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Long-range charge transfer in biopolymers

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Abstract. The results of theoretical and experimental studies on the charge transfer in biopolymers, namely, DNA and peptides, are presented. Conditions that ensure the efficient long-range charge transport (by several tens of nanometres) are considered. The known theoretical models of charge transfer mechanisms are discussed and the scopes of their application are analyzed. Attention is focused on the charge transport by the polaron mechanism. The bibliography includes 262 references.

I. Introduction

Nearly 50 years ago, scientists became preoccupied with the questions of whether a charge (electron or hole) can migrate along a DNA chain and if so, in what way this is accomplished.[1,2] This problem emerged because many biochemical processes can be explained only by assuming that a charge can migrate by rather long distances along the DNA chain.[3–10] The same concerns peptides in which the energy conversion and transport processes and also the most important biochemical reactions involve charge transfer. The charge transport induces conjugated proton transfer processes, which underlie many biochemical reactions. As an example, mention should be made of the vital processes such as photosynthesis,[11–15] which provides the main gain of Earth's biomass and makes possible breathing.[9,16–18]

Breathing can be considered as a sequence of elementary redox events involving organic and inorganic cofactors.[19] The difference between the redox potentials of NADH (the protonated form of nicotinamide adenine dinucleotide), which is the first to be oxidized, and oxygen, which is the final electron acceptor, is the 'driving force' of charge transfer. The Gibbs free energy of the overall cycle is 2.3 eV. The distance by which the charge is transferred is $\sim$14 Å. Many other biochemical reactions are also accompanied by charge transfer.[20,21]

However, apart from sustaining vital reactions, charge transfer may bring about the oxidative damage in DNA.[22–26] The oxidative stress may be exemplified by oxidation of guanine (G), which has the lowest ionization potential among the four DNA bases.[27] As the guanine base is subjected to oxidation, the emerging hole can migrate along the DNA double strand until it reacts with water or oxygen to afford mutagenic 8-oxoguanine (Fig. 1).

In DNA regions that for various reasons contain no guanine, thymine (T) undergoes redox reactions even despite its relatively high oxidation potential. For the TT sequence, the reaction proceeds by a tandem mechanism with the key stage of proton transfer conjugated with charge transfer.[28,29]

One of the reasons for the appearance of oxidative stresses that induce charges in the DNA chain is the presence of reactive oxygen species, for instance, $HO^{\bullet}$, $O_2^{-\bullet}$. They appear in the body under the action of external factors (UV light, radiation) and also as a result of normal metabolic processes. Often, the site of oxidative attack and the site of the DNA chain damage occurring upon hole migration are fairly remote from one another.[30] To prevent the harmful effect of reactive oxygen species, DNA should be activated and neutralize the oxidative damage. Lately, ideas were voiced that these protective processes can be helped by, *e.g.*, introducing molecules with higher susceptibility to oxidation as compared with natural compounds (such as guanine) which can draw to themselves the oxidation event thus protecting the vitally important genome from damage.[30,31] In implementing this mechanism, it is impossible to do without charge transfer to the oxidation 'quencher' that withdraws an electron from the reactive oxygen species.

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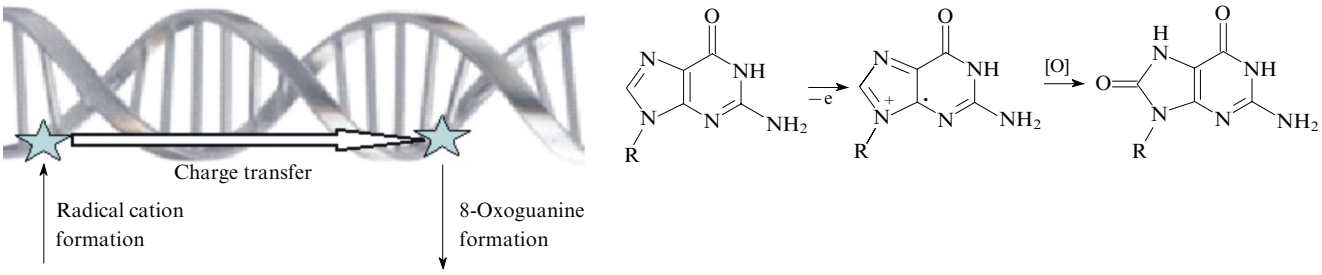


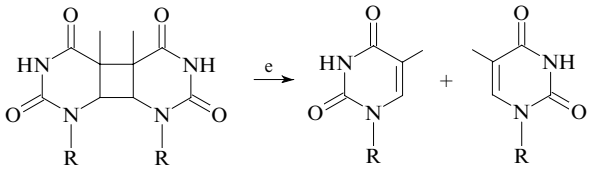
Figure 1. Illustration of guanine oxidation.[9]
In one of the DNA strands, a guanine radical cation is formed. The charge in the form of the guanine radical cation is transferred along the chain until it meets a reactive radical anion ($O_2^{-\bullet}$ or $HO^{\bullet}$). In this site of the strand, they may react to form 8-oxoguanine. The arrow shows the direction of charge migration along the chain.

The 'healing' process can occur because, due to the different reactivity of various sequences of DNA bases, driving force appears that causes the charge to move away from a DNA region that carries genetic information (usually this region is enriched with guanine bases) to a DNA region that carries no such information.

There are many types of stress, and all living organisms ranging from bacteria to humans suffer from it during the vital activity. Normal functioning requires the mechanisms that would provide adequate response of the organism to stress thus minimizing (and even eliminating) its harmful effects. Studying charge transfer processes and concomitant phenomena might help to answer the question of how living cells recognize the genome damages and respond to them.

On exposure to UV radiation, thymine bases can form dimers. One of examples of healing is retrocycloaddition of the thymine dimer (Scheme 1).[32]

Scheme 1



In this reaction, the electron does not disappear and, hence, a single electron can cleave several thymine dimers.

It was suggested[33] that DNA contains sequences that can 'sacrifice' themselves in order to protect more important genome parts from the oxidative damage. The key role in this mechanism also belongs to charge transfer (migration of a radical cation through the chain).

The above examples show that charge transfer processes play a crucial role in biological systems. Their consequences may be vitally important or may lead to oxidative damages followed by mutagenesis. Simultaneously, in living organisms, 'self-recovery' processes can occur in which the charge transfer also plays an important role.

By now, it became clear that studying biomacromolecules (such as DNA) is important for the development of not only biology and medicine but also of molecular electronics. Such molecules behave as conductors.[34–43] Particularly, the attention to unconventional conducting systems is explained by the fact that modern electronic devices have already reached the limits of miniaturization; hence, active search is carried out for compounds that can compete with and even substitute the elemental base of modern solid-state electronics. In addition to size limitations, the excessive specific heat evolution which accompanies the work of, *e.g.*, computer processors, is also a serious limiting factor. The human brain can also be considered as a powerful computer which, however, consumes much less energy. In this regard, there is much to learn from the nature, which has already found efficient and low-expense approaches to the analysis and processing of information.

The molecular structure of a DNA chain resembles a spiral staircase with stairs formed by conjugate heterocyclic DNA bases oriented almost in parallel to one another. Overlap of their electronic π-orbitals provides adequate electronic exchange interaction for the bases and stability for the whole structure. A similar organization is typical of π-orbitals of some crystals built of organic aromatic molecules and exhibiting metal-type conduction.[44] This analogy makes it possible to assume that the DNA conductivity proceeds precisely along the chain of π-conjugate bases[42,43,45–47] and also that DNA can be used as a molecular conductor.

Particular attention was drawn to DNA as a potential electric conducting system immediately after it was reported that DNA does actually allow for long-range charge transfer (by several tens of nanometres).[48,49] Having assessed the prospects of DNA as a molecular conductor that exhibits certain important advantages (such as, *e.g.*, comparatively easy preparation, low energy density consumed, flexibility), many research groups in the fields of biology, chemistry and physics started large-scale studies of charge transfer processes in DNA and other biological structures.

As regards their nature, proteins and DNA are semiconductors with a wide forbidden gap. Nonetheless, they exhibit a very broad range of conductivity. Thus, DNA can be electric current conductor,[50] semiconductor,[51] insulator[52] and even a superconductor.[53] In experiments that demonstrated the superconductivity of DNA, it was placed in a narrow gap between rhenium–carbon contacts. After cooling below 1 K, the 'proximity-induced' superconductivity was observed: the superconducting Cooper pairs diffused by a limited distance in the DNA thus providing local superconductivity. In the further studies of this effect, oligonucleotides were doped with metal gallium particles.[54] As the temperature lowered down, gallium passed to the superconducting state, which induced superconductivity of DNA. Doping with nanoparticles was also proposed as a method of modifying the electrophysical properties of DNA and peptides.

The DNA superconductivity was interpreted resorting to the views of its bipolar mechanism [55–59] according to which the efficient electron–phonon coupling counterbalances the Coulomb repulsion and polarons with opposite spins are paired. The immensely wide range of variation of electrophysical properties was attributed to different structures of studied DNA and different methods of sample preparation and also to different experimental conditions.

The results of studying the electrical conductivity of DNA fragments synthesized by specially developed methods have shown [60, 61] that they surpass the other types of molecular wires as regards this parameter. In addition to good conductivity of DNA, their important advantage is the possibility of creating conducting DNA segments of strictly definite length. The creation of such segments during the preparation of synthetic organic materials is an exceptionally difficult task. DNA fragments can be functionalized by addition of various structures, *e.g.*, metal clusters, fullerenes, carbon nanotubes (CNT), to their 5′-phosphate or 3′-hydroxyl ends. For instance, a nanobioelectric device consistsing of a DNA fragment with both ends chemically attached to a carbon nanotube, *i.e.*, CNT–DNA–CNT, was developed.[62] This procedure was used to study the interaction of a chain segment with DNA-methyltransferase SssI (M.SssI). The addition of M.SssI to the chain is extremely sensitive to the sequence of bases. Provided the addition has proceeded, then M.SssI catalyzes the cytosine methylation in the presence of SAM cofactor (S-adenosylmethionine). This process induces changes in the DNA conductivity and serves as a unique method for measuring the activity of enzymes at the molecular level.

The procedures employing CNT proved to be very helpful and informative in studying the properties of various individual synthetic oligonucleotides and their complexes with other molecules.[63–69] Thus, the conductivity of several types of one-strand and double-strand DNA segments comprising several tens of bases covalently attached to CNT, was studied.[65] In one experiment, the gap between two CNT was 27±2 nm, which corresponds to the contour length of DNA built of 80 pairs of bases. For the potential difference of 1 V, the current through an individual molecule was fairly high and reached several tens of picoamperes.

Studies of the electroconducting properties of proteins raised the problem of attaching them to electrodes. After its successful solution, protein monolayers have been integrated into electronic devices.[70–73] The use of such systems in photoelectric transducers provided the quantum efficiency of ~12%.[71] However, besides the positive effects, serious drawbacks were revealed, namely, the instability of synthesized monolayers with respect to external factors and the poor reproducibility of results. These problems were partly solved in another study.[74] Its authors were able to attach gold particles to immunoglobulin G; in turn, the gold particles were connected to control electrodes. The charge transport in this transistor depended on the conformation of the protein molecule. Moreover, CdSe quantum dots were successfully attached to a protein molecule and it was shown that the properties of this transistor can be controlled by light. The created approach is quite promising and can serve as the basis for the development of molecular electronic and nanobioelectronic devices.

Having thought over the design and subsequent synthesis of various structures based on only the four DNA bases, it is possible to create various nanodevices according to the bottom-up approach.[75–77] However, the attempts to use DNA molecules as building blocks of nanodevices are self-contradictive. The point is that the sequences of DNA bases that provide efficient charge transfer are not always suitable for building spatial structures necessary for nanodevices.[78] Indeed, the efficient charge transfer requires rather rigid uniaxial regular structures, whereas the architecture of nanoelectronic devices should contain bends and branches, which may complicate the charge transfer. However, the latest achievements in the 'DNA-origami' field allow us to hope that these complications can be overcome.[77, 79, 80]

Thus, being uniform and rigid with respect to deformation, the ideal DNA structure is suitable for charge transport.[81] However, the real DNA structure is much more complicated and its conductivity depends on many factors.[82] Various distortions of the regular chain structure decrease the probability of charge transfer. These results were obtained by the time-resolved fluorescence method [83] in analysis of the oxidation products [84] and based on changes in the optical absorption spectra.[85]

The artificial substitution of other molecules for natural bases in the DNA chain also affects the probability of charge transfer.[86, 87] The dependence of conducting properties on the structure was demonstrated in numerous experiments on measuring the charge transfer in DNA monolayers [88–90] and in isolated macromolecules.[69, 91]

In some cases, slight discrepancies between the results acquired by different research groups are noted and the results of some experiments cannot be explained based on the modern views on charge transport; however, the efficient charge transfer in DNA can be considered as a well-established fact.[92–96] In line with this, it is expedient to quote the review by Genereux and Barton:[92] 'Certainly the debate among researchers has shifted from 'Is DNA CT possible?' to 'How does it work?'' The shift of the attitude of the scientific community to the problem of DNA conductivity is quite clear if we consider how the titles of articles changed during the last 20 years: from, *e.g.*, 'DNAs conductance still confounds' [93] to 'Distance-independent DNA charge transport across an adenine tract'.[94]

The main goal set by the authors of the present review was to familiarize the readers with experimental results and theoretical concepts in the field of charge transfer in biomacromolecules. The presented material was not intended to provide complete coverage of numerous lines of research in this field. For more detailed acquaintance with the state-of-the-art of particular works, references to specialized reviews are given.

II. Experimental methods of studying charge transfer

The system under study represents a natural or synthetic biomacromolecule with the attached electron density donor (D) and acceptor (A): $D-b_n-A$. The bridge consists of n structural units b, that is, DNA bases or peptide groups; and b_n is the system being studied. The donor serves for injecting the charge into the system, while the acceptor traps or 'detects' in some other way the charge that has reached it.

Several methods are used to study the charge transfer in biological systems. The key methods are either time resolved

(*e.g.*, laser flash-photolysis) or steady-state ones. The charge transfer in DNA includes the following three main stages:

— generation of charge on the donor and its transfer to the chain;

— the charge transfer *per se* along the chain;

— trapping of the charge by the acceptor and its detection.

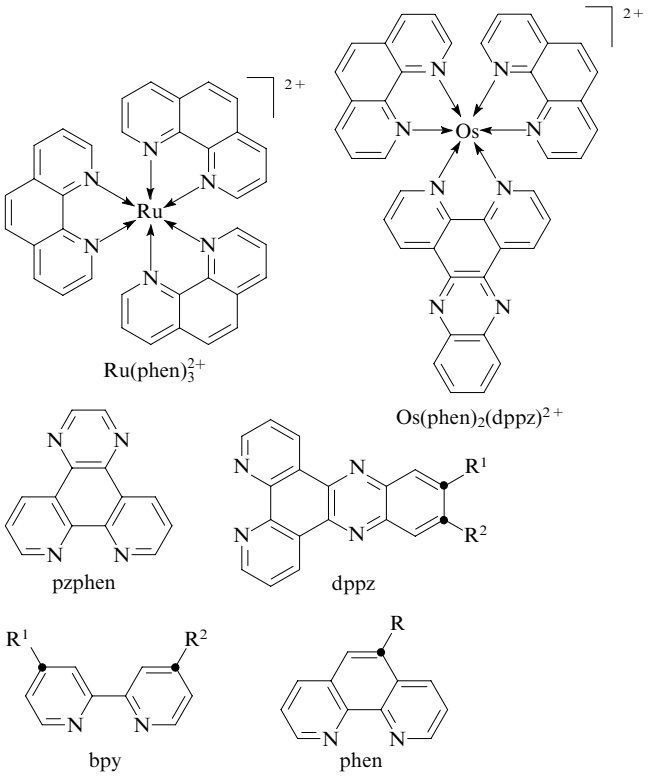
In pulse techniques, the charge on the donor is generated upon absorption of a light quantum. Steady-state methods use permanent charge sources (electrochemical cells or continuous illumination). The acceptor can detect the incoming charge by different methods, based either on changes in the spectra (absorption/excitation spectra) or on charge-induced chemical redox reactions. Other methods of studying the charge transfer are used, for example, scanning tunnelling microscopy adapted to measuring voltammetric characteristics [97–99] and also atomic-force microscopy.[100]

Most often, redox reactions induce a positive charge (hole), which can migrate along the chain. The excess electron can also migrate along the DNA chain. Due to a certain difference in the electron affinity between purine (adenine and guanine) and pyrimidine (thymine and cytosine) bases, a hole migrates mainly through purine bases while an electron migrates through pyrimidine bases. Insofar as the difference of redox potentials between thymine and cytosine is smaller than between adenine and thymine, a particular DNA sequence exerts a weaker effect on the transport of electrons as compared with holes.

The electron density donors and acceptors should meet several requirements. First of all, they should well interact with DNA bases to provide efficient charge transfer from the donor to the chain. Since the access to the bases is shielded by peripheral phosphate groups, one of possibilities is the addition of D and A molecules directly to DNA bases on chain ends. Another possibility is the incorporation (intercalation) of D and/or A molecules between DNA bases. Second, depending on its future function, a molecule should either initiate the electron transfer with a high quantum yield or serve as an efficient detector of this process. Third, donor and acceptor molecules should not chemically react with the DNA chain in both its ground and photoexcited states. Finally, D and A molecules that meet these requirements should be available and their preparation should be simple and inexpensive. It is also desirable to have the means for tuning their photophysical, spectroscopic, redox and other parameters to the particular experimental conditions.

It proved to be very convenient to use metal complexes as the molecules to be attached. Then, by selecting one or another ligand, it is possible to meet many requirements to donors and acceptors. The intercalation of a metal complex was first carried out in 1961.[101] In essence, this method consists of incorporating the ligand of a metal complex (usually a planar conjugated heterocyclic molecule) between two neighbouring DNA bases parallel to them. This provides an overlap between π-orbitals of the ligand and DNA bases sufficient for efficient charge transfer. The structural modifications that occur in the DNA chain upon intercalation are insignificant, namely, the chain becomes longer by a value approximately equal to one interbase distance and slightly untwists.[102] The DNA stability somewhat increases, as indicated by the increase in its melting temperature.[103, 104]

At present, complexes of platinum group metals, namely, Ru, Rh, Os, Ir serve most often as the additives. As an example, the compositions of two metal complexes and typical ligands are shown below †.



Among the most interesting and widely used complexes, there are Ru(bpy)$_2$(dppz)$^{2+}$ and Ru(phen)$_2$(dppz)$^{2+}$. In aqueous solutions, they do not luminesce due to deactivation of their electron-excited states by hydrogen bonds formed by the dppz ligand with water molecules. However, in solutions containing DNA double helix, the dppz ligand is shielded from the solvent (due to intercalation) so that luminescence appears, which makes it possible to use spectral methods for detecting the charge-transfer redox reactions.[105–110]

It was found that the probability of charge transfer from a metal complex to a DNA chain depends on the size and planarity of intercalated ligands,[111] increasing in the series bpy < pzphen < dppz.

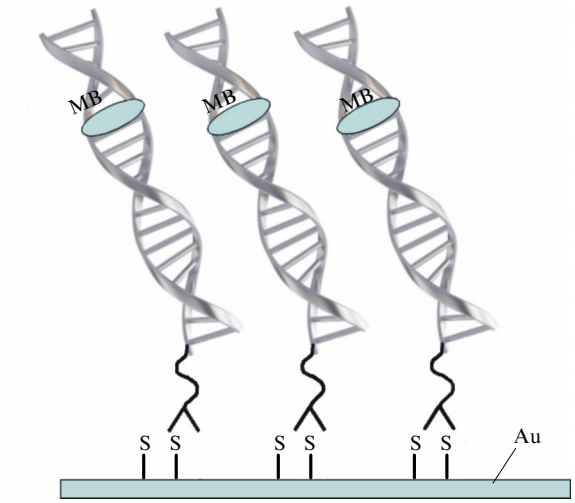
Metal complexes absorb light in the visible range upon the metal to ligand charge transfer. First of all, this is very convenient for detecting redox processes by spectroscopic methods and, second, this makes possible the targeted modification of redox properties of metal complexes by their photoexcitation. From the photoexcited state, the charge can be transferred to the DNA chain because metal complexes in this state may exhibit strong oxidative or reductive properties.[112, 113] Ligands are functionalized by attachment of long alkyl chains,[107, 108, 114] which are chemically bonded to the DNA chain. This provides a strong bond between metal complexes and DNA bases.

† In positions marked by points, the substituents (R) that modify the redox and spectroscopic properties of metal complexes can be attached. Under the structures, their generally accepted designations are shown.

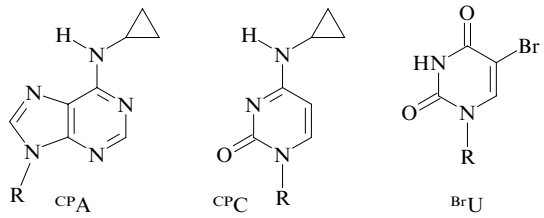
Analysis of the mechanisms of natural biochemical reactions and the results of numerous experiments on model systems have shown that the site in which the charge is generated and the site in which this charge, after migrating along the DNA chain, induces a photophysical response or chemical reactions may be separated in space. Such reactions have been called 'chemistry at a distance'.[115] The first example of reactions at a distance was the efficient fluorescence quenching upon charge transfer through a DNA chain from one intercalated excited complex $[Ru(phen)_2(dppz)]^{*/2+\bullet}$ (donor) to another intercalated complex $[Rh(phi)_2\ (phen)]^{3+}$ (phi is phenanthrene-9,10-quinonediimine).[48,49] In these experiments, the photoexcited ruthenium complex is not a sufficiently strong reducing agent to pass an electron directly to the DNA chain; however, it reduces the rhodium complex located at a considerable distance from the donor ruthenium complex. The numerous examples of the use of metal complexes as the donors and acceptors of electron density in the charge transfer in DNA and the accompanying chemical reactions are considered in more detail in a review.[116]

Other electron density donors and acceptors capable of being either incorporated into the DNA structure [for instance, Methylene Blue dye (MB)][117] or attached by a covalent bond to the chain end have been used in the studies of charge transfer processes. There are a lot of molecules capable of serving as donors and acceptors. Thus anthraquinone with various substituents can serve as both the donor and the acceptor.[118]

A large array of experimental data was obtained when studying the electrochemical phenomena induced by charge transfer under steady-state conditions. Such processes were investigated both in solution and in DNA monolayers supported on a surface. According to a very convenient procedure, DNA molecules are attached by alkyl chains with terminal sulfur atoms to the surface of a conducting metal, most often gold, to form ordered monolayers. Upon application of a potential difference to these molecules, the electrons or holes are transferred to active groups, *i.e.*, acceptors, to induce electrochemical transformations, which are then detected. One of the early electrochemical experiments involved oxidation of the aromatic MB dye the molecules of which were incorporated into the DNA structure.[117] In these experiments, the dye underwent a reversible redox reaction upon a change in the potential difference between the Au substrate and the solution.



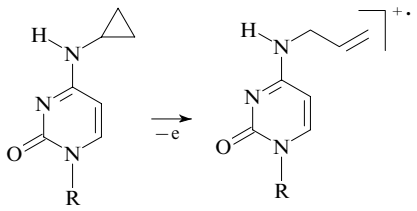
The methods of detecting charge transfer processes are very diverse being determined by the choice of a particular charge acceptor. Cyclopropyl- and bromine-substituted DNA bases proved to be very convenient as such acceptors. Their structures is shown below.



From here on, R designates a DNA chain.

Cyclopropyladenine (^{CP}A) and cyclopropylcytosine (^{CP}C) are used as the traps of charge carriers; bromouridine (^{Br}U) is often used as the acceptor. Scheme 2 illustrates the opening of a three-membered ring during the oxidation of cyclopropylcytosine.

Scheme 2

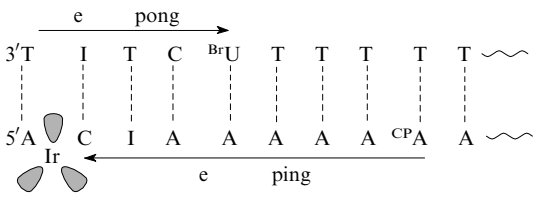


For cyclopropylguanine (^{CP}G) and ^{CP}A, a very short opening time for a three-membered ring ($\sim 10^{-11}$ s) upon single-electron oxidation was observed.[119–121] Analogous properties are typical of ^{CP}C (Refs 122 and 123) and ^{Br}U (Refs 124–126). The convenience of using these compounds as the charge traps lies also in the fact that reaction products can be identified rather easily.

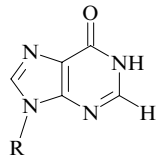
Bromouracil is also used for charge injection. Its advantage over related thymine lies in the fact that it has a more negative reduction potential and more easily passes an electron to the chain.[127] The use of bromouracil for charge injection was first reported in several studies.[126,128,129] The regularities similar to those found in electrophysical measurements were also observed in numerous electrochemical experiments.

Using more diverse methods for incorporating donors and acceptors into the DNA structure, one can observe interesting effects. For example, the 'ping–pong' effect was observed in the forward and back electron transfer in a synthetic DNA fragment (Scheme 3).[104]

Scheme 3



Here, I is the synthetic analogue of adenine



An iridium complex was incorporated into the adenine sequence of the DNA double helix. Cyclopropyladenine was incorporated into the same sequence at a certain distance from the complex. Bromouridine was incorporated into the complementary helix built of thymine bases. For convenience, three chains were used: a short chain which included 5 pairs of DNA bases (5-mer) was covalently bound to the metal complex; the second chain (13-mer) contained modified ^{CP}A; the third complementary chain (18-mer) contained ^{Br}U or ^{CP}C. Excitation of the iridium complex (excitation wavelength $\lambda = 365$ nm) triggered the cyclopropyladenine oxidation

$$Ir^{3+} + e \longrightarrow Ir^{2+}$$

$$^{CP}A - e \longrightarrow {}^{CP}A^{+}$$

This is the 'ping' reaction. In turn, after returning to its ground state, the iridium complex can again reduce bromouracil at a distance

$$Ir^{2+} - e \longrightarrow Ir^{3+}$$

$$^{Br}U + e \longrightarrow {}^{Br}U^{-}$$

This is the 'pong' reaction of backward charge transfer. The adenine base sequence was chosen because it is the most resistant to charge trapping.[130] In this experiment, iridium complexes somewhat enhanced the stability of the DNA double helix. Such enhancement is typical of intercalation of metal complexes with flat aromatic ligands.[131, 132]

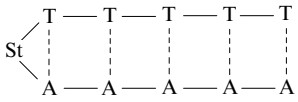
The details of studies of electrochemical properties related to the DNA-mediated charge transfer can be found in several reviews.[8, 133–135]

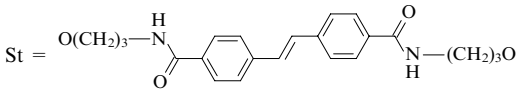
In experiments where the sequences of bases were either random or built of blocks of different length for different bases, the rate and the probability of charge transfer depended appreciably on a particular system.[28, 29, 136] However, minor variations in the chain structure, for instance, the substitution of 5-methylcytosine for cytosine did not bring about any noticeable changes in the redox properties of modified DNA associated with charge transfer.[137]

Another factor affecting the probability of charge transfer is the distance between the donor and the acceptor. Obviously, as the distance at which the charge is transferred increases, the probability of transfer decreases. This is explained by dynamic (temperature) or static (various faults of the regular structure) fluctuations. It is assumed that the probability of charge transfer decreases according to the exponential law *vs*. the charge transfer distance (r)

$$\kappa \approx \exp(-\beta r), \qquad (1)$$

where the attenuation coefficient β characterizes the possibility of charge transfer from one site to another and depends on the nature and the height of the barrier between them. One of the first measurements of rate constants for the charge transfer was carried out in a hairpin-type synthetic system of oligonucleotides.[138] A chromophore [stilbene-4,4-dicarboxamide (St)] closes the free ends of two complementary segments of the DNA chain. In experiments, various sequences of bases and lengths of the hairpin chain were used in order to elucidate the dependence of the charge transfer rate on these parameters. The St chromophore served as the photooxidant and the charge transfer detector.





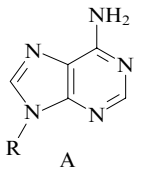
Photoillumination gives rise to the singlet state chromophore ($St^{-\bullet}$), which selectively photooxidizes guanine to form radical cation $G^{+\bullet}$. By monitoring the kinetics of the $St^{-\bullet}$ radical anion excitation and quenching, it is possible to study charge separation and recombination processes. The rate constants of forward and backward charge transfer were found to be 5×10^7 and 5×10^6 s^{-1}, respectively.

By using improved procedures for sample preparation and selecting proper donors and acceptor, faster charge transfer was observed.[139] Stilbene diether $O(CH_2)_2O.(p\text{-}C_6H_4)CH_2{=}CH_2(p\text{-}C_6H_4)O(CH_2)_2O$ (Sd) and stilbene dicarboxamide (Sa) were used as the donor and the acceptor. They closed the end of the DNA hairpin on both ends. Upon selective photoexcitation ($\lambda = 350-355$ nm) of the St terminal group, its singlet excited state $^1St^*$ can be observed (by fluorescence and stimulated radiation at $\lambda_{max} = 385$ nm). Simultaneously, charge transfer generates the $St^{-\bullet}$ radical anions ($\lambda_{max} = 575$ nm) and $Sd^{+\bullet}$ radical cations ($\lambda_{max} = 525$ nm). Laser flash photolysis measurements have shown that for 3 to 8 DNA base long conducting bridge, the charge transfer time is several nanoseconds and the time of a single charge hopping between the neighbouring bases is ~ 0.6 ns.

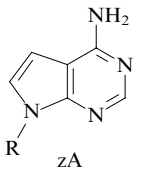
Subsequent studies[140–143] report further increase in the charge transfer rate in short hairpin DNA fragments and a rate constants of $\sim 10^9$ s^{-1}. In the same studies, the activation energies for charge transfer and energies of medium reorganization were measured.

The main obstacle to the use of DNA as 'molecular wires' is the relatively low charge transfer rate. Hence, the desire to enhance this rate is natural. One of the methods for its enhancement is the formation of a regular structure resembling the DNA composed of synthetic analogues of bases.

It was found that replacing adenine by its analogue, 7-deazaadenine (zA), in short chains $G(A)_5G \rightarrow G(zA)_5G$ increases the rate constant for charge transfer by $> 10^3$ s^{-1} (Ref. 144).



A



zA

To pursue this line of research, poly-7-deazaadenine $(zA)_n$ was synthesized. The rate constant for charge transfer in $(zA)_n$ was 4.2×10^{10} s^{-1} (Ref. 145), *i.e.*, one order of

magnitude higher that the rate constant for polyguanine (4.3×10^9 s^{-1}). This is so far the highest rate constant for charge transfer.

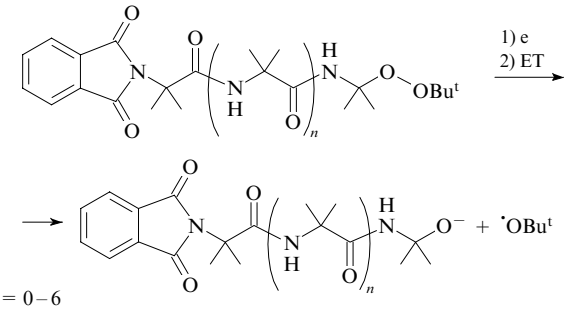
When attempting to increase the rate of this process along the chain, bear in mind that the transfer from the donor to the chain can be the limiting stage of the overall charge transport process. The charge injection rate depends on the redox potentials of the donor and the DNA bases and also on the structure of the $D-b_n$ systems (as explained by the Marcus theory [146]) and can be limited by the rate of medium reorganization.

Peptides and proteins exhibit high physiological activity, take part in metabolism and regulate the vital biological processes in which charge transfer is a necessary stage. Polypeptides lack the exchange $\pi-\pi$-electron interaction, which is believed to provide the basis of charge transfer in DNA. Nonetheless, the regularities of charge transport observed in polypeptides are quite similar to such processes in DNA. The main element of polypeptides is the helix by which the charge is transferred. These systems were studied in solutions [147, 148] and on the surface of metals.[149–153] Certain common features were revealed for the charge transfer in DNA and polypeptides. First, the charge is transferred better by the α-helix of peptides [148, 152] than by the molecules of some aromatic hydrocarbons;[154] second, as for DNA, the critical length r_c exists such that for $r < r_c$, the attenuation coefficient β in the exponential dependence (1) is in the range from ~0.1 to 1 $Å^{-1}$ and at longer distances, it is at least one order of magnitude smaller.[155, 156]

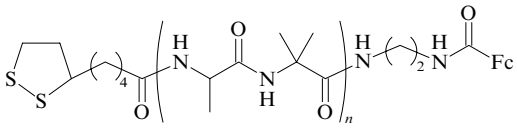
If the polypeptide structure represents a well-ordered helix with intramolecular hydrogen bonds, then the rate constants for charge transfer are higher as compared with poorly ordered systems. Thus, helical polypeptides of various lengths were synthesized and served for the formation of monolayers on a gold substrate. Ferrocene (Fc) was attached to the opposite end.[157] For electron transfer, a weak dependence on the peptide chain length was observed; the attenuation coefficient was very small ($\beta \approx 0.04$ $Å^{-1}$).

Phthalamide (donor) and peroxide (acceptor) were attached to the ends of a synthetic polypeptide chain formed by aminobutyric acid.[158] Scheme 4 shows the reaction observed in an electrochemical experiment on the cleavage of the peroxide group (a dissociative-type acceptor) upon the charge transfer from phthalimide.

Scheme 4



Later, 8-, 16-, 32- and 64-mers of helical peptides containing alternating sequences of L-alanine and α-aminobutyric acid were synthesized.[159] These peptides were attached with their one end to a gold substrate *via* Au–S bonds and formed monolayers. As the number of intermolecular bonds increased and the chain became longer, the inclination angle of peptide helices with respect to the support plane increased: the angle was ~41° for 8-mer and 67° for 64-mer. The resulting monolayers were reported to have the greatest thickness (~88 Å for 64-mer) among similar systems and to form well ordered structures. The charge transfer proceeded as follows. First, an electron is transferred from the left terminal amide group to gold. The resulting radical cation migrates over amide groups to reach ferrocene and be reduced there. This is the total route of electron transfer from ferrocene to gold. The efficiency of this process is directly related to the peptide chain 'quality' (its regularity and ordering). The chemical structure of synthesized peptides containing 6,8-dithiooctanoic acid on the left end to be attached to gold and the oxidation-active ferrocene group (electron donor) on the other end (n = 8, 16, 32, 64) is shown below.



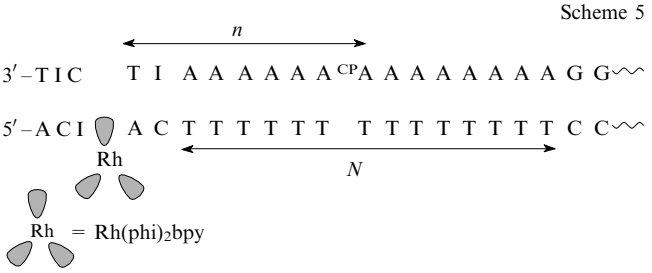
The attempts to elucidate the reasons for the high efficiency of charge transfer in polypeptides took into account the effect of their environment [160] associated with fast relative rotations (changes in the angles between peptide bonds).[161] In certain cases (if the peptide structure represents a well-developed helix with intramolecular hydrogen bonds), there are grounds to consider the charge transfer as a single-step reaction.[158] The questions of the relationship between the DNA or peptide structure and their conducting properties were considered in a review.[9]

A substantial improvement in electroconducting properties of biomacromolecules was achieved in experiments on the preparation of synthetic fragments of DNA and peptides with the use of modern automatic systems. At present, sufficiently long DNA segments built of virtually random base sequences can be synthesized. This makes it possible to solve one of the major problems, namely, to create quisi-one-dimensional virtually defect-free structures of a given length, which is the necessary condition for the efficient charge transfer.[4, 5, 48, 138, 162–165] In was found that the best building block for assembling synthetic charge-transfer chains is adenine paired with thymine. This is due to certain peculiarities of its electronic structure beneficial for charge capture [166] and transfer. [167, 168] Substitution of a CH group for the N(7) atom in adenine to afford zA improves the charge transfer. This even somewhat increases the overlap of π-systems of neighbouring bases as compared with original adenine.

The synthesis of DNA segments comprising sequential 4, 6 and 14 pairs of bases $(A:T)_N$ was reported [94]

Scheme 5 illustrates a the charge transfer experiment (N is the length of the sequence of A:T bases; n is the

Scheme 5



distance from the ruthenium complex to cyclopropyladenine; a chain segment that includes 14 A:T base pairs is shown).

The transfer was detected by the reduction of ^{CP}A in the adenine sequence. To the one side of $(A:T)_N$ segments, the $[Rh(phi)_2(bpy)]^{3+}$ complex was attached to serve as the photooxidant for ^{CP}A. Cyclopropyladenine was incorporated into the chain at a distance $n \leqslant N$ from the ruthenium complex and served for detecting the charge transfer according to Scheme 3. When studying the probability of charge transfer as a function of the distance n measured by opening the cyclopropyl fragment, it was found that the attenuation coefficient for the charge transfer was as low as 0.0013 $Å^{-1}$ and the probability of transfer was very high. For instance, the transfer probability for a distance of 100 Å was ~88%. The terminal $(G:C)_2$ group served to prevent the charge propagation along the chain by locking the charge carrier in a limited region. This limitation can lead, in particular, to the backward transfer of charge, *i.e.*, it may actually lead to recombination of the generated charges.[10, 169–172]

The analogous opening of a three-membered ring in other cyclopropyl-substituted bases, such as N(2)-cyclopropylguanine (^{CP}G) and N(4)-cyclopropylcytosine (^{CP}C) (Refs 120, 123, 167) also allowed these molecules to be used as the detectors for charge transfer.

The ratio of two characteristic times, namely, 'electronic' (t_{el}) and 'chemical' (t_{chem}), is very important. Since the charge migrates along the chain by the hopping mechanism, it can be assumed to stop on each base for a certain time. The parameter t_{el} is the time during which the charge is located on the acceptor with a sufficiently high probability. Parameter t_{chem} is the time necessary for an electrochemical reaction to proceed or a photophysical response to the charge that has arrived to occur. For successful implementation of this experiment, it is necessary to check the fulfilment of the condition $t_{chem} \leqslant t_{el}$, *i.e.*, the charge should reside in the reaction site for a time sufficient for one or another reaction to occur. Particularly, this is why the cyclopropyl-substituted DNA bases are used: they have a very short time for the reaction of three-membered ring opening ($t_{chem} \leqslant 10^{-11}$ s).

The charge transfer in a synthetic DNA fragment consisting of 100 base pairs (34 nm) was reported [173] to proceed with a very high efficiency. Using an automatic DNA synthesizer, three oligonucleotides were prepared, namely, a 100-mer with bases in regular positions, a 100-mer with a specially introduced chain defect; and a regular 17-mer. Comparing the results for the regular and defective 100-mers has shown that the charge transfer in the defective oligonucleotide is virtually absent, which convincingly points to the charge transfer along the π-conjugated chain of DNA bases. At the same time, the probabilities of charge transfer for regular 17- and 100-mers proved to be almost the same, which suggests that the charge transfer depends little on the distance by which it proceeds.

In addition to experimental results, which fit the existing concepts on the mechanisms of charge transfer processes, the data were published that do not match these concepts. Thus, some experiments (*e.g.*, on quenching of fluorescence of a photoexcited 2-aminopurine molecule upon the charge transfer to guanine) revealed the periodic dependence of the charge transfer probability on the length with the period of 3–4 base pairs.[167, 174] Earlier, similar periodicity was observed in studying the conductivity of methyl-substituted oligophenylethylene;[175] this was attributed to the appearance of segments confined by different twist angles of monomer units with respect to the oligomer axis. This mechanism cannot explain the periodic dependence for a DNA with the constant helix twist angle. The observed periodicity may suggest that for some reasons, an adenine sequence with the length divisible by to the length of the charge localization region transfers the charge better than a sequence of the same bases of a different length, although the mechanism is still unclear.

Yet another interesting and significant factor was elucidated: in certain systems, as the distance between the donor and the acceptor increases, the transfer occurs in a single step. The mechanism changes from a multi-step process typical of the hopping model (in which the charge localization on a DNA base can be detected) to a single-step process (for which only initial and final charge states can be detected). The mechanism of such charge transport is still unclear.[116, 176] An analogous phenomenon of coherent charge transport was observed in a well-developed α-helix of a peptide with intramolecular hydrogen bonds.[158]

III. Charge transfer mechanisms

To control the charge transfer processes, one has to understand their mechanism. The first theory that explained the laws of a donor to acceptor charge transfer in condensed phase was the theory of Marcus.[177–181] This theory combined ideas of chemical kinetics and thermodynamics with the views on how molecular movements and variations in the nuclear configuration affect the charge transfer rate. Marcus has shown that the probability of electron transfer in the reaction that proceed through a transition state

$$D + A \longrightarrow [D\cdots A] \longrightarrow D^+ + A^-$$

can be expressed (to an accuracy up to the main terms) as follows:

$$k_{et} = |H_{DA}|^2 \exp\left[-\frac{(\lambda + \Delta G_0)^2}{4\lambda kT}\right], \qquad (2)$$

where H_{DA} is the intensity of electronic coupling between the reactants and reaction products in the transition-state nuclear configuration; λ is the reorganization energy of the medium; ΔG_0 is the Gibbs free energy; k is the Boltzmann constant.

One of the main parameters in the Marcus theory is the difference between the oxidation potentials of D and A, which is the driving force of the electron transfer reaction. Moreover, since the electron transfer is accompanied by changes in the charge distribution in [D···A] complex, the reorganization of the medium occurs. The energy of this reorganization λ is also an important parameter in this theory. One of interesting consequences from the Marcus theory is the prediction of the bell-shaped dependence of k_{et} on ΔG_0, which was be observed experimentally [182] only ~30 years after the first Marcus publications.[177, 178] McConnell [183] has shown that in the system $D-b_n-A$, the probability of charge transfer decreases exponentially with the distance between D and A [see Eqn (1)]. The reciprocal of the attenuation coefficient β shows the distance at which the probability of transfer decreases by a factor of e. For

instance, for saturated hydrocarbons, $\beta \sim 1$ Å^{-1} (Refs 154 and 184) and for conducting polyenes and polyphenylene vinylenes, it is $\beta \sim 0.04$ Å^{-1} (Ref. 185). However, these results are true for the charge transfer between closely located donor and acceptor molecules. If the charge is transferred by long distance, the Marcus theory cannot be used.

At present, two main approaches are used for describing the long-range charge transfer. One approach is based on the tunnelling mechanism, while the other relies on the hopping mechanism.[92, 162, 186–192] In both cases, the charge is assumed to be preferentially located in a single site.

The tunnelling phenomenon discovered in the late 1920s by Gamow[193] in relation to nuclear α-decay marked the beginning of 'new quantum physics'. The conclusions of this theory are also true for tunnelling of an electron or a hole. The exponential decay of the probability of charge transfer in the tunnelling is determined by the fact that electron wave functions of two neighbouring states decay exponentially and it is their small overlap that determines the exponentially decreasing probability of the tunnel transition. Sometimes this transition is called coherent, meaning that electron does not exchange energy with the environment and is not localized. The tunnelling mechanism of charge transfer was indirectly confirmed in several experiments, for example, in Ref. 194 for the hole migration through several A : T bases. A kinetic model of charge transfer based on the tunnelling effect has been developed.[141] The energy of medium reorganization upon the charge transfer to the nearest neighbouring base is 0.83 eV and the rate constant is 1.2 ns^{-1}.

The tunnelling mechanism is true if the distance by which the charge is transferred is not too long ($< 3-4$ DNA base pairs). However, charge can be transferred by much longer distances. In this case, the hopping mechanism is involved according to which charge is transferred from one species to another by heat-activated jumps. Probably, this mechanism was first proposed by Meggers *et al.*,[3] who studied long-range charge transfer processes is DNA oligomers. They elucidated that the transfer occurs by a multi-step hopping mechanism through the chain of guanine bases, where guanine residues represent the 'halting points' and have a positive charge during a single jump. Due to charge localization on guanine, intermediate products are formed. The sequence of adenine bases can also serve as an efficient charge-transfer route.[162] In the hopping mechanism, the probability of charge transfer follows a power law, *i.e.*,[195]

$$k_{ct} = r^{-\alpha},$$

for transport in one direction (α values are from 1 to 2). When the charge can hop in both directions with equal probability, its one-dimensional random walk according to diffusion mechanism is observed.

The simplest way to consider charge hopping is within the framework of the strong coupling approximation.[196] In molecular electronics, this approximation describes a situation where the charge carrier is strongly bound to the molecule that bears it but interacts rather weakly with other neighbouring molecules. Nonetheless, there is probability for the charge to hop to a neighbouring molecule due to the finite, although weak, coupling between neighbouring molecules.

Direct experimental evidence for the hopping mechanism is the detection of charge transfer intermediates. The hopping process is implied to be adiabatic, so that after each jump the charge comes into equilibrium with the environment. The k_{ct} *vs.* r dependence serves as an indirect indication of the difference between transfer mechanisms.

The switching of the conduction mechanism from tunnelling to hopping was observed experimentally.[162] If in the $D-b_n-A$ system, the bridge length is $n \leqslant 3$, then $\beta = 0.6$ Å^{-1} and the probability of charge transfer quickly decays with the distance. However, starting from $n = 4$ and to $n = 16$, a much smoother dependence of k_{ct} on the distance was observed. It was concluded that for $n \leqslant 3$, tunnelling occurs, whereas at $n > 3$ heat-induces jumps take place.

The most well-known theory describing the long-range charge transport in biological systems is the electrosoliton theory put forward by Davydov.[197–200] This theory is based on the assumption that energy liberated, for instance, in adenosine triphosphate hydrolysis may exist as localized chain oscillations rather than dissipate throughout the environment. The charge-coupled state of these oscillations that exists due to the non-linear electron–phonon interactions was called the self-localized electron or electrosoliton.

For some time it seemed that the Davydov theory can explain many phenomena associated with the transfer of energy and charge. However, the results of subsequent thorough numerical modelling have shown that the theoretically predicted electrosoliton state is stable only at very low temperatures ($T < 10$ K) and the electrosoliton lifetime does not exceed several picoseconds.[201–203] This is why the Davydov theory in its original version is far from being popular in explaining the charge transport in biological systems. Nonetheless, studies along this line were carried on taking into account the non-linear effects of interparticle interaction. The possibility of transfer of vibrational energy and charge in DNA and protein molecules was considered.[204–208] It was demonstrated that the polarization-induced lattice deformations can give rise to a self-localized state capable of supersonic transport of energy and charge. Details of Davydov's theory and its further development can be found in several reviews.[202, 209, 210]

In the hopping mechanism, the charge is assumed to be completely localized on one of bases. However, the theory and certain experimental data suggest that the charge is delocalized over several, more often, three or four bases.[123] This is explained by the fact that for a charge it is energetically advantageous to polarize its environment and create a self-localized state, *i.e.*, a polaron. In a regular chain, the polaron state is translation-invariant; hence, it can move. If the lattice is random like the natural DNA lattices, the polaron motion can acquire the heat-activated hopping character.

The polaron mechanism was probably pioneered in a study[211] in which the experimental data on charge transfer were confronted to theoretical concepts on the charge transport by polaron hopping through the DNA chain. A theoretical description of polarons in DNA and the necessary model parameters can be found in several publications.[212–214]

At present, the polaron mechanism is very popular in explanation of the charge transfer. Polarons are employed in various models and quite different approximations.[215–218] Theoretical approaches to the description of

polarons with small [219–222] and large [223] radii are somewhat different.

The diffusion mobility of polarons [224, 225] and their mobility in an applied electric field [216, 226–230] were calculated. In analyzing the polaron migration in an electric field, it was shown that there exists a threshold potential difference below which the conductivity in DNA is absent.[228, 229]

The current through a single DNA chain can be very large (up to 5 nA for the potential difference of 2 V).[222] For an asymmetrical sequence of DNA bases in short chains, the rectifying effect was observed.[229] The results of these studies well agree with experimental data.[231]

It is assumed that in the absence of potential difference, polarons posses only diffusion mobility. However, there exists a possibility of spontaneous migration of polarons due to the positive gradient of chain curvature.[232] Polaron is prone to perform random walk in a chain, but the driving force associated with the chain curvature determines the direction of its drift.

Consideration of polaron dynamics at non-zero temperatures is very important for practice.[221, 226, 233, 234] It was shown that as the temperature increases, the probability of charge transfer becomes higher.[167, 174, 235] In this case, we observe competition between the following opposing factor, one reducing the probability of transfer by enhancing the fluctuations (increase in the dynamic disorder) and the other increasing the probability of heat-activated jumps. However, the effect of the second factor should disappear at distances exceeding ~ 15 Å.[236] So far, no adequate explanation has been found for the temperature dependence of the charge transfer according to which the conductivity increases with increase in temperature.

Although direct experimental methods fail to confirm the polaron transport mechanism, the latter gains in popularity, as it is able to explain a lot of experimental facts and predict new interesting phenomena.

For the charge transfer mechanisms discussed above (tunnelling, hopping and polaron mechanisms), the details of interaction between 'particles' are not too important. In many cases, it is sufficient to introduce the harmonic approximation into interactions to make these models suitable for describing the charge transfer. However, the real interaction potential is non-linear. This is why the idea borrowed from the non-linear dynamics theory according to which solitons exist in non-linear systems proved to be very attractive.[237–241] A soliton represents a migrating lattice deformation with a definite stable profile. This deformation represents a potential well in which the charge can get. Thus, a coupled state can be formed, which was called the solectron in which the charge adiabatically follows the soliton.[242, 243] This mechanism could have explained certain charge-transfer experiments. However, taking into account the considerable opposite effect of the electronic subsystem on the dynamic variables, the solectron can most probably be considered in the framework of the non-adiabatic approximation.

In calculations associated with charge transfer, one has to operate with the model concepts on the structure of DNA or polypeptide chains. The original systems are always very complicated; this is why various simplifying assumptions are used. Such simplifications make it possible to convert the problem to a form that allows for its detailed analytical consideration or numerical simulation. Most often, a model is built for a particular property under study.

The simplest model considers a single DNA strand in which the role of 'beads' (particles) is played by bases and the interaction between them is due to overlap of π-systems of neighbouring aromatic bases. A quasi-one-dimensional model which additionally considers the interactions between both DNA strands, is used rather often. The double helix DNA model [244, 245] is among the most popular models. It is suitable for interpreting local distortions (pairing–unpairing of hydrogen bonds between the bases, which play the role of breathers) when considering the dynamics of DNA helix untwisting.[246] The model proposed by Yakushevich [247–250] proved to be helpful in explaining the DNA transcription. This model takes into account the rotational dynamics (as opposed to other models that mainly consider longitudinal shifts of particles) and, like many other one-dimensional non-linear DNA models, identifies the local excited states (such as solitons).[251] A very convenient (as regards computation efficiency and applicability to description of many DNA properties) coarse-grained DNA model has been developed by Manevich and co-workers [252, 253] They considered [253] the heat conduction in DNA; however, the coarse-grained model can also be successfully applied to study other properties.

The studies of charge transfer mainly use one of the simplest models, namely, the one-dimensional model of particles with the overlap of π-systems of neighbouring bases. Calculations within the framework of this model are carried out in the tight-binding approximation.

Thus, several mechanisms of charge transfer were proposed, each having its own scope of applicability, describing the transfer in a particular system (DNA and polypeptides) with a particular structure (for structural units of different lengths and different sequences). The choice of mechanism is not always unambiguous.

IV. Polaron mechanism of charge transfer in DNA

This Section briefly considers the evolution of the concept of polarons in DNA. The complete Hamiltonian of the DNA–charge system is as follows:

$$H = \sum \frac{c}{2}(x_i - x_{i-1})^2 + \sum \frac{m}{2}\dot{x}_i^2 + \sum_i \varepsilon_i \psi_i \psi_i^* + \\ + \sum_i t_{i,i-1}(\psi_i \psi_{i-1}^* + \text{c.c.}), \quad (3)$$

where c is the bond rigidity constant; x_i is the displacement of the coordinate of the ith particle from its equilibrium position, m is the particle mass (the potential of interaction between neighbouring particles is assumed to be harmonic), ε_i is the on-site energy of the electron with the ith particle; ψ_i is the amplitude of the discrete wave function on the ith particle; $t_{i,i-1}$ is the hopping integral which depends on the interaction between neighbouring systems and determines the probability of the electron hopping from the $(i-1)$th to ith particle and back; c.c. means complex conjugation. Taking into account the non-linearity of particle interaction brings about only minor quantitative changes in conclusions with the main qualitative characteristics remaining unchanged. The last sum in expression (3) describes the electron–phonon interaction in the tight binding approximation.[212, 254–256] Below, for the sake of definiteness, we consider an electron, although this approach can also be

used for holes, provided certain modifications are introduced into parameter values.

For a uniform chain (in the absence of statistical disorder), $\varepsilon_i = \varepsilon = \text{const}$ and, without loss in generality, it can be assumed that $\varepsilon = 0$, because this parameter determines the electron energy origin. The hopping integral $t_{i,i-1}$ is often written in the Su–Schriffer–Heeger approximation,[257,258] which is linear as regards the shift of particles from their equilibrium positions

$$t_{i,i-1} = -[v_0 - \alpha(x_i - x_{i-1})], \tag{4}$$

where v_0 is the hopping integral for the equilibrium configuration, α is the parameter of the electron–phonon interaction.

It is convenient to use dimensionless values assuming that in Eqns (3) and (4), the mass, the bond elasticity constant and the energy are all equal to unity

$$m = c = v_0 = 1.$$

Then, the dimensionless parameters of time and length are

$$t = \sqrt{\frac{m}{k}},$$

$$L = \sqrt{\frac{v_0}{c}},$$

and the dimensionless parameter of the electron–phonon coupling is

$$\frac{\alpha}{\sqrt{cv_0}} \to \alpha.$$

In the steady state, $\dot{x}_i = 0$ and the expression for the total polaron energy in the dimensionless form can be written as

$$H = \frac{1}{2}\sum_{i=1}^{N-1} y_i^2 - \sum_{i=1}^{N-1}(1 - \alpha y_i)(\psi_i^*\psi_{i+1} + \text{c.c.}), \tag{5}$$

where

$$y_i = x_i - x_{i-1}.$$

Variables $\{y_i\}$ and $\{\psi_i\}$ are interrelated[213]

$$y_i = -2\alpha\psi_{i-1}\psi_i.$$

As a result, the number of independent variables in expression (5) is halved and reduces to a set of discrete wave functions $\{\psi_i\}$. In the steady state, the wave function can be considered as real and the polaron itself is assumed to be symmetrical with respect to its centre with the coordinate $i = 0$. We designate the wave function amplitude as ψ_0 in the central point and ψ_i ($i = 1, 2, \ldots$) in the other points, *i.e.*, we will consider the right-hand part of the polaron. Then, the Hamiltonian takes the form

$$H = -4\sum_{i=0}^{\infty}\psi_i\psi_{i+1} - 4\alpha^2\sum_{i=0}^{\infty}(\psi_i\psi_{i+1})^2 \tag{6}$$

with the wave function normalization

$$\psi_0^2 + 2\sum_{i=1}^{\infty}\psi_i^2 = 1.$$

To determine the polaron parameters (amplitudes of wave functions on particles, the energy and the radius), it is necessary to minimize the energy in expression (6) with respect to $\{\psi_i\}$ values. As a result of minimization, the following system of algebraic equations can be obtained:

$$\psi_i + 2\alpha^2\psi_0\psi_i^2 = \frac{\mu}{2}\psi_0, \tag{7}$$

$$\psi_{i+1} + \psi_{i-1} + 2\alpha^2\psi_i(\psi_{i+1}^2 + \psi_{i-1}^2) = \mu\psi_i, \; i = 1, 2, 3, \ldots,$$

where μ is the undetermined Lagrange multiplier introduced to ensure that this system of equations meets the condition of wave function normalization.

For a finite number of particles N, this system completely determines the solution. However, for higher N values, the computation procedure is complicated but a more efficient method of solution can be used. The approach is based on the fact that far from the centre, the wave function decays exponentially with the distance, *i.e.*,

$$\frac{\psi_{i+1}}{\psi_i} = g,$$

where g is the geometric progression ratio. Hence, for, *e.g.*, ψ_0, ψ_1 and ψ_2 the first three equations of system (7) can be solved. For ψ_i ($i > 3$), one can use the condition of geometric progression. Figure 2 illustrates the solution.

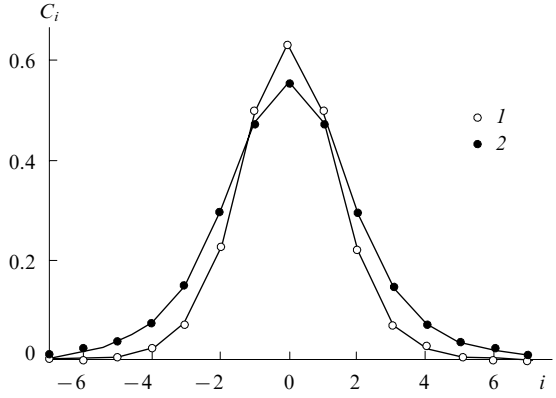


Figure 2. Wave functions $C_i = |\psi_i|$ for two polarons with $\alpha = 1.5$ (1) and 1.0 (2).[259]
Polaron is located in the midpoint of a chain with the number of particles $N = 101$ ($-50 \leqslant i \leqslant 50$). Points are the exact results obtained by numerical minimization of energy (6); curves correspond to calculations with the use of analytical expressions.

Above, we considered a polaron with a small radius the solution for which is obtained for relatively high values of the electron–phonon coupling parameter. To find the analytical expressions for a large-radius polaron (for small α), one can use a continuum approximation. The analytical solution for the large-radius polaron is derived based on the second equation of system (7).

By subtracting $2\psi_i$ from both sides of this equation, substituting $2\psi_i^2$ for the sum $(\psi_{i+1}^2 + \psi_{i-1}^2)$ and introducing a small parameter $\delta^2 \equiv \mu - 2$, we obtain the equation

$$\frac{1}{\delta^2}(\psi_{i+1} + \psi_{i-1} - 2\psi_i) + 4\frac{\alpha^2}{\delta^2}\psi_i^3 = \psi_i. \tag{8}$$

After the change of variables

$$\psi_i = \frac{\delta}{\alpha\sqrt{2}} q_i,$$

this equation takes the form

$$\frac{1}{\delta^2}(q_{i+1} + q_{i-1} - 2q_i) + 2q_i^3 = q_i. \tag{9}$$

For the large-radius polaron, we can pass to a continuous limit and arrive to the following continous equation:

$$q'' = q - 2q^3. \tag{10}$$

with solution

$$q = \operatorname{sech}(x),$$

or in the discrete form

$$\psi_i = \frac{\alpha}{\sqrt{2}}\operatorname{sech}(\alpha^2 i). \tag{11}$$

The polaron radius is $\sim 1/\alpha^2$. The relative shift of neighbouring particles has also a simple form

$$y_i \simeq -\alpha^3 \operatorname{sech}^2(\alpha^2 i).$$

As for the small-radius polaron, the agreement between the 'exact' result and analytical expressions is very good. Solution (11) was obtained rather long ago [260, 261] for models slightly different from that considered above and by much more complicated methods.

The polaron centre may be located in two intermediate states, namely, on the particle and in the middle between particles. The dimensionless energies of polarons in these two states differ only slightly: $E_1 = -2.64539$ and $E_2 = -2.64513$ (the quantity v_0 can serve as the energy unit). Hence, the activation barrier for the polaron transition from one particle to another is very small and the polaron can migrate over the lattice virtually freely. This provides the grounds to consider polarons as the charge carriers in DNA.

To describe a moving polaron, it is necessary to consider the coupled equations for the dynamic variables $\{x_i\}$ and the wave function $\{\psi_i\}$

$$\ddot{x}_i = (x_{i-1} - 2x_i + x_{i+1}) + \alpha\left[(\psi_i\psi_{i-1}^* + \text{c.c.}) - \right. \tag{12}$$
$$\left. -(\psi_{i+1}\psi_i^* + \text{c.c.})\right],$$
$$\mathrm{i}h\dot{\psi} = (1 - \alpha q_{i-1})\psi_{i-1} + (1 - \alpha q_1)\psi_{i+1},$$

which are derived from Hamiltonian (3). Here, i is the imaginary unit, h is the dimensionless Plank constant

$$h\frac{1}{v_0}\sqrt{\frac{m}{c}} \to h.$$

It is possible to pass to variables $y_i = x_i - x_{i-1}$, which allows for approximate solution of this system of equations. The generally accepted method consists of reducing Eqns (12) for discrete variables to a system of equations for the corresponding continuous variables for which the analytical solution exists. In the continuum limit, the discrete variables can be expanded into a series being restricted to the several first terms

$$y_{i\pm1} = y_i \pm \varepsilon(y_i)_x + \frac{1}{2}\varepsilon^2(y_i)_{xx},$$
$$\psi_{i\pm1} = \psi_i \pm \varepsilon(\psi_i)_x,$$

where subscripts indicate a spatial derivative of the corresponding order, ε is the series expansion parameter. By substituting these expansions into system (12) and assuming that y_i and ψ_i are now continuous variables, we can obtain the following continuity equations:

$$\ddot{y} = k y_{xx} + 2\alpha(\psi\psi^*)_{xx}, \tag{13}$$
$$\mathrm{i}h\dot{\psi} = -2(v_0 - \alpha y)\psi - v_0\psi_{xx}.$$

The solution of these equations is

$$\psi = B\operatorname{sech}\left[\beta(x - v_\mathrm{p}t)\right]\exp\left[\mathrm{i}(\kappa x \pm \omega t)\right], \tag{14}$$
$$y = -A\operatorname{sech}^2\left[\beta(c - v_\mathrm{p}t)\right],$$

where $\mathrm{i}(\kappa x + \omega t)$ is the wave function phase. Solution parameters, *i.e.*, the wave function amplitude B and the polaron rate v_p, are expressed as the shift of the amplitude A of neighbouring particles as follows:

$$B = \sqrt{\frac{\beta}{2}}, \tag{15}$$
$$\beta = \sqrt{\alpha A},$$
$$v_\mathrm{p} = \sqrt{1 - \sqrt{\frac{\alpha^3}{A}}}.$$

The solution of form (14) describes a solitary soliton-like wave that moves at a rate v_p. From expression (15), it follows that the polaron rate fits the range from zero to the sound velocity

$$0 \leqslant v_\pi < 1.$$

For $v_\mathrm{p} = 0$, the solution of Eqn (14) is reduced to that for a stationary polaron. The complex wave function oscillates with parameters $\kappa \sim h \ll 1$, and $\omega \sim 1/\mathrm{h} \gg 1$. It is interesting that the system of equations similar to (13) appears in the description of a quite different phenomenon, namely, the Langmuire waves in plasma.[262]

The applicability of the continuum solution was checked by numerical simulations with model parameters close to DNA parameters,[212] namely, the rigidity coefficient in the harmonic potential expression (3) $c = 0.85$ eV Å^{-2} and $m \approx 2.18 \times 10^{-22}$ g (half-sum of masses of DNA bases), $v_0 = 0.36$ eV and $\alpha = 0.6$ eV Å^{-1}. Numerical integration of system of equations (12) was carried out. Figure 3 illustrates the evolution of the initial state taken to be a moving polaron. Obviously, the polaron is very stable.

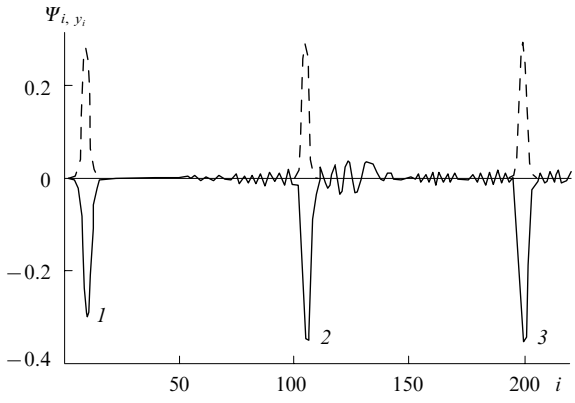


Figure 3. Polaron migration along the lattice.[259]
The polarons are shown for consecutive moments $t = 0$, 150, 300 for polaron migration from left to right.
In the moment $t = 0$, polaron is on the site $i_0 = 10$. The solid line corresponds to relative displacements of particles y_i, the dashed line is the absolute value of the wave function $|\psi_i|$; $\alpha = 1.5$, $A = 0.33$, $v_p \approx 0.65$ (dimensionless parameters are shown).

In the above example, the polaron travels over the lattice at $T = 0$ K. The real charge transfer occurs at a finite temperature and the polaron can be destroyed gradually due to its interaction with thermal fluctuations. Figure 4 shows the distribution of polaron over the lattice at physiological temperature.

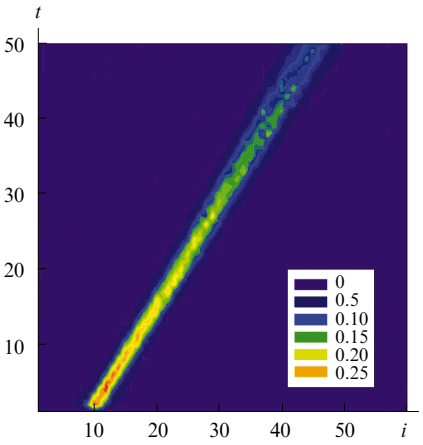


Figure 4. Distribution of the probability density for the polaron wave function depending on time (t) and position in the lattice (i).[259]
The lattice has $N = 60$. Initial condition: the polaron centre is located on particle $i_0 = 10$ and moves to the right. Temperature $T = 310$ K. Averaged for 50 random trajectories.

Obviously, at this temperature too, the polaron is sufficiently stable. For example, the probability of charge transfer by a distance of 40 particles ($\sim$135 Å) exceeds 80%. In calculations, the DNA parameters shown above were used.

Thus, polaron can carry the charge in organic and inorganic systems [59] and also in DNA. This was confirmed by additional numerical modelling of the polaron stability with respect to dynamic (temperature) and static fluctuations.

For the polaron to be considered as a carrier of charge and energy, at least two conditions should be fulfilled. First, once a charge is transferred to the chain, a finite time is required for the polaron formation. Second, the polaron should acquire some initial velocity in order to efficiently carry the charge. One of the ways to achieve this is to employ the above [232] mechanism of polaron motion due to chain curvature. Otherwise, polaron would perform random walk by hopping and the charge transfer would slow down to become inefficient.

V. Conclusion

Summarizing briefly the results in the field of long-range charge transfer in biopolymers, several conclusions can be drawn. First, the high probability of transfer by distances of several tens and hundreds of Ångströms was confirmed. Numerous experiments carried out recently have shown that the decay coefficient for‘ the probability of charge transfer with the distance in dependence (1) can reach the values of $\sim 10^3$ Å^{-1}. Second, the charge transport can be realized as a single-step coherent process, which is quite surprising because as regards the electronic structure, DNA can rather be classified as a wide-gap semiconductor to which the traditional concepts of ballistic charge transport that provide metallic conduction are formally inapplicable.

The main achievements in the field of efficient long-range charge transfer in DNA and polypeptides came from several laboratories of the USA, Japan, Switzerland and Germany. Useful procedures for the preparation of synthetic oligonucleotides have been worked out and methods for the introduction of charge donors and acceptors have been developed. Requirements have been formulated and necessary conditions have been found for the synthesis of systems with high electrical conductivity. These requirements concern the possible types of DNA structure (the choice of optimal base sequences), the chemical structure and the methods of introduction of electron density donors and acceptors into the DNA chain and also the development of efficient methods for detecting electrical signals. Attention should be focused on the widely cited (in particular, in the present review) studies of the research group headed by Caltech professor Jacqueline Barton (USA). In 2011, she was awarded the highest scientific prize of the USA for the discovery of long-range charge transfer in DNA and for proving that the electron transfer depends on the DNA packing and dynamics. Her studies have shown how proteins can detect the damages in DNA and demonstrated the importance of DNA-mediated charge transfer for biology.

The authors of numerous studies in the field of charge transfer in biopolymers pointed to the prospects of these systems not only for biology (for suppressing or weakening the oxidative stresses, for sensors and diagnosis) but also for different fields of nanotechnology. The reason for such interest lies in the low consumed power, flexibility, and stability to external factors. It is very important that the methods for synthesizing well-conducting one-dimensional structures with strictly determined length have been developed. The preparation of these structures is a challenge for the modern technology of synthetic metals with the highest conductivity.

The progress in studying biopolymer-based conducting systems can be accelerated once reliable theoretical fundamentals explaining the charge transport are developed. At present, it is assumed that the polaron theory agrees better with the latest experimental data, namely, a considerable increase in the rate and probability of charge transfer has been achieved. Despite the successful development of the theory of polarons in solids observed in the past decades, the adaptation of its ideas and concepts to particular structures of biomacromolecules is necessary.

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