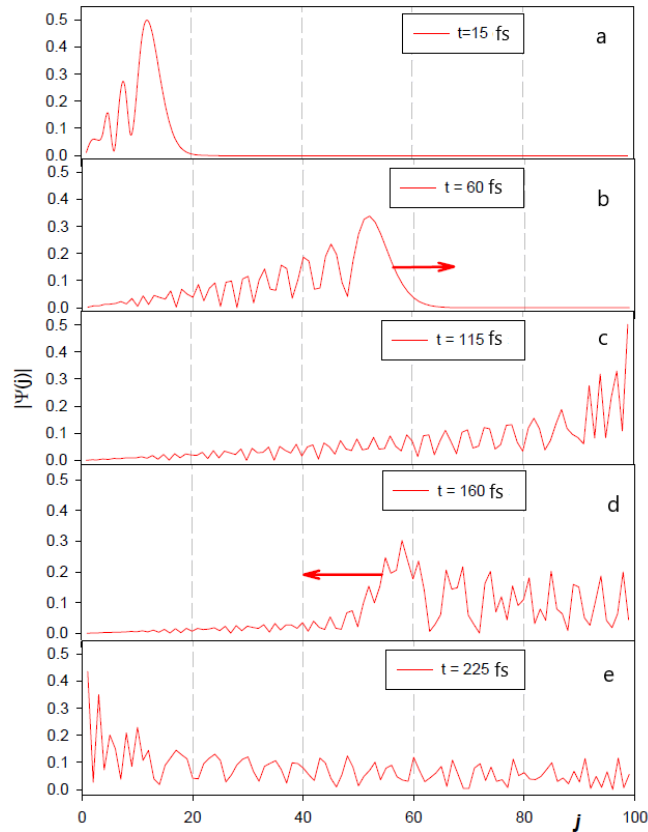


Fig. 9. The wave packet of the wave function at different moments of time (the moments of time are shown in the insets to the figure). At the moment of time $t = 115$ fs (panel c), the wave packet is reflected from the right boundary of the lattice. In panel (d), the wave packet moves to the left. Panel d shows the wave function at the moment when the front of the wave function meets the left boundary of the lattice.

The exact solution of the maximally simplified problem (4) for the evolution of a wave packet in the absence of an electric field, when the Schrödinger equation for the j -th site has the form $i\psi_j = \psi_{j-1} + \psi_{j+1}$, is given in [52, 53].

If the wave function is localized as a δ -function on some lattice site j_0 , then from the form of the Schrödinger equations for sites $j = j_0 \pm 1$ at the first moment of time: $\psi_{j_0 \pm 1} = -i\hbar^{-1}t_0\psi_{j_0}$ it follows that the initial wave δ -function is divided into two symmetric wave packets that begin to move in opposite directions with a normalization equal to 1/2 for each. After several reflections of the wave packet from the lattice boundaries and interference of the wave function, the time-averaged density of the wave function on each site tends to a constant value

§ The wave packet is formed only on a discrete lattice. In the continuous case, the initial localized condition for the wave function spreads out and the “center of gravity” of the wave function does not change its position.

$\langle \psi_j^* \psi_j \rangle_{t \rightarrow \infty} \Rightarrow 1/N$, where N is the number of lattice sites.

It is precisely this behavior of the wave function after charge transfer from the donor to the DNA chain that makes the formation of a polaron unlikely due to the lack of time for the formation of a polaron.

Detailed modeling of charge dynamics in homogeneous chains and charge transfer from the donor to the acceptor (when modeling the donor and the acceptor by simple trapping potentials) was performed in [54].

Model of charge transfer in DNA

Let the N -th lattice site be connected to an electron acceptor, which forms a “drain” of the wave function from the lattice to the acceptor, thereby simulating the charge transfer to the acceptor according to the D-b_n-A system. A simple way to simulate the “drain” process is to add the term $-i\hbar/\tau$ to the Schrödinger equation (4), where τ is the characteristic “drain” time [55]. Then the Schrödinger equation for the wave function at site N has the form (for a lattice with free boundaries):

$$i\hbar \frac{\partial \psi_N}{\partial t} = -\left(t_0 - \alpha z_{N,N-1}\right) \psi_{N-1} - i \frac{\hbar}{\tau} \quad (11)$$

The classical potential has the form (5) with the dynamic equations (6).

The simulation at finite temperatures is performed as follows: the lattice is thermalized to a temperature T without a wave function. The simulation is continued by adding an initial condition for the wave function in the form of $\Psi(t=0) = (1, 0, \dots, 0)$. The probability of charge transfer to the acceptor is determined by the decrease in the normalization of the wave function $P(t) = 1 - Q(t)$, where $Q(t) = \sum_j \psi_j(t) \psi_j^*(t)$ at time t . Unity is the normalization of the wave function at time $t = 0$.

Figure 10 shows the change in the probability of capture of the charge carrier by the acceptor $P(t)$ depending on time for two lattice lengths: $N = 100$ and $N = 200$ at $T = 100$ K. These dependencies are well approximated by the dependencies: $P(t) = 1 - Nr(t) = 1 - \exp(-t/\tilde{\tau})$. And the parameter $\tilde{\tau}$, which differs from τ , depends on the lattice length and temperature.

The decay of the normalization of the wave function $Nr(t)$ is exponential. The exponential decrease of the wave function with time is explained as follows. Let the drain be localized at an arbitrary j_0 -th site. Then expression (11) for the rate of change of the wave function at this site can be rewritten as:

$$\frac{\partial \psi_{j_0}}{\partial t} = \frac{-i}{\hbar} \left[-\left(t_0 - \alpha z_{j_0, j_0-1}\right) \psi_{j_0-1} - \left(t_0 - \alpha z_{j_0+1, j_0}\right) \psi_{j_0+1} \right] - \frac{\psi_{j_0}}{\tau} \quad (12)$$

If, as a result of reflections with interference, the wave function is distributed with approximately the same density $\psi_j(t) \psi_j^*(t)$ along the chain and the average values $z_{j_0, j_0 \pm 1}(t)$ during thermalization are also the same, then the first term on the right-hand side of (11) vanishes. Then $\psi_{j_0}(t)/dt = -\psi_{j_0}(t)/\tilde{\tau}$ with the exponential solution

$$\psi_{j_0}(t) = Ae^{-t/\tilde{\tau}} \quad (13)$$

It also follows from Figure 10 that there is a dependence of the probability of charge transfer on the length of the chain. And this dependence has an explanation: If the charge wave function has (on average) a constant value along the chain, then the amplitude of the wave function at each site is $\approx 1/\sqrt{N}$, including at the end site from which the drain comes. Then the coefficient A in (13) is also proportional to $1/\sqrt{N}$.

A realistic case of charge transfer in DNA corresponds to shorter chains at physiological temperature $T = 310$ K. Let us consider this case in more detail for $N = 10$ and $N = 15$. Figure 11 shows the probability of capture of a charge carrier by the acceptor for two values of the lattice lengths and two values of τ . The probability of capture increases with decreasing lattice length and decreasing parameter τ .

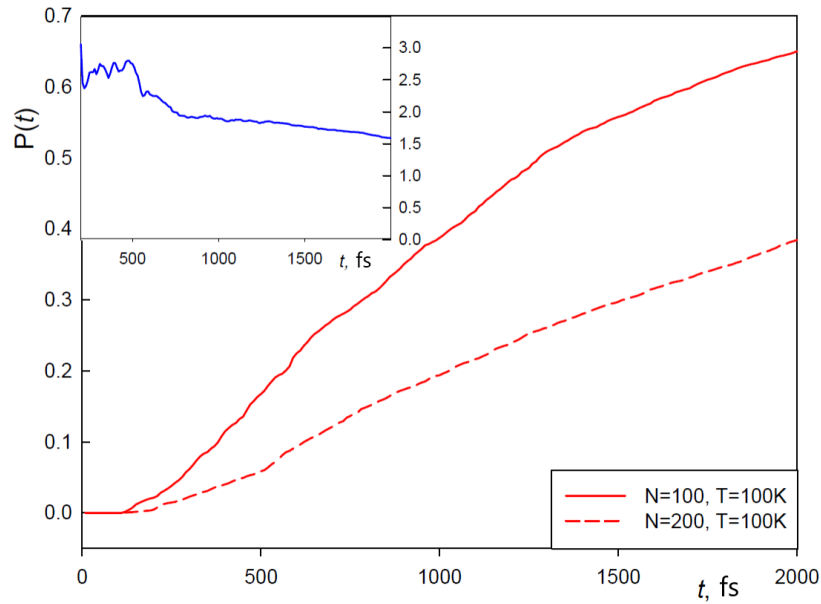


Fig. 10. The probability of capture of a charge carrier by the acceptor at $T = 100$ K for a lattice with lengths $N_1 = 100$ and $N_2 = 200$. The parameters: $\gamma = 10^{-3} \text{ fs}^{-1}$, $\tau = 20 \text{ fs}$, 10 MD trajectories. The inset shows the ratio of the probabilities of charge transfer $P_{N_1}(t)/P_{N_2}(t)$ for different lattice lengths. This ratio tends to $\sqrt{2}$ at large times.

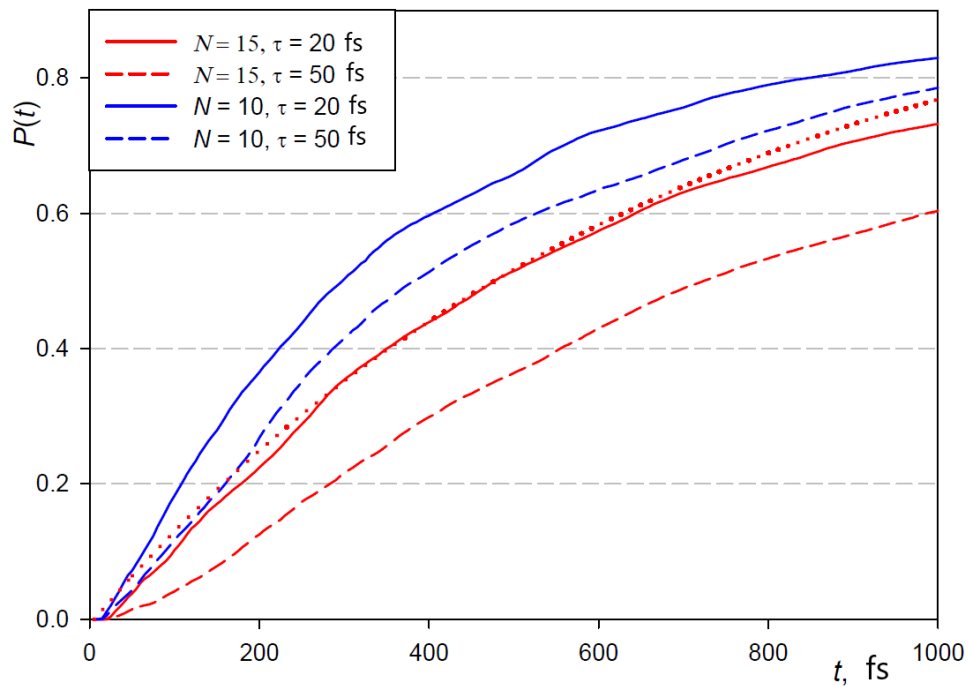


Fig. 11. The probability of capture of a charge carrier by the acceptor depends on the length of the lattice N and the parameter τ . The line of red dots is an exponential approximation of the dependence $P(t)$.

CONCLUSION

It is shown that charge transfer (CT) mechanisms that have proven themselves well in molecular systems, such as the Marcus mechanism, the hopping mechanism, and tunneling, cannot be responsible for charge transport in DNA due to the rapid decrease in the CT probability with increasing distance. The polaron paradigm, which uses different models of dynamic and quantum interactions, has long been considered to be the main CT mechanism in biological systems, including DNA. In these models, at temperatures close to $T = 0$, very interesting results were obtained. However, it turned out that at physiological temperatures polarons are destroyed quite quickly due to the electron-phonon interaction, which is responsible for both the formation of the polaron and its destruction by thermal fluctuations. We considered a well-known method for modeling the polaron based on the inclusion of a dissipative term for the wave function in the Schrödinger equation. This approach leads to a weak dependence of the probability of charge transport on temperature and can be a mechanism for charge transfer in DNA.

REFERENCES

1. Eberhard S., Finazzi G., Wollman, F.-A. The dynamics of photosynthesis. *Annu. Rev. Genet.* 2008. V. 42. P. 463–515. doi: [10.1146/annurev.genet.42.110807.091452](https://doi.org/10.1146/annurev.genet.42.110807.091452)
2. Loll B., Kern J., Saenger W., Zouni A., Biesiadka J. Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II. *Nature.* 2005. V. 438. P. 1040–1044. doi: [10.1038/nature04224](https://doi.org/10.1038/nature04224)
3. Cordes M., Giese B. Electron transfer in peptides and proteins. *Chem. Soc. Rev.* 2009. V. 38. P. 892–901. doi: [10.1039/B805743P](https://doi.org/10.1039/B805743P)
4. Verkhovskaya M.L., Belevich N., Euro L., Wikström M., Verkhofsky M. Real-time electron transfer in respiratory complex I. *Proc. Natl. Acad. Sci. U.S.A.* 2008. V. 105. No. 10. P. 3763–3767. doi: [10.1073/pnas.0711249105](https://doi.org/10.1073/pnas.0711249105)
5. Stubbe J., Nocera D.G., Yee C.S., Chang M.C.Y. Radical Initiation in the Class I Ribonucleotide Reductase: Long-Range Proton-Coupled Electron Transfer. *Chem. Rev.* 2003. V. 103. No. 6. P. 2167–2202. doi: [10.1021/cr020421u](https://doi.org/10.1021/cr020421u)
6. Heller A. Spiers Memorial Lecture. On the hypothesis of cathodic protection of genes. *Faraday Discuss.* 2000. V. 116. P. 1–13. doi: [10.1039/B006196O](https://doi.org/10.1039/B006196O)
7. van Loon B., Markkanen E., Hubscher U. Oxygen as a friend and enemy: How to combat the mutational potential of 8-oxo-guanine. *DNA Repair* 2010. V. 9. P. 604–616. doi: [10.1016/j.dnarep.2010.03.004](https://doi.org/10.1016/j.dnarep.2010.03.004)
8. Kanvah S., Schuster G.B. The sacrificial role of easily oxidizable sites in the protection of DNA from damage. *Nucl. Ac. Res.* 2005. V. 33. No. 16. P. 5133–5138. doi: [10.1093/nar/gki801](https://doi.org/10.1093/nar/gki801)
9. Giese B., Carl B., Carl T., Carell T., Behrens C., Hennecke U., Schiemann O., Feresin E. Excess Electron Transport Through DNA: A Single Electron Repairs More than One UV-Induced Lesion. *Angew. Chem. Int. Ed.* 2004. V. 43. P. 1848–1851. doi: [10.1002/anie.200353264](https://doi.org/10.1002/anie.200353264)
10. Chen F., Tao N.J. Electron Transport in Single Molecules: From Benzene to Graphene. *Acc. Chem. Res.* 2009. V. 42. P. 429–438. doi: [10.1021/ar800199a](https://doi.org/10.1021/ar800199a)
11. Liu L., Frisbie C.D. Length-Dependent Conductance of Conjugated Molecular Wires Synthesized by Stepwise Click Chemistry. *J. Am. Chem. Soc.* 2010. V. 132. P. 8854–8855. doi: [10.1021/ja103239b](https://doi.org/10.1021/ja103239b)
12. Marcus R.A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.* 1956. V. 24. P. 966–978. doi: [10.1063/1.1742723](https://doi.org/10.1063/1.1742723)
13. Marcus R.A. Electrostatic Free Energy and Other Properties of States Having Nonequilibrium Polarization. I. *J. Chem. Phys.* 1956. V. 24. P. 979–989. doi: [10.1063/1.1742724](https://doi.org/10.1063/1.1742724)

14. McConnell H.M. Intramolecular Charge Transfer in Aromatic Free Radicals. *J. Chem. Phys.* 1961. V. 35. P. 508–515. doi: [10.1063/1.1731961](https://doi.org/10.1063/1.1731961)
15. Giese B., Wessely S. The Influence of Mismatches on Long-Distance Charge Transport through DNA. *Angew. Chem., Int. Ed.* 2000. V. 39. P. 3490–3491. doi: [10.1002/1521-3773\(20001002\)39:19<3490::AID-ANIE3490>3.0.CO;2-S](https://doi.org/10.1002/1521-3773(20001002)39:19<3490::AID-ANIE3490>3.0.CO;2-S)
16. Henderson P.T., Jones D., Hampikian G., Kan Y., Schuster G.B. Long-distance charge transport in duplex DNA: the phonon-assisted polaron-like hopping mechanism. *Proc. Natl. Acad. Sci. USA* 1999. V. 96. P. 8353–8358. doi: [10.1073/pnas.96.15.8353](https://doi.org/10.1073/pnas.96.15.8353)
17. Ly D., Sanii L., Schuster G.B. Mechanism of charge transport in DNA: internally-linked anthraquinone conjugates support phonon-assisted polaron hopping. *J. Am. Chem. Soc.* 1999. V. 121. P. 9400–9410. doi: [10.1021/ja991753s](https://doi.org/10.1021/ja991753s)
18. Murphy C.J., Arkin M.R., Jenkins Y., Ghatlia N.D., Bossmann S., Turro N.J., Barton J.K. Long Range Photoinduced Electron Transfer through a DNA Helix. *Science* 1993. V. 262. No. 5136. P. 1025–1029. doi: [10.1126/science.7802858](https://doi.org/10.1126/science.7802858)
19. Wan C., Fiebig T., Kelley S.O., Treadway C.R., Barton J.K., Zewail A.H. Femtosecond dynamics of DNA-mediated electron transfer. *Proc. Natl. Acad. Sci. USA* 1999. V. 96. No. 11. P. 6014–6019. doi: [10.1073/pnas.96.11.6014](https://doi.org/10.1073/pnas.96.11.6014)
20. Turro N.J., Barton J.K. Paradigms, supermolecules, electron transfer and chemistry at a distance. What's the problem? The science or the paradigm? *J. Biol. Inorg. Chem.* 1998. V. 3. P. 201–209.
21. Elias B., Genereux J.C., Barton J.K. Ping-Pong Electron Transfer through DNA. *Angew. Chem. Int. Ed.* 2008. V. 47. P. 9067–9070. doi: [10.1002/anie.200803556](https://doi.org/10.1002/anie.200803556)
22. Arikuma Y., Nakayama H., Morita T., Kimura S. Electron Hopping over 100 Å Along an α Helix. *Angew. Chem. Int. Ed.* 2010. V. 49. P. 1800–1804. doi: [10.1002/anie.200905621](https://doi.org/10.1002/anie.200905621)
23. Nano A., Furst A.L., Hill M.G., Barton J.K. DNA Electrochemistry: Charge-Transport Pathways through DNA Films on Gold. *J. Am. Chem. Soc.* 2021. V. 143. P. 11631–11640. doi: [10.1021/jacs.1c04713](https://doi.org/10.1021/jacs.1c04713)
24. Delaney S., Barton J.K. Long-Range DNA Charge Transport. *J. Org. Chem.* 2003. V. 68. No. 17. P. 6475–6483. doi: [10.1021/jo030095y](https://doi.org/10.1021/jo030095y)
25. Genereux J.C., Barton J.K. Mechanisms for DNA Charge Transport. *Chem. Rev.* 2010. V. 110. No. 3. P. 1642–1662. doi: [10.1021/cr900228f](https://doi.org/10.1021/cr900228f)
26. Astakhova T.Yu., Likhachev V. N., Vinogradov G.A. Long-range charge transfer in biopolymers *Russian Chemical Reviews*. 2012. V. 81. No. 11. P. 994–1010. doi: [10.1070/RC2012v081n11ABEH004308](https://doi.org/10.1070/RC2012v081n11ABEH004308)
27. Arnold A.R., Grodick M.A., Barton J.K. DNA Charge Transport: from Chemical Principles to the Cell. *Cell Chemical Biology*. 2016. V. 23. P. 183–197. doi: [10.1016/j.chembiol.2015.11.010](https://doi.org/10.1016/j.chembiol.2015.11.010)
28. Diaz E., Lima R.P.A., Dominguez-Adame F. Bloch-like oscillations in the Peyrard-Bishop-Holstein model. *Phys. Rev. B* 2008. V. 78. P. 134303. doi: [10.1103/PhysRevB.78.134303](https://doi.org/10.1103/PhysRevB.78.134303)
29. Maniadis P., Kalosakas G., Rasmussen K.O., Bishop A.R. ac conductivity in a DNA charge transport model. *Phys. Rev. B* 2005. V. 72. Article No. 021912. doi: [10.1103/PhysRevE.72.021912](https://doi.org/10.1103/PhysRevE.72.021912)
30. Lakhno V.D. Davydov's solitons in homogeneous nucleotide chain. *International Journal of Quantum Chemistry*. 2010. V. 110. P. 127–137. doi: [10.1002/qua.22264](https://doi.org/10.1002/qua.22264)
31. Basko D.M., Conwell E.M. Stationary Polaron Motion in a Polymer Chain at High Electric Fields. *Phys. Rev. Lett.* 2002. V. 88. No. 5. Article No. 056401. doi: [10.1103/PhysRevLett.88.056401](https://doi.org/10.1103/PhysRevLett.88.056401)
32. Vinogradov G.A. Subsonic and supersonic polaron dynamics in polyacetylene. *Synthetic Metals*. 2023. V. 299. Article No. 117477. doi: [10.1016/j.synthmet.2023.117477](https://doi.org/10.1016/j.synthmet.2023.117477)

33. Lakhno V.D., Fialko N.S. Mechanism of soliton stopping in a molecular chain without dispersion. *Computer Research and Modeling*. 2009. V. 1. No. 1. P. 93–99. doi: [10.20537/2076-7633-2009-1-1-93-99](https://doi.org/10.20537/2076-7633-2009-1-1-93-99)
34. Lima R.P.A., Malyshev A.V. Charge transfer mechanisms in DNA at nite temperatures: From quasiballistic to anomalous subdi usive charge transfer. *Phys. Rev. E*. 2022. V. 106. Article No. 024414. doi: [10.1103/PhysRevE.106.024414](https://doi.org/10.1103/PhysRevE.106.024414)
35. Lakhno V.D., Fialko N.S. Conditions for the Existence of Polaron States in Classical Molecular Chains at Finite Temperatures *Mathematical biology and bioinformatics*. 2014 V. 9 No. 1. doi: [10.17537/2014.9.1](https://doi.org/10.17537/2014.9.1)
36. Lakhno V.D., Fialko N.S. On the dynamics of a polaron in a classical chain with finite temperature. *Journal of Experimental and Theoretical Physics*. 2015. V.120. P. 125–131. doi: [10.1134/S106377611501015X](https://doi.org/10.1134/S106377611501015X)
37. Fialko N. S., Sobolev E., Lakhno V. D. On the calculation of thermodynamic quantities in the Holstein model for homogeneous polynucleotides *Journal of Experimental and Theoretical Physics*. 2017. V. 124. P. 635–642. doi: [10.1134/S1063776117040124](https://doi.org/10.1134/S1063776117040124)
38. Su W.P., Schrieffer J.R., Heeger A.J. Solitons in Polyacetylene. *Phys. Rev. Lett.* 1979. V. 42. P. 1698–1701. doi: [10.1103/PhysRevLett.42.1698](https://doi.org/10.1103/PhysRevLett.42.1698)
39. Su W.P., Schrieffer J.R., Heeger A.J. Soliton excitations in polyacetylene. *Phys. Rev. B* 1980. V. 22. No. 4. P. 2099–2111. doi: [10.1103/PhysRevB.22.2099](https://doi.org/10.1103/PhysRevB.22.2099)
40. Sun S., Zhang Y., Liu X., An Z. *J. Phys. Chem. C*. 2019. V. 123. P. 28569–28575. doi: [10.1021/acs.jpcc.9b07330](https://doi.org/10.1021/acs.jpcc.9b07330)
41. Berlin Y.A., Burin A.L., Ratner M.A. Elementary steps for charge transport in DNA: thermal activation vs. tunneling. *Chem. Phys.* 2002. V. 275. P. 61–74. doi: [10.1016/S0301-0104\(01\)00536-5](https://doi.org/10.1016/S0301-0104(01)00536-5)
42. Meng R., Yin S., Zheng Y., Yang L., Xie S., Saxena A. Phase-breaking e_ect on polaron transport in organic conjugated polymers. *Org. Electron*. 2017. V. 49. P. 33–38. doi: [10.1016/j.orgel.2017.06.026](https://doi.org/10.1016/j.orgel.2017.06.026)
43. Conwell E.M., Basko D.M. Hole Traps in DNA. *J. Amer. Chem. Soc.* 2001. V. 123. No. 46. Article No. 11441. doi: [10.1021/ja015947v](https://doi.org/10.1021/ja015947v)
44. Conwell E.M., Rakhmanova S.V. Polarons in DNA. *Proc. Natl. Acad. Sci. U.S.A.* 2000. V. 97. P. 4556–4560. doi: [10.1073/pnas.050074497](https://doi.org/10.1073/pnas.050074497)
45. Zak J. Stark ladder in solids? *Phys. Rev. Lett.* 1968. V. 20. Article No. 1477. doi: [10.1103/PhysRevLett.20.1477](https://doi.org/10.1103/PhysRevLett.20.1477)
46. Kittel C. *Quantum Theory of Solids*. Wiley, New York, 1987.
47. Astakhova T.Yu., Vinogradov G.A., Kashin V.A. Effect of External Factors on Physical and Chemical Transformations Polaron in an Electric Field as a Generator of Coherent Lattice Vibrations. *Russian Journal of Physical Chemistry B*. 2019. V. 12. P. 977–986. doi: [10.1134/S1990793118050147](https://doi.org/10.1134/S1990793118050147)
48. Lakhno V. D., Korshunova A. N. The modelling of selftrapped state formation in homogeneous polynucleotide chain. *Russian Journal Nonlinear Dynamics*. 2008. V. 4. No. 2. P. 193–214. doi: [10.20537/nd0802007](https://doi.org/10.20537/nd0802007)
49. Zhang Y.L., Liu X.J., An Z. Temperature dependence of polaron stability in conjugated polymers. *Europhys. Lett.* 2015. V. 111. Article No. 17009. doi: [10.1209/0295-5075/111/17009](https://doi.org/10.1209/0295-5075/111/17009)
50. da Cuna W.F., de Oliveira Neto P.H., Gargano R., e Silva G.M. Temperature Effects on Polaron Stability in Polyacetylene. *Int. J. Quant. Chem.* 2008. V. 108. P. 2448–2453. doi: [10.1002/qua.21798](https://doi.org/10.1002/qua.21798)
51. Likhachev V.N., Astakhova T.Y., Vinogradov G.A. “Electron ping-pong” on a one-dimensional lattice: Wave packet motion up to the first reflection. *Theor. Math. Phys.* V. 175. No. 2. P. 681–698. doi: [10.1007/s11232-013-0054-9](https://doi.org/10.1007/s11232-013-0054-9)
52. Likhachev V.N., Astakhova T.Y., Vinogradov G.A. “Electron ping-pong” on a one-dimensional lattice: Multiple reflections of the wave packet and capture of the wave

- function by an acceptor. *Theor. Math. Phys.* V. 176. No. 2. P. 1087–1099. doi: [10.1007/s11232-013-0090-5](https://doi.org/10.1007/s11232-013-0090-5)
53. Fialko N.S., Lakhno V.D. Long-range charge transfer in DNA. *Regular & Chaotic Dynamics*. 2002. V. 7. No. 3. P. 299–313 doi: [10.1070/RD2002v007n03ABEH000212](https://doi.org/10.1070/RD2002v007n03ABEH000212)
 54. Berlin Y.A., Grozema F.C., Siebbeles L.D.A., Ratner M.A. Charge Transfer in Donor-Bridge-Acceptor Systems: Static Disorder, Dynamic Fluctuations, and Complex Kinetics. *J. Phys. Chem. C*. 2008. V. 112. P. 10988–11000. doi: [10.1021/jp801646g](https://doi.org/10.1021/jp801646g)

Received 29.06.2025.

Published 03.09.2025.